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Improve dyeing levelness of iron-complexed dye on vegetable tanned leather

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Abstract: Dyeing levelness on vegetable-tanned leather is often affected by the presence of iron. Although adding vegetable tannins is very cost-effective for increasing the fullness of the leather, the polyphenolic compound of vegetable tannins can react with excess ferrous ions from ion-complexed dyes and form black complexes and precipitates on leather. Herein, we present a quantitative measurement of dyeing levelness in a series of vegetable tannins and ferrous ions concentrations. Then we provide a practical solution for lowering the formation of black complexes and hence improving the dyeing levelness of leather.

Keywords: dyeing levelness; vegetable tannins; ferrous ions

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Topic I Advances in leather science basic research

Covalently surface-functionalized α-zirconium phosphate nanoplatelets for enhanced ultraviolet barrier, antibacterial, and flame-retardant properties of collagen fibers towards multifunctional leather manufacture

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Abstract: Manipulating the dispersibility and reactivity of two-dimensional nanomaterials in the (bio)polymeric matrix by surface functionalization strategy has aroused much attention in the fabrication and applications of novel multifunctional organic-inorganic nanocomposites. Here, α-zirconium phosphate nanoplatelets (ZrP NPs) has been surface-functionalized with gallic acid (GA), ZrP–GA NPs, for modification of the collagen fiber matrix, and the effects of ZrP–GA NPs on the ultraviolet barrier, antibacterial, and flame-retardant properties of the resultant collagen fiber matrix have been investigated. The results showed that ZrP–GA NPs can be fabricated via covalently surface-grafting reaction of ZrP NPs and GA. Microstructural analysis revealed that the NPs can be evenly dispersed and bound within the collagen fibrils and onto the collagen strands in the collagen fiber matrix. Moreover, the resultant collagen fiber matrix maintained typical D-periodic structures of collagen fibrils and native branching and interwoven structures of collagen fiber networks with increased porosity and enhanced ultraviolet barrier properties. Antibacterial activities testing results indicated that the collagen fiber matrix exhibited excellent antibacterial activities owing to the grafting of GA serving as the building blocks of ZrP–GA NPs. Furthermore, owing to the incorporation of ZrP–GA NPs, the collagen fiber matrix possessed enhanced flame-retardant properties. Therefore, we envisioned that these results can guide potential applications of two-dimensional nanomaterials for the development of reasonable tanning materials and related tanning technologies towards emerging multifunctional leather manufacture.

Keywords: collagen fibers; α-zirconium phosphate nanoplatelets; functionalization; ultraviolet barrier; antibacterial activities; flame-retardant properties

Exploration of the interaction mechanism between neutral salts and skin collagen using molecular dynamics simulation

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Abstract: The salt effect on skin collagen is a macroscopic manifestation of the microscopic interaction between neutral salts and collagen, which is great significance in Leather-making. However, this micro-effect mechanism is not yet clear, since the microscopic interaction is hard directly observed from the macro-level of skin collagen. In this study, the interaction mechanism between typical neutral salts (NaCl, $CaCl_2$, Na_2SO_4) and collagen was investigated via molecular dynamics (MD) simulation. The non-covalent interaction energy analysis showed that the main interaction between salt and collagen was electrostatic, and the order of the magnitude of this effect was $CaCl_2$ > Na_2SO_4 > NaCl. The conformational and radial distribution function analyses indicated that Cl^-, Ca^{2+} and SO_4^{2-} were the contributing ions for the interaction of NaCl, $CaCl_2$ and Na_2SO_4 with collagen, respectively. $CaCl_2$ tended to form salt bridges within collagen molecules, and the binding effect between Ca^{2+} and collagen enhanced the electrostatic repulsion between molecules, thus showing the effect of dispersing collagen fiber bundles in leather tanning. Na_2SO_4 with SO_4^{2-} as a contribution ion more likely formed cluster-like salt bridges between collagen molecules, weaken the electrostatic repulsion and promoted aggregation, and therefore used as a dehydrating agent in tanning. The effect of NaCl on the intermolecular action of collagen is intermediate between $CaCl_2$ and Na_2SO_4, inhibiting acid swelling and assisting in loosening fibers in tanning acid immersion. MD simulations revealed the mechanism of interaction between neutral salts and collagen at the microscopic level, which can provide theoretical guidance for tannery production.

Keywords: collagen; neutral salts; interaction mechanism; molecular dynamics simulation

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Topic I Advances in leather science basic research

Study on tanning effect of fiber dialdehyde starch combined with titanyl sulfate

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Abstract: The abuse of chrome tanning agent in leather processing has caused great harm to human health and the natural environment. Chrome-free tanning agent is of great significance because it can eliminate the notable environmental pollution of chrome tanning. As a kind of dialdehyde polysaccharide, dialdehyde starch is widely used in leather tanning. Titanium tanning agent is also considered as a potential tanning agent. However, the tanning effect of dialdehyde starch and titanium tanning agent is not ideal. In this study, a system of dialdehyde starch with different aldehyde group contents was prepared by the oxidation of tapioca with sodium periodate. The molecular weight of dialdehyde starch decreased, while their aldehyde group content increased with increasing dosage of sodium periodate. The degradation products of dialdehyde starch with different molecular weight were obtained by degradation. The tanning effect of disaldehydes starch degradation products combined with titanyl sulfate was studied. Under the experimental conditions, the leather was tanned with dialdehyde starch degradation products, and then the leather was re-tanned with titanyl sulfate. The effect of single tanning of dialdehyde starch degradation products and combined tanning with titanium oxide sulfate on the tanning effect of sheep skin was investigated. The results show that the tannability of leather can be improved by combining disaldehyde-degradation products with titanyl sulfate.

Keywords: dialdehyde starch; titanyl sulfate; tanning

Ultra-flexible, anti-freezing and adhesive goatskin-derived conductive organohydrogel e-skin as strain, temperature and humidity tri-mode sensors

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Abstract: The development of flexible electronic skin (e-skin), which could mimic the sensing function of biological skin, has significant value in many fields including human health monitoring, soft robotics, wearable electronic devices and human-machine interaction. As a potential candidate for e-skin, the application of conductive hydrogel is limited by various factors such as complicated fabrication process, insufficient mechanical performance, poor environmental stability and difficulty in degradation. Herein, a top-down fabrication approach was adopted to construct a multifunctional goatskin-derived conductive organohydrogel e-skin, in which the collagen fiber scaffold of goatskin was filled with the polyacrylamide network. This goatskin-derived organohydrogel displayed excellent mechanical strength (fracture stress of 2.87 MPa) and stretchability (fracture strain of 542%). Unlike conventional conductive hydrogels, this organohydrogel remained its multi-functionality even at -20 °C and after long-term storage under room environment condition. Additionally, this organohydrogel demonstrated considerable adhesion and anti-bacterial properties, allowing it to conform closely to human skin without causing bacterial infection. The e-skin sensors, assembled with this organohydrogel, possessed multiple stimuli-responsive modes to respond to the changes in strain, humidity and temperature, allowing their precise monitoring of various body movement, facial expression, voice communication and physiological signal. Notably, the discarded e-skin could be effectively degraded under the natural environment condition, reducing the generation of electronic waste. In brief, this work gives new insights into the development of intelligent multifunctional e-skin and demonstrates a new pathway for the high-value utilization of animal skin.

Keywords: goatskin; e-skin; tri-mode sensors

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Topic I Advances in leather science basic research

Functional organogel e-skin as strain, temperature and humidity sensors for health monitoring

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Abstract: The rapid development of intelligent electronic technology has facilitated the transition of electronic devices from rigid systems to flexible ones. Flexible electronic skin (E-skin) that mimics natural animal skin has attracted widespread attention owing to its significant applications in health management, soft robotics, and human-machine interaction, and so on. However, the increasing demand for more advanced functionalities imposes higher requirements on E-skin, such as high mechanical strength, flexibility, and biocompatibility. Herein, a top-down fabrication strategy was adopted to prepare an intelligent multifunctional organogel-based E-skin by using flexible but tough goatskin as the basic framework followed by the filling treatment with a poly (methyl acrylate-acrylamide) (P(MAA-co-AM)) network. This organogel exhibited excellent mechanical strength and puncture resistance, with a fracture stress of 3.86 MPa and the breaking elongation of 230%, respectively, thus serving as the second skin layer to protect human body. Unlike conventional water-containing hydrogels, this organogel possessed exceptional biocompatibility and environmental stability, enabling it to operate normally at low temperature (e.g. -20 ℃) and after long-term storage (> 15 d). More importantly, the crucial properties for practical application, such as adhesion, conductivity, and antibacterial performance, have been successfully integrated into this organogel system. A flexible, stretchable, and durable organogel-based sensor was further developed that can accurately monitor large-scale and subtle movements of human body within a wide range of temperature and duration. Moreover, it could simultaneously achieve strain, temperature and humidity responsiveness on the same platform, enabling the real-time monitoring of human health status. This work provides a new approach for the biomimicry and multifunctionality of intelligent E-skin, aiming to replicate or even surpass the performance of real animal skin.

Keywords: goatskin; top-down; organogel; E-skin; multi-functionality; health monitoring

Comparative analysis of the surface properties of leathers produced with different tanning systems

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Abstract: Due to the growing demand for sustainability and customization by companies in the luxury and fashion chain, the main efforts of the researchers involved in leather technology, today, are pointed to the development of novel tanning processes, capable of satisfying the needs of the even more demanding market. On the other hand, changing tanning agents itself, without changing the whole tanning process paradigm, does not guarantee the expected performances; on the contrary, this continuous search for alternative tanning systems of different typology, to ensure growing levels of sustainability and biodegradability of the products, may cause novel technical issues and novel categories of leather defects. Therefore, in order to guarantee the undisputed high-quality features of leather, in terms of product performance, which determine its primacy in the panorama of contemporary markets characterised by the emergence of numerous alternative materials, it is necessary to plane tools and strategies for monitoring the most crucial parameters within the main production phases; in particular, the monitoring of surface properties can avoid the occurrence of possible novel issues and any other possible effect provided by the novel tanning agents, able to affect the common leather features. The present work is aimed to provide further information on the possible role of technical parameters potentially able to affect the final leather surface performances. More in detail, the present investigations have been pointed to the ζ potential and the isoelectric point determination of leather surface (at different steps of the production process), and their effects on the final surface features of chrome tanned and novel generation of chrome-free leathers. In fact, surface charge can significantly affect the interactions between the leather surface and the chemicals used in the retanning, fat-liquoring, dyeing and finishing processes. A detailed knowledge of surface charge after tanning in different conditions will allow the optimization of the whole leather production process moving through more sustainable and environmentally friendly technologies.

Keywords: leather qualification; surface properties; isoelectric point; leather reactivity; finishing issues; chrome-free leather properties

Histological and microscopic analysis of the characteristics of Ethiopia's cattle hides

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Abstract: Ethiopia is one of the countries which possesses the largest livestock population in the world. About 22 cattle breeds are reported. There has not been any objective based scientific study revealing natural intrinsic qualities of Ethiopia's cattle hides, and breed and region-specific qualities in particular. This research work is to analyze the histological and microscopic characteristics of Ethiopian breeds of cattle hide. A total of 12 cattle breeds were taken from five different regions of Ethiopia. Crust leather samples were taken; grain and cross section of the leathers were observed under SEM. Fresh raw hide sample taken was preserved in 18.50% formalin solution and histological analysis was carried by using Hematoxylin & Eosin staining protocols. Two types of pores are present on the grain pattern of Ethiopian cow hide, small and big. The average diameter of the big pores is about 105 μm and that of small pores is about 20 μm. The number of pores per unit area varies not only from species to species but also from breed to breed within the same species, and also from location to location within a single hide. The higher the number pores per unit area the finer will be the grain. It was observed that the average number of pores per square inch for Ethiopian cattle hides varies from 12,000 to 20,000. The highest number of pores was observed in Afar, Bale, Arsi, Fogera and Raya cattle breeds, indicating that the grain pattern of these cattle hides are finer than other breeds. It was reported as 11,000 for Indian cattle hide. The number of pores for Ethiopian cattle hides is relatively higher due to presence of more small pores. The grain layer for Ethiopian cattle hides varies from 13 to 27%. The collagen fiber bundles which constitute the bulk of the corium are quite big in Ethiopian cattle hides and highly compactly woven. The grain layer varies from 5 to 30% as per the data from histology images. It was concluded that the Ethiopian cattle hides have finer grain pattern and compactly woven fiber structure.

Keywords: Ethiopia cattle breed; pores; structures

Synthesis of hyperbranched flame retardants and their application in polyurethanes

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Abstract: Aqueous polyurethane materials, owing to their superior thermal stability and mechanical performance, have been extensively utilized in coatings, foams, household products, electrical apparatus, and other domains. However, the profound combustibility of polyurethane materials circumscribes their broad application. Through the reaction of 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and maleic anhydride (MA), DOPO derivatives as flame retardants were synthesized. Subsequently, through reaction with diisopropanolamine (DIPA), a novel hyperbranched polymer, MA-HBP, was synthesized. By modifying this with phosphorus trichloride (PCl_3), tetrakis(hydroxymethyl)phosphonium sulfate (THPS), and triethyl phosphate (IPPP), nitrogen and phosphorus-containing hyperbranched flame retardants were prepared. Finally, the synthesized flame retardants were incorporated into the synthesized aqueous polyurethane by chain extension, generating flame retardant aqueous polyurethane. The synthesized tetrakis(hydroxymethyl)phosphonium sulfate modified flame retardant exhibited the highest residual char yield of 39.97% in the muffle furnace and an expansion height of 1.59 cm. The triethyl phosphate modified flame retardant prepared flame retardant polyurethane exhibited the best flame retardancy, with the limiting oxygen index increased from 22.1% to 27.8% and the vertical combustion grade reaching V-0 level.

Keywords: overbranched flameretardants; maleic anhydride; waterborne polyurethane

Charge modulation for efficient mass transfer of protease in leather bating process

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Abstract: Bating is an important process for making soft and clean leather by removing non-collagenous proteins from hide and moderately dispersing hide collagen network with protease. However, the slow mass transfer of protease in hide makes it stay longer in the surface layer of hide than in the middle layer, which may result in an excessive hydrolysis of the hide surface and a reduction in the leather quality. We have found that the mass transfer of protease in hide can be modulated by manipulating the electrostatic interaction between protease and hide. Here, glutamic acid (Glu) and sodium gluconate (SG) were used to adjust the surface charge of trypsin (typical bating protease). The results showed that Glu and SG increased the negative charge of trypsin and scarcely affected its proteolytic activity and effective diameter. The effects of Glu and SG on the transfer behavior of trypsin in bating was investigated using fluorescent tracing. Obviously, Glu and SG enhanced the trypsin transfer, thereby decreasing the collagen damage. This was because the increase in the negative charge of trypsin caused by Glu and SG led to an increase in the electrostatic repulsion between trypsin and hide (with negative charge) and a decrease in their affinity, which accelerated the penetration of trypsin into the hide. Additionally, Glu and SG with high carbon content increased the C/N ratio of bating effluent, which was beneficial to the biological treatment of tannery wastewater. This work provides a promising strategy for protease transfer enhancement and high-quality bating.

Keywords: bating; protease; mass transfer; electrostatic interaction; charge modulation

Study of the variability of the surface measurement of leathers in different conditioning atmospheres

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Abstract: In the metrological controls aimed at verifying the commercial transactions of finished leathers, one of the factors considered to be decisive for a standardized measurement of leather surface is the preliminary conditioning of batches in specific conditions of temperature and relative humidity. In all the reference documents on the measurement of the leather surface, in fact, the conditioning is always foreseen with the aim of uniforming the humidity content inside the materials and, therefore, eliminating a factor of variability for the results. In particular, the "Code of practice for the area measurement" (1998) and the EN ISO 11646:2014 standard for the measurement using pin-wheel machines, specify (§3 and §5.1.1) a 48-hour ageing to a single condition of 20°C and 65% R.H. (20/65); the standard EN ISO 19076:2023 on measurement using optoelectronic machines, on the other hand, always indicate a 48-hour conditioning to one of the 3 conditions set out in the EN ISO 2419:2019 (20/65, 23/50 and 27/65) "Leather, Standard atmospheres for conditioning and testing" .

To determine the effective influence of conditioning, in the present study the variability of the surface on different leather batches on the above conditionings has been evaluated; to the standard conditions indicated in ISO 2419, conditioning at higher temperatures and low humidity (35°C and 10% R.H.) and in cold humid (10°C and 85% R.H.) conditions has been included. In the study, not only the dependence on environmental factors has been evaluated, but also the dependence on time: the measurements, in fact, have been carried out both after 24 and 48 hours of conditioning.

Keywords: metrology; leather; area measurement; surface measurement; surface variability; conditioning; ageing; international contract N. 7; ISO 2419; ISO 11646; ISO 19076

Synergistic effect of silica aerogel and titanium dioxide in porous polyurethane composite coating with enhanced passive radiative cooling performance

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Abstract: A series of porous polyurethane (PPU) composite coatings containing silica aerogel (SA) and/or titanium dioxide (T) were prepared through a wet phase inversion method. The microstructure, radiative cooling, mechanical and hydrophobic properties of the composite coatings can be well controlled by altering the content of the two fillers. The typical PPU-SA10@T10 composite coating showed an interleaving porous structure, and the incorporated SA and T fillers were uniformly stacked in the pore cavities. Taking advantages of the strong light-back scattering and molecular oscillation functions, the solar reflectance, thermal emittance in the atmospheric transparency window, and the net cooling power of the PPU-SA10@T10 coating reached 0.917, 0.973, and 87.8 W/m^2, respectively, which results in a sub-ambient cooling of 7.8 °C at midday under a solar irradiance of ~640 W/m^2. Moreover, the PPU-SA10@T10 coating possessed well balanced mechanical properties and superior hydrophobicity (water contact angle was 121.7°). The present work provides a viable way for developing radiative cooling coating with desirable mechanical properties and water-repellency.

Keywords: porous polyurethane composite coatings; silica aerogel; titanium dioxide; passive radiative cooling; synergistic effect; soft substrates

Advances in research of collagen-like peptides: from triple helices to fibrils

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Abstract: One of the major contributions of Dr. Heidemann to the field of collagen research is to utilize peptides to investigate the molecular properties of collagen. Since his pioneer work in the late 1970s, research on collagen-like peptides has not only advanced our understanding of the molecular basis of the structure and function of collagen, but also expanded into an active field of its own for the development of novel collagen mimetic biomaterials for medical and industrial applications. A recent achievement is the development of peptides that, upon forming a collagen triple helix, can further self-assemble into collagen like fibrils. In addition to being a molecular scaffold of collagen-mimetic materials having enhanced native-like properties and tunable functionality, these fibril-forming, collagen mimetic peptides (FCMPs) are effective molecular tools for further research on collagen fibrils – a significant step in our research effort elucidating the structural hierarchy of fibrillar collagen going from triple helices to fibrils. In this talk I will present our work on the design and development of such FCMPs. These FCMPs consist of more than 100 amino acid residues in modular amino acid sequences and are obtained by bacterial expression using designed genes. I will also present some of our new findings using the FCMPs on triple helix folding, fibril assembly, triple helix crosslinks, and the stability of the collagen structure. Further research on the FCMPs will lead to new insight on the biological functions and chemical and physical properties of collagen, and new design features for novel collagen-mimetic biomaterials.

Keywords: fibril-forming collagen mimetic peptides; collagen fibrillogenesis; folding and stability of collagen triple heli; new collagen based biamaterials

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Topic I Advances in leather science basic research

Tuning the supramolecular assembly of collagen through an interplay of electrostatic interaction using ionic liquids

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Abstract: Tuning the self-assembly of collagen has broad applications in the biomedical field owing to their desired biological performance as collagenous materials with tunable functionalities can further determine cellular responses. In this work, an attempt has been made to tune the self-assembly of collagen using ionic liquids viz., imidazolium chloride (IC) and choline dihydrogen phosphate (CDHP) at its physiological pH, followed by probing assembled systems using various characterization methods. Turbidity measurements of fibrillar networks were performed to ascertain the rate of fibril formation in addition of imidazolium chloride and choline dihydrogen phosphate to collagen at physiological pH, binding affinity and way of binding of collagen with CDHP and IC were studied using Microscale Thermophoresis (MST) technique. Morphological changes were examined using Scanning Electron Microscope (SEM), in addition, changes in the shear viscosity, mechanical strength, Linear Viscoelastic Region (LVER) and dynamic mechanical analysis of collagen fibrils when interacted with imidazolium and choline-based ILs were carried out using rotational rheometer and quartz crystal microbalance (QCM) measurements. The experimental result depicts that CDHP imparts better cross-linking, as well as mechanical strength compared to IC, which is already known for destabilizing the triple helix structure, is inhibiting the fibril formation. This self-assembled fibrillar system would create a better understanding of ionic forces modulating its structure-function relationship. This will further aid these cross-linked scaffolds to act as templates, favouring the growth and viability of specific cells depending upon the pore geometry of the prepared scaffold.

Keywords: collagen self-assembly; ionic liquids; fibrillation; microscale thermophoresis; rheology

The effect of tanning on water retention of skin collagen

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Abstract: Water plays an important structural role in hierarchical collagen fiber. This study investigates the water-holding capacity and moisture types of leather from various tanning. Tanning significantly improves the water-holding capacity of leather. In particular, inorganic Cr or Al/Zr tanning demonstrates an impressive increase of 18% compared with raw skin, while organic TWS tanning exhibits a modest enhancement of 5%. Furthermore, the water within the skin collagen was classified as free water and bound water using the constant centrifugal method. Natural raw skin holds 0.56 g/g-dry of free water and 1.04 g/g-dry of bound water with most of which bonded with side-chain and 0.23 g/g-dry with backbone of collagen. After cross-linking, the content of free water increases substantially to about 0.9 g/g-dry, no significant difference for various tanning methods. However, tanning changed the bound water. The organic TWS tanning surprisingly decreased the total bound water to 0.78 g/g-dry, and the sharp drop was observed on side-chain to 0.57 g/g-dry. Whereas inorganic Cr or Al/Zr cross-linking changes the type of bound water in spite of the constant total. The content of bound water on backbone obviously increased, concomitantly with the slight decrease on side-chain. Then the water bound with backbone was further categorized as Ramachandran bridges and double water bridges. Interestingly, inorganic Cr or Al/Zr cross-linking enhanced double water bridges, which was reduced by organic TWS cross-linking. This study provides valuable insights into the difference of collagen conformation caused by cross-linking.

Keywords: leather; water types; collagen; cross-linking

Effect of protease–bactericide interaction on the protease-assisted soaking performance

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Abstract: Protease-assisted soaking has received increasing attention in recent years. However, few reports have elaborated on how bactericides, which are used to prevent hides/skins from decaying in the soaking process, affect the protease-assisted soaking performance. In this study, the effects of three bactericides, such as 2-methyl-4-isothiazolin-3-one (MIT), sodium propyl 4-hydroxybenzoate (SPHB), and cetyl trimethyl ammonium bromide (CTAB), on the catalytic activity of protease were investigated. Results showed that MIT and SPHB had little effect on the proteolytic activity, while CTAB had a negative effect. Fluorescence spectroscopy, synchronous fluorescence spectroscopy, molecular docking, and molecular dynamics simulation were used to analyze the protease–bactericide interaction, and the data revealed that MIT and SPHB are bound to the non-catalytic sites of protease, while CTAB affected the catalytic triad of protease. Further, the protease and bactericides were used alone, simultaneously and sequentially in the soaking process, and their soaking performances were evaluated. It was found that the use of protease increased microorganisms in the soaking float, and MIT exhibited the best bactericidal effect. Additionally, the simultaneous use of protease and MIT inhibited bacteria effectively and scarcely affected the removal of noncollagenous proteins from hide and the loosening of hair by protease. These findings contribute to a better understanding of the scientific use of protease with other auxiliaries in the soaking.

Keywords: protease; bactericide; leather; soaking

Effect of size of dialdehyde sodium alginate tanning agent on its multiscale mass transfer and tanning performance in leather

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Abstract: Green, low-carbon and circular development is an inevitable trend for the leather industry. Dialdehyde polysaccharide is a type of sustainable tanning agent that could eliminate chrome discharge from the source of leather manufacture. However, higher molecular weight of the dialdehyde polysaccharide than the traditional tanning agents will probably affect the mass transfer characteristic and crosslinking effects of the tanning agent. Herein, dialdehyde sodium alginate (DSA) was chosen as the model object. The structure-activity relationship between the size of DSA and the tanning effects of DSA was explored. Four DSAs with gradient sizes (Mw 14,000-83000) were prepared by regulating the oxidation conditions. 5-(4,6-dichlorotriazinyl) aminofluorescein (DTAF) was grafted on DSA by a nucleophilic substitution reaction. The labeled DTAF-DSAs also possessed gradient sizes (Mw 11000-28000). Then DSAs and DTAF-DSAs were used in tanning. It was found from the fluorescent tracing technique that the smaller the Mw of tanning agent, the faster the penetration rate. DSAs with Mw ranged between 10000-87000 transferred and evenly distributed in the elementary fiber hierarchy (Φ 2-10 μm), and exhibited crosslinking/tanning effects. The tanning performance of DSAs (characterized by shrinkage temperature and thermal denaturation temperature of tanned leather) mainly depended on its aldehyde group content rather than its size under the same tanning conditions. The higher the aldehyde group content, the stronger the tanning performance. The hierarchical micro-structures of DSA tanned leather were observed by scanning electron microscopy. According to EDS, the oxygen element content in fibrils of DSAs tanned leather had increased. Meanwhile, the hierarchical pore structures of DSA tanned leather were analyzed by micro-CT, mercury intrusion porosimetry and nitrogen adsorption method. These results indirectly proved that DSA could penetrate into the fibril level and even reach the space between collagen molecules, which changed the hierarchical fiber structures and pore structures (pore size 10~50 nm) of leather through crosslinking/tanning. The biodegradability and macroscopic physical properties of leather were also changed by tanning. The larger the size of the tanning agent, the higher the biodegradation rate and thickening rate of the leather. DSA with a moderate Mw (28000-60000) could impart leather satisfactory organoleptic properties such as softness and fullness. Therefore, the size of DSA is one of the most essential factors that affect the tanning effects of DSA. The results are expected to provide a theoretical foundation for the design and development of dialdehyde polysaccharide tanning agents and assist the green manufacturing of chrome-free eco-leather.

Keywords: chrome-free tanning; dialdehyde sodium alginate; mass transfer; molecular size; hierarchical structure; leather matrix

Supramolecularly mediated preparation of high-concentration collagen solution for 3D bioprinting

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Abstract: The distinguished biocompatibility of collagen renders it a promising material for 3D bioprinting. Despite recent advances in this field, one major challenge lies in eliminating entropically-driven aggregation of collagen during the process of 3D bioprinting, as high-concentration collagen prints tissue engineering materials with better geometric fidelity and precision than low-concentration one. Here, we report a novel strategy to prepare high-concentration collagen that uses non-covalent, selective and controllable binding of engineered cucurbit [7] uril carrying at its periphery multiple polyethylene glycol pendants (CB [7] PEG) with aromatic residues (Phe/Tyr) on collagen. Once the engineered cucurbit [7] uril is removed in a controlled manner via competitive binding, the high-concentration collagen could aggregates to generate high-density hydrogel. With the strategy reported in this study in hand, collagen-based 3D tissue engineering materials that display better geometric fidelity and precision are in sight.

Keywords: 3D bioprinting; high-concentration collagen; tissue engineering; cucurbit [7] uril

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Topic I Advances in leather science basic research

Preparation and properties of aminated graphene oxide reinforced gelatin-chitosan composite films

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Abstract: In this work, an ethylenediamine-modified graphene oxide (GON) derivative was prepared and subsequently incorporated into gelatin-chitosan composite films at varying concentrations (0.01%, 0.05%, 0.10%, 0.50%, 1.00% w/w) via the casting technique. Experimental results showed that graphene oxide underwent partial reduction in the presence of ethylenediamine. When GON was introduced, there was a markable reduction in the moisture content, swelling rate, and water vapor permeability of the composite film. Notably, at a GON concentration of 1.0%, the moisture content plunged to 9.09%, the swelling rate was reduced by roughly 38.62%, and the water vapor permeability diminished by approximately 22.60%. Concurrently, as the GON concentration escalated, the film's transparency decreased and its color became darker. UV-Vis 10.2 spectrophotometry analysis indicated that the inclusion of GON notably augmented the opacity of the composite film and diminished light transmittance. Specifically, at 280 nm and 600 nm, the transmittance of the GON/GC5 composite film reduced by 55.96% and 31.45% respectively, thereby considerably enhancing the composite film's ultraviolet blocking efficacy. Additionally, the tensile strength of the GON/GC composite film substantially was improved as the concentration of GON increased. At a GON concentration of 1.00%, the tensile strength reached 23.88 MPa, signifying an increase of around 20%. Thermogravimetric analysis further revealed that the addition of GON enhanced the thermal stability of the composite film.

Keywords: aminated graphene oxide; gelatin; chitosan; biocomposite films; mechanical strength; ultraviolet protection

Biodegradable tanning and re-tanning agents based on alginate: towards recyclable leather

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Abstract: The aim of this research has been to obtain biodegradable tanning and re-tanning agents with antimicrobial activity from renewable sources within the wide remit of a sustainable manufacturing process based on circularizing the design and de-carbonising the products. To this purpose, alginate and zinc oxide nanoparticles together with ultrasound (US) clean, green and scalable technology have been exploited, while exploring new processes for leather tanning using environmentally friendlier inputs. Our objectives included: (i) obtaining sodium alginate derivatives (SADs) using US technology; (ii) evaluating their tanning effectiveness at both laboratory and pilot level; (iii) US- assisted functionalization of SADs using zinc oxide nanoparticles; (iv) testing the antimicrobial activity of functionalized SAD-nanoZnO; (v) designing a tanning process aiming at 100% biodegradable leather using vegetable tannins (tara) and SAD-nanoZnO; (vi) investigating the physical-mechanical properties of leather and environmental performance of the tanning process. This work has revealed the synergistic effects of SAD-nanoZnO and tannins on leather matrix and established a valid novel hybrid tannage that endows the leather with required organoleptic properties and physical performance. The novel SAD-nanoZnO tanning agent and and the tanning process will produce zero chrome/aldehyde/syntan-containing solid wastes and recyclable leather, thus contributing to a cleaner production and puting industry on a new path of a sustainable development.

Keywords: alginate derivatives; nanoparticles; ultrasound technology; biodegradable leather; antimicrobial activity

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Benign leather processing using ovine collagen hydrolysate produced by indigenous sheepskin microbial community

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Abstract: The leather industry has been making strides in reducing the environmental impact of leather production throughout the product life cycle. Inspired by the natural wool loosening process, LASRA has identified bacterial species that produce proteases as an alternative to the conventional beamhouse operation for depilation. Further optimization of the process led to natural depilation by drumming at acidic conditions, demonstrating that acetic acid introduced as the only chemical to the system could achieve complete depilation of fresh sheepskins.

Metagenomic analysis revealed the microbial community involved in the acetic acid depilation process, making it possible to fine-tune the depilation liquor. By altering the process conditions, total decomposition of sheepskins was achieved, and ovine collagen hydrolysate was obtained. This treatment not only enables eco-friendly depilation but also valorizes tannery waste into value-added products, reducing the cost of sustainable depilation.

We explored the efficacy of ovine collagen hydrolysate as an additive in pre-tanning or post-tanning stages and investigated its influence on chemical discharge and leather quality. Our results showed that ovine collagen hydrolysate, when added as a pre-tanning agent, increased the strength of the crust leather while maintaining its softness. When added as a post-tanning agent, it replaced conventional retanning agents, resulting in satisfactory leather quality with lower pollutant discharge. At the pre-tanning stage, ovine collagen hydrolysate was incorporated into the collagen matrix of the substrate, increasing the uptake of tanning agents by providing additional crosslinking sites. At the post-tanning stage, the added hydrolysate reinforced the collagen matrix and improved the emulsification and absorption of fatliquors.

In conclusion, the metagenomic analysis of the indigenous microbial community of the acetic acid depilation process enabled the integration of eco-friendly leather processing, valorization of leather waste, production of value-added products, and improvement of leather quality. Our study demonstrated the feasibility of the benign leather processing approach with economic viability.

Keywords: benign processing; metagenomics; collagen hydrolysate

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Topic II Sustainable technologies for leather manufacture

Integrated cleaner technology of leather making for beamhouse and tanning processing

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Abstract: In order to effectively control the pollutant emissions in the tanning process and promote the green transformation and upgrading of the leather industry, after years of research, based on the fluorescence probe visualization technology, the mass transfer law of the enzyme protein in the skin, the dispersion mechanism of the enzyme fiber, the efficient hydrolysis mechanism of the lipase-catalyzed oil, and the efficient penetration and binding mechanism of chromium in the hides and skins were analyzed. The integrated technology of clean production technology for the beamhouse-tanning processes of leather making was established, which was mainly based on clean technologies such as enzymatic unhairing based on grain protection, enzymatic fiber opening, enzymatic degreasing, ammonium-free deliming and bating, high absorption chrome tanning, efficient recycling of chrome tanning waste liquid, trichloroazine-type chrome-free tanning. The industrial application results show that the integrated technology can meet the production requirements of typical leather varieties such as cowhide sofa leather, shoe upper leather and automobile cushion leather. The dosage of sulfide, lime and chromium in the leather making process is reduced by 75 %, 80 % and 23 %, respectively. The emissions of typical pollutants such as COD, ammonia nitrogen, total nitrogen, suspended solids and chromium are reduced by 67 % -85 %, and the formation of chromium-containing sludge is reduced by 19 %. It has the characteristics of high efficiency and energy saving.

Keywords: enzymatic unhairing; high exhaustion chrome tanning; cleaner production; enzymatic fiber opening; chrome free tanning; enzymatic degreasing

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Topic II Sustainable technologies for leather manufacture

Antibacterial, antiviral, and biodegradable collagen network mask for effective particulate removal and wireless breath monitoring

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Abstract: The contaminated air containing particular matter and pathogens has caused adverse impacts on human health. Face masks are the simplest and most cost-effective method for individual protection. However, most commercial masks rely on size exclusion to achieve air purification and are commonly made of petroleum-based materials, which makes it has the defects of short service life, nondegradable, and cannot actively inactivate viruses. Besides, it is easy to cause environmental pollution and secondary infections if the used masks were disposed of improperly. Animal skin has a wide range of sources and low prices as a byproduct of the meat and milk industries. The unique three-dimensional woven structure and a large number of active functional groups in collagen fibers make it an excellent candidate for air purification. Therefore, a facile and straightforward method for creating biodegradable and self-disinfecting masks based on skin collagen network was prepared in this study. Tannic acid was used to modify the skin collagen fiber, which can not only disperse collagen fibers and increase filtering performance but also allows for the in-situ synthesis of silver nanoparticles (AgNPs) on collagen fiber surfaces. The prepared collagen-based masks can efficiently purify the polluted air through the interaction of active groups and hazardous particles (PM2.5 removal efficiency >99.9%), and they can also solve environmental issues related to waste disposal. Besides, the masks exhibit excellent antibacterial (>99.99%) and antiviral (>99.999%) capabilities due to the introduction of AgNPs. Furthermore, the integration of the mask into a wireless platform for respiratory monitoring was also demonstrated.

Keywords: collagen fiber network; biodegradable face mask; antibacterial and antiviral

"Three-in-one" strategy based on the on-demand multifunctional fluorescent amphoteric polymer for ecological leather manufacturing: disruptive wet-finishing technique

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Abstract: The traditional wet-finishing process for leather manufacturing is complicated and uses numerous chemical additives, limiting the leather industry's development in the direction of energy saving and emission reduction. Integrated with the allegro promotion of chrome-free organic tanning system, amphoteric wet-finishing materials have shown great promise for settling the current issues such as low chemical absorption-rates. Herein, we developed a disruptive "three-in-one" strategy for ecological organic chrome-free leather manufacturing based on the on-demand multifunctional fluorescent amphoteric polymer (referred to as pADD-DMENA). As expected, pADD-DMENA exhibited satisfyingly integrated "three-in-one" origins including retanning, fatliquoring and dyeing properties. Compared to conventional anionic dyed leather, pADD-DMENA dyed leather had a uniformly bright yellow color surface and superior lightfastness, durability, and washability. Furthermore, its fluorescent ontology enabled the visual tracking of pADD-DMENA in crust leather and sewage, allowing for real-time monitoring of pADD-DMENA precise distribution. Notably, because of the "three-in-one" features, pADD-DMENA significantly shortened the conventional wet-finishing process, greatly reducing machining time and demonstrating better environmental conservation of wastewater. To summarize, the development of pADD-DMENA allows the traditional wet finishing process to be completed in one step, effectively simplifying the tanning process, reducing additive of various chemicals, and broadening the way for ecological leather manufacturing in a green direction with low energy consumption and less pollution.

Keywords: amphoteric polymer; wet-finishing; multifunctional auxiliaries; visual tracking; fluorescence

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Topic Ⅱ Sustainable technologies for leather manufacture

Preparation of chrome-free tanning agent by combining mineral sourced fulvic acid with coordination effect: a novel tanning-dyeing integrated strategy

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Abstract: Mineral sourced fulvic acid (MFA) is characterized by excellent water solubility and abundant functional groups. MFA is commonly used in agriculture as a plant growth regulator, as well as it also can be used in the dyeing of wool due to its chromophoric quinonyl and auxochromic carboxyl. In addition, MFA contains a large number of carboxyl and phenolic hydroxyl and thus has excellent coordination performance. In view of this, a novel chrome-free tanning agent (MFAA) with tanning-dyeing integration was prepared by coordinating MFA extracted from low-value weathered coal with Al (Ⅲ). Quantitative analysis showed that the contents of carboxyl and quinonyl in MFA were 9.88 mmol/g and 1.52 mmol/g, respectively. The coordination mechanism between MFA and Al (Ⅲ) was analyzed by FTIR and XPS. The shrinkage temperature of leather tanned by MFAA was more than 90℃. The tensile strength and elongation at break reached 21.8 MPa and 114.1%, respectively, which were higher than those tanned by commercially available organic tanning agents. Meanwhile, the UV absorption spectrum analysis showed that the metal coordination would affect the dyeing performance of MFAA, which proved that it can be used to produce a series of dark leather with high market share. Finally, MFA was re-isolated from the tanning wastewater and applied in the cultivation of rice seeds. The results showed that MFA could promote the germination rate of seed and the growth of root and stem. Therefore, MFAA is expected to solve the pollution of Cr^{6+} and organic dyes caused by dark leather.

Keywords: mineral source fulvic acid; tanning-dyeing integration; agriculture

Preparation of hyperbranched polyglycidyl based on biomass glycerol for the chrome-free leather production

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Abstract: Currently, minimizing the environmental impact of tanning processes is the goal of many tanners, which have forced the leather industry to develop tanning systems based on natural products. Biomass-derived polyaldehyde or vegetable-aldehyde combination tanning is the current research hotspots. While, the usage of these tanning materials may result in high organic load in the effluent leads to high biological and chemical oxygen demand. Sparked from vegetable tanning, employing excess by-products of biomass glycerol and glycidol to produce high value-added chrome-free tanning agents will be in great significant. In this paper, a series of hyperbranched polyglycidyl (hPG) with different hydroxyl group and various molecular weights, widely molecular weight distribution have been developed by cationic ring-opening polymerization of glycidol and glycerol. The tanning effect of hPG on hide powder and plicking sheepskin as well as biological and chemical oxygen demand of effluent have been determined. The tanning results show that the denaturation temperature of hide powder and white-wet leather significantly improved. The highest denaturation temperature can reach 115.6℃ by employing 3% hPG. In addition, compared to tannins, the chemical oxygen demand and biological oxygen demand of effluent tanning by hPG can reduce by nearly 1/4 and 1/5, respectively. Therefore, the use of hPGs benefits to the complete elimination of chrome pollution and greatly reduce the biological and chemical oxygen demand.

Keywords: hyperbranched polyglycidyl; chrome-free tanning;denaturation temperature; biological and chemical oxygen demand; cleaner leather production

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Innovative modified natural tannins for ecofriendly leather

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Abstract: Innovative modified natural tannins for eco-friendly tanning will be developed within the LIFE I'M TAN project co-financed by EU. Employed since prehistory, although bio-based, natural tannins have reduced applicability and generate significant environmental impact due to high chemical load in waste water measured in terms of Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD). LIFE I'M-TAN will implement to semi-industrial scale the production/use of chemical modified natural tannins, for environmentally sustainable high-quality leather for footwear, handbags, leather goods with low environmental impact, low chemical hazard, sustainable costs, reduced waste disposal and a circular economy approach for recycle/reuse of waste. natural tannins such as chestnut and quebracho extracts will be chemically modified according to green chemistry principles (bio-based chemicals, zero waste) to produce high exhaustion chemical modified natural tannins. Chemical modification empower the efficacy of the tanning process, reduce the load of tanning agents required, increase bath exhaustion fundamental to recover/recycle tanning bath, reduce water consumption and COD/BOD in the waste water.

Project environmental impact on partners product/process by the end of the project are:

1) 100% reduction of hazardous chemicals such as chrome salts, aldehydes, phenols.

2) 25% COD/BOD reduction in tannery effluents.

3) 30% reduced water consumption in leather tanning by recovery/recycle of waste water.

Second objectives concern eco-design & circular economy:

4) 20% recovery/recycle of chemical modified natural tannins leather scraps to produce fertilizers and 80% low molecular waste products as additives for animal feed. The valorization of chemical modified natural tannins by-products for high value goods is an opportunity to increase industry competitiveness and human wellbeing.

Keywords: modified natural tannins; green tanning process; circular economy

Establishment of ammonium salt-free deliming methods

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Abstract: Of the leather-making processes, the beamhouse process is known to have the highest waste-water pollution load. Reducing the pollution load generated by this process is one of the key issues to be solved by the leather industry.

The pollution load caused by the unhairing process accounts for the highest proportion of the beam-house process and is said to be 30-40% of the total leather-making process. The subsequent deliming and bating processes also have a high effluent pollution load due to the use of nitrogen-containing ammonium salts such as ammonium chloride or ammonium sulphate. Nevertheless, ammonium salts are used in the deliming process because of the low cost of these chemicals and the ease of process control. This is because the reaction is completed by simply adding and stirring a certain amount of ammonium salts to the lime pelt.

Methods have been devised to use carbon dioxide instead of ammonium salts in the deliming process. This method removes calcium hydroxide with low solubility (solubility in water: 0.17 g/100 cm^3 (25°C)) by changing it to calcium bicarbonate with high solubility (solubility: 16.6 g/100 cm^3 (20°C)) through the injection of carbon dioxide into lime pelts. Using this method, the total nitrogen (TN) generated in the deliming process can be reduced by about 90% compared to the conventional method.

However, the use of ammonium salts still remains the predominant method. The reasons for this are the high cost of carbon dioxide compared to ammonium salts and the need for special equipment such as gas injection systems. Methods using carbon dioxide are therefore not widely used.

On the other hand, the use of hydrochloric acid and lactic acid as deliming agents is also theoretically known. However, when these agents are used, the acid reacts with the surface of the pelts and partially swells, making it difficult to penetrate sufficiently. It is therefore not appropriate to use acid alone as a deliming agent. The use of acid alone is not practical, as it requires frequent injections to properly control the pH. When acids are used alone, injection has to be done frequently due to the need to maintain an appropriate pH, which is not practical. In the present study, a method was put into practice which, despite being an inexpensive and simple method of deliming without the use of ammonium salts or special equipment, has few proven examples.

Keywords: deliming; ammonium salts; reducing the pollution load

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Preparation of cationic waterborne polyurethane and its application in leather dyeing

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Abstract: Cationic aqueous polyurethane was prepared by acetone method using isophorone diisocyanate (IPDI), polycarbonate diol (PCDL), polypropylene glycol (PPG), dibutyltin dilaurate (DBTDL), N-methyl diethanolamine (MDEA) and 1,4-butanediol (BDO) as raw materials. The effects of the conditions of R-value, PCDL: PPG ratio and MDEA addition amount on the performance of the prepared polyurethane emulsion were investigated, and the results showed that the best comprehensive performance of CWPU was achieved when the R-value was 1.1, the PCDL: PPG ratio was 1:1 and the MDEA addition amount was 6 wt%. And the optimal color fixation process was derived by the addition order, amount and pH of CWPU as indicators for application in leather dyeing. The color fastness of leather after color fixation can reach 4-5 grade for dry rubbing, 3 grade for wet rubbing, 4-5 grade for solvent washing and sunlight fastness, the K/S value of the leather is increased to 36.071, the dyeing rate has been improved significantly and it has wide applicability to different color dyes.

Keywords: cationic waterborne polyurethane; leather; fixing agent; dyeing

A novel composite retanning system based on pH-responsive hydrogen bonding and hydrophobic interaction for cleaner leather processing

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Abstract: Aldehyde-tanned leather is one of the promising choices to avoid the widespread chrome pollution in leather industry. However, due to the lack of metal ions, the aldehyde-tanned leather faces a significant challenge of not being able to effectively fix traditional anionic retanning materials, which seriously affects the quality of aldehyde-tanned leather. Herein, a novel composite retanning system consisting of a nonionic fluorinated surfactant with poly(ethylene oxide) and arylic resin was constructed, which breaks through the dependence of conventional leather materials on metal ions in terms of fixation. The main acting mechanism is that at the final stage of retanning, after reducing the float pH, pH-responsive hydrogen bonding and hydrophobic interaction synergistically drivenonionic fluorinated surfactant to self-assemble into bigger polymer composite aggregates, and then these aggregates are forced to deposit and fill in leather fiber gaps, thus obtaining more desirable retanning results. Furthermore, the retanned leather has better biodegradability and higher uptake rates for subsequent dye and fatliquoring agent, which can further eliminate the threat of formaldehyde to health, accelerate the degradation of waste leather in the nature, and reduce the chemical residual in wastewater, respectively. Consequently, this novel retanning system will benefit to satisfy evolving demands for related technologies toward cleaner leather production.

Keywords: organic chrome-free tanning; aldehyde-tanned leather; composite retanning system; pH-responsive hydrogen bonding; hydrophobic interaction; cleaner production

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Study on the stepwise combined-tanning system of TWS-TWLZ tanning agent

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Abstract: In this study, the delimed and bated cattle hide was pre-tanned with 2% TWS tanning agent, after the salt-free pickling the pre-tanned leather was combined-tanned by using TWLZ tanning agent. The results showed that, with this combined tanning system, the shrinkage temperature of the TWS-TWLZ tanned leather increased with increasing the amount of TWLZ tanning agent. When the amount of TWLZ was 6%, the moisture and heat resistance of the crust leather tended to be balanced, and the shrinkage temperature reached the peak of 84.5°C. Compared with the conventional TWLZ tanning, the shrinkage temperature of the combined-tanned leather increased by 12.1°C; the dispersion of TWLZ was much evener in the cross-section of leather, showing an increasing uptake rate as well, thus leading to a flat and fine grain surface, full body and bones, loose fibers, and higher mechanical strength for the combined-tanned leather. The TWS-TWLZ stepwise combined-tanning system represents a clean chrome-free tanning process.

Keywords: TWS tanning agent; TWLZ tanning agent; salt-free pickling; combination tannin chrome-free tanning; leather making

Preparation and application of cyanuric chloride cationic chrome-free tanning agent

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Abstract: Traditional chrome-free tanning agents, especially organic chrome-free tanning agents, tend to enhance the electronegativity of the fibers of crust leather during the tanning, which is negative for the absorption and binding of anionic materials in the subsequent processes. In this research, two kinds of cyanuric chloride-based cationic chrome-free tanning agents (TADM and TYDM) were synthesized, and their preparations were characterized by Fourier transform infrared spectrometer (FT-IR) and nuclear magnetic resonance spectroscopy (1H-NMR). The thermal properties and morphology of the tanned leather were analyzed by using thermogravimetric analysis and scanning electron microscope (SEM). The results indicated that the multi-point active chlorine groups in syntans had an excellent cross-linking effect on collagen fibers, which increased the shrinkage temperatures of leathers tanned by TADM and TYDM to 74.3℃, and 75.4℃, respectively. The tanned leathers exhibited flat and fine grain, clear pore texture, and highly dispersed collagen fibers. The tensile strength, tear strength, and load elongation of the TADM tanned leather were 22.38MPa, 65.86N/mm, and 21.88%, respectively, and those of the TYDM tanned leather were 35.85MPa, 72.87N/mm, and 27.46%, respectively. Based on dyeing experiments, both TADM and TYDM tanning agents can improve the absorption of anionic dyes and subsequent chemical materials. In addition, the TADM and TYDM tanning agents had excellent environmental benefits by significantly reducing the levels of total solids (TS), dissolved solids (DS), suspended solids (SS), and chloride compared with traditional chrome tanning technology.

Keywords: chrome-free tanning; no-pickling; cleaner production; syntans

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Filtration membranes based on collagen fiber network for efficient wastewater treatment

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Abstract: The presence of bacteria, antibiotics and other pollutants in wastewater poses a significant threat to the ecosystem and human health. Due to their low-cost and easy operation, filtration membranes have been widely used for wastewater treatment. In this study, abundant animal hides, which are by-products of the meat processing industry, were proposed as raw materials to fabricate a sustainable filtration membrane due to their natural, hierarchical, and renewable collagen fibrous network (CFN) with inherent biodegradability. After the removal of non-collagen compositions from animal hides, such as hair and fat, through a facile pretreating process base on green chemistry principles, a thin CFN based membrane (CFN-M) could be produced. Additionally, inspired by conventional leather tanning technology, tannic acids (TA) were selected as plant polyphenol tanning agent to modify collagen fibers based on tanning chemistry to improve the thermal stability of CFN-M. Moreover, the TA cross-linked CFN-M (TA@CFN-M) exhibited excellent antibacterial properties due to the production of reactive oxygen species (ROS) by the catechol functional group. The resulting TA@CFN-M achieved >99.9% water disinfection efficiency with a flux of 150 L m^{-2} h^{-1} via gravity-driven operation. Moreover, Fe-TA@CFN-M was obtained by cross-linking TA@CFN-M with Fe^{3+}. This Fe□TA@CFN-M showed excellent Fenton catalytic performance and could remove 96% of TC in wastewater within a residence time of 16.8 s. This work, based on the green chemistry principle, sheds light on designing new sustainable membranes for efficient wastewater treatment.

Keywords: collagen fibrous network; filtration membrane; wastewater treatment

Bisphenols: how the challenges of a new legislation can be addressed in leather chemicals and leather articles

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Abstract: Syntans are a key class of products in the leather manufacturing process. They are either made from phenol or from bisphenol S. Both are common residual monomers in these leather chemicals. Bisphenol F can form as a side product in the condensation of phenol with formaldehyde and is also found in many syntans. In a European initiative to reduce bisphenol A, a common starting material for many plastic articles with proven endocrine side effects, also Bisphenols S and F came into focus. The regulatory agencies called for evidence and currently run a public consultation for a proposed restriction of all bisphenols with the goal to prevent substitution of bisphenol A by other bisphenols. Proposed are limits of bisphenols for leather chemicals and for leather articles, so it will affect the whole value chain of leather.

In this presentation recent examples will be given how bisphenols S and F could be reduced significantly through process chemistry optimization, maintaining the performance properties of the optimized products on leather. The second part of the presentation will focus on data obtained from extraction of bisphenols from leather. Examples will be shown how optimized syntans contribute to optimized leathers concerning bisphenol levels.

Keywords: syntans; bisphenols; extraction of bisphenols from leather

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Waterborne polyurethane leather coating based on dynamic covalent bonds with ambient temperature self-healing properties

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Abstract: Waterborne polyurethanes with higher mechanical properties, excellent self-healing efficiency under moderately controlled conditions are a sort of interesting and useful finishing materials for a wide range of applications. Herein, we prepared a waterborne polyurethane with ambient temperature self-healing by a simple method introducing dynamic ditelluride bonds in the main chain. The particle size of the synthetic emulsions was evaluated by dynamic light scattering and the results showed that the emulsions had a uniform particle size distribution with a single peak distribution. The test of zeta potential values shows that all the emulsions have zeta potential values greater than 35, indicating that the synthesized emulsions have good storage stability. Finally, the mechanical properties of the material were tested by a tensile testing machine and the film of synthesized waterborne polyurethane presents strong tensile strength (~17.5 MPa), satisfactory elongation at break (~860 %), and rapid self-healing (healing efficiency 85.4 % of stress, 91.99 % of strain, at ambient temperature visible light irradiation for 30 min). Moreover, the leather coating finished with waterborne polyurethane showed favorable self-healing properties. The present work will be hopefully developed as a facile designing method to fabricate environmentally friendly water dispersion polymers with fast ambient temperature self-repairing performance.

Keywords: waterborne polyurethane; ditelluride bonds; self-healing; leather coating

Optimization of lipase defatting conditions and the law of electrophilic interaction with collagen protein

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Abstract: Degreasing is an important part of animal hide processing. The current chemical degreasing technology has deficiencies such as insufficient degreasing and high pollutant emissions, and lipase degreasing has become a key focus of future research and development in the leather industry. In this paper, the affinity relationship between lipase and key components of animal hides under the influence of different pH values and surfactants was investigated, and the optimum conditions for lipase reaction in the tanning process were explored.

The experiments were conducted by using soaked cowhide powder as the substrate, treating the leather powder back to water and adjusting the pH value, adding the gel-purified lipase protein, and characterizing the lipase protein content and activity in the supernatant after 8h of reaction by the Komas Brilliant Blue method and the olive oil emulsion method. The results showed that the electrophilic interaction between the enzyme protein and collagen was weakest when the pH value was at the lipase protein pI. Based on this, non-ionic surfactants TO5~TO10 were added to the reaction system, and the results showed that the surfactants would increase the pH at the weakest electrophilic interaction between the two and affect the lipase activity, and the effect of different surfactants varied; the experimental results were applied to the actual tanning, and it was concluded that the optimum pH=7.0 for leather deliming, the best softening time was 60 min, and the pH was reduced to about 7.0 after softening. pH is lowered to about 7.0, adding lipase for secondary treatment, adding soda ash to raise the pH to 10.0-10.5, and adding suitable surfactant at the same time, through the synergistic effect of enzyme-alkali-surfactant, the penetration performance of lipase in animal hides is improved, and the residual grease in hides can be reduced to about 4.2%. This paper provides the basis for the construction of lipase efficient degreasing technology, which provides more possibilities for the sustainable development of leather industry.

Keywords: leather; lipase; degreasing; protein affinity

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Process effect, pollution analysis, and product quality comparison of wet-blue prepared from seawater vs. industrial water based on benchmarking method

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Abstract: In order to reduce the fresh water intake in the leather-making industry, seawater was used instead of industrial water to prepare the wet-blue. Firstly, the main components and key indicators of the seawater after simple pre-treatment and the industrial water were compared and analyzed; then, using wet-salted bovine hide as raw material and industrial water as a benchmarking, the processes effects of seawater of soaking, liming, deliming-softening, pickling, and chrome tanning, as well as the different pollutants content in the different discharged waste liquid, and the performances of resulted wet-blue were investigated. Furthermore, the properties of the obtained crust and finished leather were also investigated. The experimental results show that compared to conventional industrial water, the application of seawater in leather-making had better soaking and liming process effects; and except for the high content of chloride ions, the content of other pollutants in the waste liquids were relatively close; and the obtained wet-blue, crust, and finished leather also had better sensory performance and physical-mechanical properties. All these experimental results indicated that using seawater instead of industrial water to prepare the wet-blue was feasible, which provided a new approach to solving the problem of freshwater resource shortage in the leather-making industry.

Keywords: leather-making engineering; seawater; wet-blue; processes effect

Human safety performance evaluation based on metal-free tanned shoe upper leather

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Abstract: Chromium-free tanning solves the chromium pollution caused by the tanning industry to a certain extent, but there is a certain risk of metal ion pollution. To improve the ecological performance of leather, a metal-free combined tanning strategy based on organic compounds containing amino groups, phenolic hydroxyl groups or aldehyde groups was designed. The metal-free combined tanning process was optimized by orthogonal experiments, and the structure and properties were characterized by Fourier transform infrared (FTIR), Inductively Coupled Plasma (ICP), differential scanning calorimetry (DSC), thermal gravimetric (TG) and scanning electron microscopy (SEM), and preliminarily established a human safety evaluation method based on cytotoxicity, oral acute toxicity, and skin sensitization. The experimental results show that the metal-free tanned eco-leather, shrinkage temperature ≥ 80℃, tear force ≥ 50N, crack height ≥ 7mm, coating fold fastness > 50000 times, color fastness to rubbing (dry/wet) ≥ grade 4, light resistance ≥ grade 3; and free formaldehyde ≤ 20mg/kg, VOC ≤ 100μg/g, total Cr, Al, Zr, Ti, Fe ≤ 50mg/kg, Cr^{6+}, azo dyes, entachlorophenol cannot be detected; and cytotoxicity ≤ grade 2; skin sensitization ≤ grade II, and no acute toxicity. On the basis of satisfying the physical-chemical properties of shoe upper leather, metal-free tanned ecological leather has better human safety performance, which can broaden the use and application scope of leather products and promote the ecological development of the leather industry.

Keywords: metal-free combined tanning; human safety performance; ecological performance; physical-chemical properties; ecological leather

Formaldehyde in surfactants used as leather auxiliaries and their effects on ECO quality of leather

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Abstract: Free formaldehyde is the key index for evaluating ECO quality of leather, and it has been strictly restricted by legislations and Standards almost all around the world. However, free formaldehyde as more than 75 mg/kg, can be still detected in leather. Amino resins were the major chemicals for investigating the resources of free formaldehyde in leather due to the fact that formaldehyde was commonly used as raw materials for their synthesis. Besides, other leather chemicals as tanning agents and dyestuffs could also contribute to formaldehyde in leather. Recently, surfactants widely used in leather auxiliaries, were tested and compared for their contribution to free formaldehyde in leather. The results indicated that some nonionic surfactants as alcohol ethoxylates (AEO) contain formaldehyde significantly. Their application in leather processing, especially in finishing operation, results in relatively high free formaldehyde in leather. This fact indicates another major resource of free formaldehyde in leather, and that some nonionic surfactants and auxiliaries should be carefully selected to control the pollution resources of formaldehyde in leather effectively.

Keywords: free formaldehyde; nonionic surfactant; alcohol ethoxylate

Development of an ecological process for the conservation of raw hides through gamma radiation

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Abstract: The objective of this work is to determine the optimal dose of gamma radiation appropriate to be used in the preservation of raw hides. In order to establish the optimal dose for long term preservation of raw hides, three doses of gamma radiation have been used: 10, 20, and 25 kGy. Irradiated and control (non-irradiated) hides were characterized physicochemically, spectral (ATR-FT-IR, EPR, Chemiluminescence), calorimetric (μDSC) physical-mechanical and microbiological according to the standards in force or in house methods. Differences in soluble nitrogen and mucopolysaccharide content were observed between irradiated and noniradiated samples. ATR-FTIR spectra indicated a decrease in the intensity of the specific collagen bands as the radiation dose increases. The chemiluminescence spectrum for the typical sterilization dose of 25 kGy showed that insignificant changes are produces up to 200 °C, after which degradation progresses faster compared to the non-irradiated sample. The oxidation processes, for the hide irradiated with the dose of 20 kGy, occurs more slowly compared to the control sample and samples irradiated with other doses. Antimicrobial analysis highlighted that irradiated raw hides are sterile for the 20 and 25 kGy doses. The analyzes carried out showed that there are some differences between non-irradiated and irradiated hides, but these differences do not influence the quality of the product after tanning.

Keywords: raw hides; preservation; gamma radiation; collagen modification

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Determination of the diffusion front in the process of accelerated tanning of leather

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Abstract: With accelerated tanning (30-60 min), the description of the movement of tanning compositions in the complex porous structure of the dermis by direct methods of hydrodynamics is difficult. The porous medium of the skin tissue has a random, irregular structure, which is difficult to describe accurately enough. In addition, the study of the penetration of chemical compositions through a porous medium is complicated by many factors. One of them is the difficulty of visualizing the flow of tanning compounds inside a porous structure in experimental studies. In this work, the penetration of tanning compositions in the process of accelerated tanning with chromium compounds was visualized by digital processing of color images. A computer program has been developed, which is based on the processing of a series of digital images formed during the impregnation of leather with a tanning composition after a certain time interval. The program allowed the authors to determine the diffusion front of the tanning agent passing through the dermis and the "shell" of the diffusion front. Visualization of the flow of tanning compositions inside the leather tissue made it possible to get closer to understanding the mechanism of their accelerated penetration into the complex structure of the dermis.

Keywords: tanning; visualization; diffusion front; diffusion front "shell"; digital processing of color images

Recovery and recycling of unused chemicals in commercial wet blue manufacture

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Abstract: There is significant waste of unused chemicals from the basic manufacture of wet blue leathers. To address this problem, changes are required, and four different problems have to be addressed:

1] The leather has to remain of high quality and meet customer specifications.

2] The techniques employed have to be manageable and provide a consistent end result.

3] The final effluents have to meet the demands or limits set by authorities.

4] In particular, stringent levels set for the chromium content of waste water discharges must be met.

As a result of developments that started more than 14 years ago a technique has been developed by BIOSK Chemicals, China to address these matters. This has been adopted by many manufactures of bovine and sheepskin leathers, and is easy to work with. It has been accepted for use within large tanneries of traditional layout, new-build situations, and small sized enterprise. Central to this technology is the collection of final floats that contain unused chemicals from the unhairing/liming process, at the end of tannage, and their reuse. These two processes are completely self-contained, and there are no discharges to effluent treatment. The only waste waters for treatment are from soaking, deliming/bating, and the wash waters from these processes. Manufacturing advantages include consistent wet blue leathers to specification, significant reductions in basic chemicals used for unhairing/liming, in the pickle process, and in offers of chrome tanning agents. In waste water treatment, the problem of sulfide removal from manufacture is eliminated and the level of inorganic salts is reduced. Of highest importance, the technology is major component for tanners to meet the most stringent demands for chromium in end-of-pipe discharges.

Keywords: recovery and recycling; wet blue manufacture; floats; unused chemicals; unhairing/liming process; discharges; tannage; effluent treatment

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Simplified beamhouse: one-step unhairing/opening collagen fiber-bundles/bating by dispase after alkali pre-swelling

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Abstract: The use of conventional lime/alkali system in beamhouse involves a series of complex operation units, which bring a lot of sulfide, suspended solids and ammonia nitrogen pollution. In this work, dispase was used for unhairing/opening collagen fiber-bundles/bating after alkali pre-swelling to replace lime/alkali process to simplify the unit operations in beamhouse. The effects of unhairing and fiber opening were investigated, and the physical and thermal properties and aggregate structure of tanned leather from alkali pre-swelling dispase process were evaluated and compared with those of the conventional one. As a result, alkali pre-swelling dispase process has good effects of unhairing and fiber opening, and the physical properties of tanned leather from this process are better than those of conventional process, while the pollution loads are greatly decreased. Especially, NaOH pre-swelling dispase process, rapidly hydrolyzes the proteoglycans in bovine hides, while the collagen hydrolysis is very little. Besides, collagen fibers dispersion, grain smoothness, the fluffy effect of collagen fibers and physical properties of tanned leather from the NaOH pre-swelling dispase process are the best, with hydrothermal shrinkage temperature comparable to that of conventional process. This work might provide a reference for simplifying the unit operations in beamhouse, reducing the environmental pollution and the development of high-quality leather.

Keywords: alkali swelling; dispase; leather making; unhairing; opening collagen fiber-bundles

Approaches of the control of collagenase activity on enzymatic unhairing process

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Abstract: As a cleaner technology, enzymatic unhairing is expected to replace the traditional $Na_2S/Ca(OH)_2$ unhairing system. However, in the enzymatic unhairing process, it is easy to cause excessive hydrolysis of collagen fibers due to the existing of collagenase component, resulting in loosen grain and even grain damage, thus lead to a poor quality for the finished leather. In order to reduce the excessive hydrolysis of collagen in enzymatic unhairing process, we have conducted continuous research on the regulation of collagenase activity in the process of enzymatic unhairing. Enzymatic unhairing process was performed under CO_2 supercritical fluid (SCF-CO_2) medium, and then the enzymatic unhaired pelt was tanned under SCF-CO_2 medium. The hydrolysis degree of collagen fiber was higher than that of conventional enzymatic unhairing while the shrinkage temperature of the tanned leather was increased. To reduce the activity of collagenase, enzymatic unhairing of cattle skin was carried out at low temperature (18-25 ℃). The results showed that the unhairing can be completed after 8 to 19 h in the temperature range of 18℃ to 25℃, and the content of soluble collagen in the unhairing solution is lower than that of conventional enzymatic unhairing at 35℃. Moreover, the application of collagenase inhibitors in the enzymatic unhairing process was studied. It was found that the addition of metal ions such as Cu(II), Mg(II), Zn(II), carboxylates such as sodium salicylate, sodium malonate, sodium succinate, etc., can effectively inhibit the collagenase activity in AS1.398 enzyme, while maintain relatively high caseinase activity, and reduce the hydrolysis of collagen during unhairing. Collagenase complex inhibitors such as Cu(II) + Fe(III), Cu(II) + sodium succinate, Cu(II) + sodium salicylate, which can reduce the relative activity of AS1.398 enzyme hydrolyzed collagen fiber to 6% ~ 36%, while the relative activity of hydrolyzed casein protein is higher than 68%. Histological observation and morphology analysis showed that the addition of collagenase inhibitor could improve the condition of grain surface and reduce the damage of collagen fibers. These approaches provide a potential solution to the excessive hydrolysis of collagen fibers in the enzymatic unhairing process.

Keywords: enzymatic unhairing; collagenase; collagenase inhibitor; enzymatic activity; leather-making

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The effect of hydrophobicity of acrylic resin retanning agent on the properties of non-chrome metal salts tanned leather

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Abstract: Non-chrome metal tanning agent is an ideal alternative to chrome tanning agent. However, the performance of the resultant leather is inferior to that of chrome leather due to the lack of retanning agents that are specially designed for chrome-free leather. In this work, in order to solve the problem of strong hydrophilicity prevalent in chrome-free leather and to provide guidance for improving the properties of chrome-free leathers, acrylic resin (AR) was selected as the model of retanning agents, and the effect of hydrophobicity/hydrophilicity of AR on the properties of non-chrome metal salt tanned leather were investigated. The results show that the appropriate hydrophobicity/hydrophilicity of AR is important to the properties of chrome-free leathers. When the mole ratio of hydrophilic/hydrophobic monomers in AR is 67/33, the AR could fully penetrate into the chrome-free leather and achieved the highest degree of fiber dispersion, which endow the crust leather with satisfactory dry heat stability, tear strength, and tensile strength. These results suggested that designing AR with suitable hydrophobicity/hydrophilicity is of great significance to improve the comprehensive performance of chrome-free leather.

Keywords: chrome-free; retanning; hydrophobicity/hydrophilicity; leather properties

Studying the possibility of using pine extracts in the leather and fur industry

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Abstract: The article discusses the possibility of using extracts obtained on the basis of pine bark as tanning and coloring agents for the leather and fur industry. Processing pine bark into plant extracts opens up the possibility of rational disposal of large-tonnage waste from the woodworking industry, with the production of a product suitable for processing leather and fur semi-finished products. The use of solvents of various nature in the extraction process makes it possible to change the physicochemical and technological properties of the finished extracts. Aqueous solutions of surfactants, alkalis, alcohols were used as extractants.The method of obtaining pine extracts and their concentration has a great influence on the technological properties of extracts and the quality of the tanned semi-finished product. The study of the relationship between the concentration of pine extracts and their wetting ability makes it possible to identify the most favorable parameters for the processing of leather and fur raw materials and to obtain a tanned semi-finished product of satisfactory quality. The qualitative composition of extracts affects the nature of the interaction of pine extracts with collagen and, as a result, the heat resistance of the resulting semi-finished product. Extracts derived from pine bark not only modify natural collagen, turning it into skin, but also have good coloring properties. The dyeing of the leather fabric during the tanning process is even. The color is deep and resistant to dry and wet friction. Coloring of the hairline in the case of perch tanning is not observed, only its light toning occurs. When carrying out tannin tanning with pine extracts by the spread method, dyeing of the hair cover is not observed. In addition, the tanning process by the spread method excludes the formation of toxic wastewater, characteristic of traditional tanning of leather and fur raw materials.

Keywords: pine extracts; tanning; dyeing; chemical composition; extractants

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Ultrasound-assisted extraction of oak bark soluble fraction as a potential source of tannins

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Abstract: The extraction of bioactive compounds from bark has been practiced throughout time. Their ability to act as tannins and antioxidants has been exploited by the tanners since ancient times. Compared to leather tanned using metals, aldehydes or bisphenols, vegetable tanned leather does not pose any risk to the environment and is totally safe to wear and to handle. In addition, it has unique attributes like long life, breathing, natural colors, smell and touch, reparability, acoustic properties, perfect for crafting (perfect for moulding, embossing, burnishing), aesthetic patina offered by ageing. Its antimicrobial activity is intrinsic and not due to the use of antimicrobial chemical agents.

Currently, the use of oak bark by-product/waste is aligned with the circular economy paradigm which encourages the use of renewables derived from waste, opposing the consumption of virgin resources in the production of goods. The increasingly strict restrictions on the use of organic solvents and the need to leverage new technologies and drive towards more sustainable industrial processes, thread towards the of non-conventional extraction methods such as ultrasound assisted extraction. However, the use of this technology is still in its infancy, as the mechanisms have not been sufficiently studied and solutions are not easily available on an industrial scale. The optimization of the extraction of soluble bioactive compounds is still a trending topic. In this study, a continuous extraction system based on a Dual Frequency Reactor (DFR) was used and the effect of the solvent (water, low concentration NaOH solution, low concentration of sulphite-bisulphite solution), solute/solvent ratio (from 1/20 w/v to 1/10 w/v),

extraction temperature (35, 50 and 60 °C) and extraction time (5 to 30 min) was evaluated through the content of phenolic compounds, content of soluble compounds and tannins. The molecular profile of the extracts was obtained by FTIR-ATR spectroscopy, while their tanning ability was tested on both hide powder (laboratory level) and hides (micropilot level) using thermal microscopy (MHT method) and dynamic differential microcalorimetry (micro-DSC). The optimal experimental condition (0.5% NaOH solution; 1/10 w/v; 55-58 °C; 30 min) showed a significant positive effect compared to conventional methods. These experimental values allows for technologically, financially and energetically feasible extraction and excellent tanning ability of the extracts.

Keywords: vegetable tanning; ultrasound extraction; circular economy; antimicrobial activity

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Biodegradable and recyclable OMW leather developed for automotive interior industry

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Abstract: Mingxin is one premier automotive leather manufacturer to supply variety of chrome, no chrome and vegetable tanned automotive leather for automotive seat, steer wheel, armrest as well as DP/IP application. With increased appeal of green and recycle concept drived by Premier Chinese electronic car brand, as Mingxin developed OMW leather free of Chrome and also free of aldehyde, the tanning agent OMW is made from olive mill waste water which contains variety of polyphenols including Tyrosol, Hydroxytyrosol, Catechol, Oleiropein, Caffeic, Gallic, Vanillic and Coumaric acids. These phenolic compounds have a strong tanning action, extraordinary antioxidant properties and also nice distinctive olive smell. However, leather tanned with OMW tanning abstract has strong negative charge and moisture absorption which make it difficult to keep the size stability of cut piece required by automotive industry. To overcome these technical obstacle, Mingxin developed hybrid tannage by adding cationic based polymer (CAP) with multi functional group at the end of OMW tanning process to increase the cationic charge of wet white and its reactive power with anionic retanning & fatliquoring material used in subsequent process. Attribute to the synergistic effect of OMW tanning fixed together with CAP material, leather made from this process has much tighter grain, much better softness and tear strength and also much less COD in waste water. The attractive part of this leather different from traditional chrome and no chrome leather is distinctive natural smell, biodegradable property, synonymous with circular economy and much less carbon footprint.

Keywords: OMW leather; hybrid tannage; distinctive olive smell

Convenient flow injection analyzer for each element monitoring system in tannery sewage

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Abstract: A low-cost detection device based on a flow injection pump and a spectrophotometer was developed for the automatic spectrophotometric detection of Cr^{3+}, Cr^{6+}, NH^{+}_{4}-N, NO^{-}_{2}-N, NO^{-}_{3}-N, and PO^{+4}-P in various sections of a tannery water plant. The equipment was computer controlled by a program written in Qt. The effects of reagent concentration, sample salinity, and foreign ion interference on the samples were investigated. The national standard method was used to judge the accuracy of the test, select the standard solution test method arbitration, and calculate the spiked recovery. A positive hexagonal carousel was set up in the device to place the standard liquid pool, into which the test liquid and standard color developer were pumped by peristaltic pump respectively, and the cuvette used a 1 cm quartz channel pool, which was pumped into the test after the sample finished color development. This device can be used for tanning production staff to quickly judge the effect of each chemical in the process and improve production efficiency.

Keywords: flow injection analyzer; automatic spectrophotometric detection; tannery sewage

Achieving the evolution of radiation protection materials by integrating the merits of leather

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Abstract: The widespread applications of ionizing radiations such as X/ γ-rays in industrial production as well as daily life call urgently for lightweight, high-efficiency and high-strength wearable radiation protection materials. In the recent years, we have designed and fabricated the first-generation natural leather-based radiation protection material, and evolved it into the third generation by integrating the merits of leather. The first generation of leather-based radiation protection materials focus on the loading and dispersion of the functional component, i.e. elements with high atomic number (Z). The structural and chemical merits of leather is preferable to reduce the particle size of high-Z elements, and therefore to enlarge the radiation performance. In this regard, an "impregnation–desolvation" strategy has been developed to introduced the high-Z elements following the process of tanning, which loaded high-Z element ions via coordination, hydrogen bond and electrostatic interaction. Additionally, high-Z element oxide nanoparticles have been loaded into leather with the help of poly(acrylic acid) resin, which is inspired by the retanning process. The resultant materials both demonstrated good radiation shielding performances stemming from the uniform dispersing capability of leather to high-Z elements.

The second generation of leather-based radiation protection materials are devoted to offset the drawback of weak absorption in certain energy region. Inspired by the coating process of leather manufacturing, the first-generation materials are evolved by coating a thin polyurethane layer containing the second kind high-Z element to gain enhanced radiation shielding capability by the synergistic effect of bis-high-Z elements. The thin coating layer has successfully complemented the weak absorption region of the material, and has elevated the radiation protection performance to a large extent.

The third generation of leather-based radiation protection materials are committed to further levitate the radiation protection capability without increasing the material density. To achieve this goal, advanced structural design has been carried out, and Barbican-inspired core–shell nanoparticles comprised of bis-high-Z elements are fabricated and incorporated into natural leather. By regulating the interaction between X//γ-ray photons with high-Z elements, the attenuation and absorption of photon energy have been maximized, and the radiation protection performances have been raised to a new stage.

In a word, by integrating the merits of leather, we have fabricated advanced leather-based radiation protection materials, and have achieved the evolution of radiation protection materials with light weight, high efficiency and high strength.

Keywords: natural leather; tanning; re-tanning; coating; radiation protection

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Ionic conductive leather based electronic skin with excellent sensing and environmental stability

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Abstract: Electronic skin (E-skin) is an artificial skin that mimics the function of human skin, which is considered as the most attractive candidate to replace human skin. Herein, a novel ionic conductive hydrogel/ leather based E-skin (ICHL) was constructed via temperature induced in-situ forming technology, which solved the challenges of uneven distribution of conductive components and complex manufacturing process faced by traditional conductive leather. Due to the efficient integration of components, ICHL with interpenetrating network structure and multiple physical interactions achieved an efficient balance among conductivity, mechanical strength and versatility. Firstly, Hofmeister effect was used to induce and rearrange the aggregation state of hydrogel polymer chains, which successfully balanced the inherent contradiction between conductivity and mechanical properties of ionic conductive hydrogel, laying the foundation for its recombination with leather. Secondly, the "permeation and self-assembly" of hydrogel in leather was achieved by temperature induction to construct ICHL. The interpenetrating network structure between the two improved the mechanical properties of ICHL and the effective fixation of conductive networks. Meanwhile, the interpenetrating network of hydrogel in ICHL provided a continuous, highly conductive platform for ion transport. In addition, the glycerin/water system endowed ICHL with low temperature tolerance and moisturizing properties, providing its normal work in harsh environments. Finally, these characteristics enabled ICHL to realize real-time monitoring of human body, which exhibited broad application in wearable flexible sensors and E-skin. This study provides a simple strategy for the design of natural leather based E-skin. Meanwhile, it illustrates novel and multifunctional manufacturing platform for high-performance E-skin.

Keywords: leather based electronic skin; ionic conductive hydrogel; permeation and self-assembly

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A unidirectional water penetration leather designed with dual-gradient structure enables efficient sweat release

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Abstract: Excessive sweat secreted from the skin often causes sticky and cool feelings in outdoor sensations. Leather as a wearable material can absorb sweat but hardly evaporate it. It is generally accepted that Janus membrane with surface energy gradient or aperture gradient can endow the unidirectional water penetration property to facilitate sweat removal and regulate skin temperature. Hence, a dual-gradient hierarchical leather (i.e., leather with both surface energy and aperture gradient, denoted as DGH-L) was synthesized. Specifically, the hydrophilic urethane resin and hydrophobic fluorinated polymer were in-situ deposited onto different sides of the leather to obtain surface energy gradient. And the aperture gradient was derived from the combination of leather with natural aperture gradient and fiber membranes with programmed pore. The DGH-L exhibited unidirectional water penetration and antigravity rise in pH range of 4.5~9. When the hydrophobic side with large pore contacted the liquid, the DGH-L driven by capillary force can pump it to the hydrophilic side with small pore through leather. Importantly, DGH-L can weaken the sticky adhesion, promote sweat removal, and avoid excessive cool feeling on the skin. This work offers a new strategy into functional leather with efficient sweat release to address personal comfort in outdoor conditions.

Keywords: functional leather; unidirectional water penetration; dual-gradient structure

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Facile "synergistic inner–outer activation" strategy for nano-engineering of nature-skin–derived wearable daytime radiation cooling materials

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Abstract: Natural skin–derived products, as traditional wearable materials are widely used in people' s daily life due to the products' excellent origins. Herein, a versatile daytime-radiation cooling wearable natural skin (RCskin) consisting of the collagen micro-nano fibers with the on-demand double-layer radiation cooling structure is nano-engineered through the proposed facile "synergistic inner–outer activation" strategy. The bottom layer (inner strategy) of the RCskin is fabricated by filling the skin with the $Mg_{11}(HPO_3)_8(OH)_6$ nanoparticles by soaking. The superstratum (outer strategy) is constituted by a composite coating with an irregular microporous structure. The RCskin harvests the inherent advantages of natural building blocks including sufficient hydrophobicity, excellent mechanical properties, and friction resistance. Owing to the subtle double-layer structure design, the solar reflectance and the average emissivity in the mid-infrared band of RCskin are ≈92.7% and ≈95%, respectively. Therefore, the RCskin' s temperature in the sub-ambient is reduced by ≈7.5°C. Various outdoor practical application experiments further substantiate that RCskin has superior radiation cooling performances. Collectively, RC-skin has broad-application prospects for intelligent wearing, low-carbon travel, building materials, and intelligent thermoelectric power generation, and this study also provides novel strategies for developing natural-skin–derived functional materials.

Keywords: collagen micro-nano fibers; natural skin; radiative cooling; structure design; wearable materials

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In-situ construction of hydrogel coating on leather surface for flexible wearable devices

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Abstract: In leather manufacturing, crust leather often requires to be endowed durability and functionality via the finishing process. Among the traditional finishing agents, film-forming defects of biomass-based ones are obvious, for example, casein as one of the most widely used finishes has the disadvantage of poor resistance to microorganisms. For this reason, in this research, to further enhance the stability, intelligence and convenience of resultant leather, based on our previous study, it is proposed to construct an in-situ growth of biomass-based double network hydrogel coating on the crust surfaces, of which a dual solvent system was used and conductive ions or nanoparticles were introduced. The results demonstrated that the strain sensor with leather as the substrate was successfully prepared under the function of "casein micelle-nanoparticles double cross-linking", which imparted leather substrate with excellent sensing and mechanical properties. This study provides a reference value for the construction of hydrogel coatings on the surface of the leather and also provides an essential idea for the realization of high-value application of leather and other flexible product. It was found that the tensile strength of the as-prepared hydrogel could reach 210 kPa. It is worth mentioning that the thickness of the coating on the leather substrate can be controllable (10 μm ~ 500 μm), and the adhesion was proved excellent. In addition, it could keep stable in a wider temperature range (- 20 ℃ - 50 ℃), and also showed high robustness and stability as a strain sensor.

Keywords: leather finishing agent; hydrogel coating; double network; strain sensor

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Construction of stable and efficient flexible underwater sensors based on Zr^{4+} ligand cross-linked CNTs and leather collagen fibers

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Abstract: In recent years, flexible sensing materials have been widely used to integrate various underwater sensors. However, the complex water environment such as water temperature, water salinity, water acidity and alkalinity, tidal energy impact, water biological damage, etc., seriously limit their practical use effect. In this work, flexible conductive leather (CNTs@Zr@OTL) was prepared by "bridging" collagen fibers with carbon nanotubes (CNTs) based on the coordination and complexation of zirconium ion (Zr^{4+}) with the unique three-dimensional collagen fiber network of natural leather as the "structural template", and a flexible pressure sensor of collagen fibers was constructed accordingly. At the same time, the effects of its use under different water environment influencing factors were explored. The composition, microstructure and sensing properties of CNTs@Zr@OTL were investigated by FT-IR, XRD, SEM, XPS and electrochemical workstation. The experimental results showed that Zr^{4+} played a "bridging" coordination role between collagen fibers and CNTs. When the dosage of CNTs was 8.5%, the resistivity of CNTs@Zr@OTL was about 7.4 Ω·cm, the shrinkage temperature was about 74.5℃, the biodegradation performance was 24 h and the wide sensing range (20%-120%), high sensitivity (300 ms response time and 100 ms recovery time), strong water stability, and excellent anti-swelling properties. We further investigate the sensing performance of the underwater sensor in three different environments: air, pure water, and seawater, and also investigate the effects of water temperature, water acidity and alkalinity, and water salt on the underwater sensor. The experimental results show that CNTs@Zr@OTL still has stable and excellent sensing performance under complex water environment. Finally, the application of simulated underwater sensors in response to small external stimuli, rain response, multi-angle response, and water depth response applications, and through the wireless module and mobile phone interconnection, to achieve SOS distress personnel, indicating its application potential in underwater motion monitoring, emergency rescue, and other fields.

Keywords: underwater sensing; collagen fibers; coordination

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Smart and high-efficiency cleaner nano tanning technology based on modular penetration and controlled release strategy

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Abstract: The conventional tanning process suffers from uneven penetration, low crosslinking efficiency, and inadequate performance due to small tanning agent size, leading to resource waste, environmental pollution, and poor tanning performance. Therefore, a simple and efficient cleaner tanning technology is urgently needed. In this study, a pH-responsive metal-loaded nanoparticles (M-NPs) tanning agent with an inert polymer surface was fabricated and proposed a novel two-step tanning approach termed "modular penetration and controlled release" (MP-CR). A multicomponent copolymer containing carboxyl, epoxy, and polyethylene glycol groups was synthesized using free radical polymerization. This copolymer was then used as a template to prepare M-NPs through an in-situ mineralization technique. This method is versatile, suitable for common metal tanning agents like Cr and Al. The resulting nano-tanning agent, with a particle size of around 100 nm, demonstrates excellent pH responsiveness, salt stability, and resistance to proteins. Compared to conventional small molecule metal tanning agents, nano-sized tanning agents can rapidly and uniformly distribute within collagen fibrils through modular penetration. Subsequently, controlled release of metal ions occurs through the disassembly of M-NPs when the pH of the tanning liquor decreases below 3. This facilitates deeper penetration of metal ions into the microfibril. Moreover, the copolymers with multiple reactive groups generate organic-inorganic synergistic tanning effects by interacting with released metal ions, resulting in a remarkable increase in the absorption rate of metal ions. As a consequence, highly effective tanning performances were achieved, and water pollution produced by heavy metal ions can also be tremendously reduced from the source.

Keywords: metal-loaded nanoparticles; modular penetration and pH-controlled release; cleaner leather manufacturing

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Self-dense skin-based conductive hydrogel for underwater salvage

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Abstract: The environment of underwater salvage is very special, and many factors such as real-time water conditions, the depth of salvage and the complexity of underwater environment could greatly affect the smooth progress of the salvage process. How to accurately judge the type of underwater salvaging item is an important topic to improve the efficiency of underwater operations. Herein, following the "top-down" strategy, a skin-based conductive hydrogel was designed and constructed by using the natural collagen fiber network of goatskin (CFNG), which was crosslinked by green, renewable and cheap vegetable tannin in the presence of conductive ions. The resulting CFNG-based conductive hydrogel exhibited high toughness, high modulus and high sensitivity. It showed 150% of the maximum fracture strain and 20 MPa of the maximum tensile strength, and excellent strain sensitivity (GF (gauge factor) =12.5), and it could perform well in a variety of extreme environments. The underwater anchor grab, constructed by this hydrogel, could recognize objects specifically in various complex environments and reflect the river/ocean environments in real time through the conversion of electrical signal to digital signal, so as to provide early warning for underwater operations. Further, the underwater anchor displayed good recycling ability and identification accuracy, which can greatly reduce the workload of river/ocean operations, ensure the construction safety, and save time and economic costs. In short, as a kind of intelligent sensing materials, the present skin-based conductive hydrogel features the characteristics of intelligence, multi-function and automation, and has significant application potential in many fields such as artificial intelligence and human-machine interface.

Keywords: underwater salvage; skin-based conductive hydrogel; underwater anchor grab

A flexible leather-based sensor via dual-in-situ growth of conductive materials for human motion detection

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Abstract: Natural leather with mechanical strength, flexibility and wearing comfortable has long been used to make wearable products. Thus, it is a favorable candidate for flexible substrate material of wearable sensor. Nowadays, many strategies such as impregnation, filtration and coating have been used to prepare leather-based sensors. However, their sensing performance is still limited by the poor uniformity of conductive network and the weak interface between conductive materials and leather. Herein, it was innovatively proposed that polypyrrole (PPy) and silver nanoparticles (AgNPs) were grown in situ on the surface of collagen fibre in picked goatskin by wet processing method. Then, the tanning process was carried out to produce the leather-based flexible wearable sensor with excellent conductivity, hydrothermal stability, chemical stability and electric heating performance. Specifically, in-situ growth of PPy and AgNPs based on wet processing technology ensured the uniform penetration and distribution of conductive materials in leather. Meanwhile, the multiple hydrogen bonds between conductive materials and collagen fibre provided the firm combination to avoid dropping of conductive materials, thus improving sensing performance. The synergistic effect of PPy and AgNPs endowed the leather-based flexible wearable sensor with high sensitivity (3.76 and 0.451 kPa^{-1}), wide detection range (0-80 kPa), low detection limit (10 Pa) and fast response capability. These characteristics enabled the sensor to monitor the subtle activities and large-scale movements of human body in real time. In addition, the obtained sensor could achieve articular thermotherapy by effectively adjusting different temperatures. This study provides a new idea for the intelligent design of traditional leather materials, multi-dimensional perception of electronic skin and artificial intelligence.

Keywords: flexible piezoresistive sensor; conductive leather; dual-in-situ growth

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Topic III Novel strategies in high-efficiency and intelligent leather processing technology

Photothermal convertible hydrogel for solar-driven water purification

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Abstract: Water scarcity is threatening human health and draining precious energy resources as a result of climate change and water pollution from small molecule dyes, heavy metals, oil, yeast and bacteria. However, the synthesis of multifunctional hydrogels with superhydrophilic, strong photothermal conversion, decontaminating and antimicrobial properties is still a major challenge. This article proposes a novel multi enhancement design strategy for carboxymethyl chitosan (CMCS) and photothermal carboxylic acid multi walled carbon nanotubes (CMWCNTS), based on an effective and simple one pot two-step preparation method to ensure superhydrophilicity and decontamination performance. Remarkably, the hydrogel exhibits tunable volume shrinkage-release response behavior and drives a dynamic switch of hydrophilic/hydrophobic phase transformation at the lower critical solution temperature. Due to the photosensitive effect, the resultant hydrogel can purify water from various harmful reservoirs containing small molecules, oils, metals, and bacteria with a water purification rate of 9.83 $kg \cdot m^{-2} \cdot h^{-1}$, using only one sunlight irradiation. This nature-inspired strategy, which can endow the hydrogel with excellent water purification rate, decontamination and antibacterial function, provides a meaningful insight into the rational design of solar absorbent hydrogels in the sustainable production of clean water to improve the quality of human life.

Keywords: passive solar-driven hydrogel; wastewater purification; photothermal carboxyl multiwalled carbon nanotubes; carboxymethyl chitosan; poly (N-isopropyl acrylamide)

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Carbon-quantum-dot-crosslinked collagen-based dual-network conductive organohydrogel for strain and bioelectric sensing applications

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Abstract: Conductive hydrogel-based flexible sensors have been widely investigated in the fields of human-computer interaction, sports and health monitoring, soft robotics, tissue engineering, and bionic e-skin. However, it is still a big problem to construct a collagen-based conductive hydrogel with excellent mechanical strength and multiple functions. Herein, carbon quantum dots containing aldehyde groups (CQDs-CHO) were firstly fabricated by using the hydrothermal method in which oxidized sodium alginate was adopted as carbon source. The CQDs-CHO were then used as a crosslinking agent to form the first dynamic reversible crosslinking network owing to its Schiff base reaction with amino group of collagen; meanwhile, the reversible metal coordination bonds between PAA (polyacrylic acid) and Fe^{3+} ions were used to construct the second crosslinking network to realize the formation of dual-network (DN) collagen-based conductive hydrogel. Further, the introduction of silver nanoparticles (AgNPs), prepared by using ethylene glycol as both reducing and stabilizing agents, led to the construction of collagen-based DN conductive organohydrogel (called PACOE) with high mechanical properties, self-healing, anti-freezing and moisturizing, antibacterial, self-adhesion and biocompatibility. Based on the combined action of Fe^{3+} ions and AgNPs, PACOE exhibited good conductivity and strain-resistance responsiveness, and could be used not only as flexible strain sensors to stably record various human movements, but also as biological electrodes to monitor physiological signals of human body. In short, this work provides a new CQDs-CHO crosslinking method for the fabrication of collagen-based conductive organohydrogel with high mechanical strength and multi-functionality, and this organohydrogel is expected to, strain sensors as well as bioelectrodes, possess broad application prospect in the fields of flexible electric devices biomedicine.

Keywords: collagen; conductive organohydrogel; strain and bioelectric sensing

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Leather-solid-waste-derived aerogel for highly thermal energy storage, photothermoelectric conversion and heavy metal adsorption

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Abstract: How to improve the energy conversion efficiency of phase change materials (PCM) and prevent its leakage has always been a challenge for renewable and sustainable energy storage technology. Aerogel with high porosity, high specific surface area and low density has been widely applied in adsorption separation, photocatalysis, energy storage and other fields. In this work, collagen fibers, obtained from the limed hide solid waste (LHSW), were firstly copolymerized with acrylic acid (AA) to prepare shape-stable composite hydrogel, and the corresponding aerogel was subsequently yielded through the freeze-drying method, and further applied as a carrier of PCM and photothermoelectric agents, and a heavy metal adsorbent. Compared with the conventional aerogels constructed by synthetic or natural polymers, this aerogel containing collagen fibers featured the porous 3D network structure with a larger space and more adsorption sites for the storage of PCM, making this aerogel possess considerable energy storage density, thermal conductivity efficiency and cycle stability. The obtained aerogel exhibited commendable adsorption properties for many metal ions such as Fe(III), Cr(III), Cr (VI), Au (III) and Ag (I), and demonstrated excellent photothermoelectric conversion efficiency. Thus, this study provides not only an efficient, green, inexpensive treatment method of LHSW, but also a high value-added porous aerogel with the shape stability of PCM, the improved optical, electric and thermal energy conversion performance, and outstanding adsorption ability to heavy metals.

Keywords: leather solid waste; aerogel; phase change materials

Topic III Novel strategies in high-efficiency and intelligent leather processing technology

Nanocatalysts induced self-triggering leather skin for human–machine interaction

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Abstract: Electronic skins that mimic the comprehensive functions of human skin are very interesting for the development of human-computer interaction (HMI). Traditional conductive leather faces the challenges of uneven dispersion of conductive elements and complex manufacturing processes, which hinders its application in electronic skin. In this paper, a novel ion-conductive leather skin was developed by using ionogel in situ self-triggering gel reaction in the layered structure of leather matrix. Core-shell liquid metal@catechin nanocatalysts can be rapidly and uniformly gelled under ambient conditions in tens of seconds. The interpermeable ion-gel network generated within the leather matrix not only provides a 3D continuous and highly conductive pathway for ion transport, but also forms multiple bonding to achieve strong interfacial interactions. These superior properties give the leather skin excellent mechanical robustness (tensile stress: 17.8 MPa; Toughness: 1590 kJ/m^3), high air transmission rate (720 mL/cm^2/h) and water vapor transmission rate (70 g/m^2/h), and wide environmental tolerance (-80 ~ 100 ◦C). Impressively, the leather skin sensor shows a stable and fast response in just 40 milliseconds. The bionic glove as a gesture-recognizable wearable controller for HMIs further proves the appeal of leather skin. This work opens up a new horizon for the development of ionic conductive leather skin, which will have a profound impact on wearable electronic systems.

Keywords: leather skin; Ionically conductive leather; liquid metal@catechin nanocatalyst; self-triggering ionogel; bionic glove

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Enhanced performance of an ecological leather-based triboelectric nanogenerator by "reinforced via inner and surface" strategy

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Abstract: Chrome-free tanning and intelligentization are hot topics in leather-related research. Leather collagen fiber is a natural material with a unique hierarchical structure, which is a promising substrate for wearable electronics due to its advantages such as breathability, biocompatibility and biodegradability. However, weak polarity and poor hydrophobicity of the leather fibers severely limit the development of high-performance leather-based self-powered flexible sensing materials. Herein, an ecological leather-based triboelectric negative material was proposed through the facile "reinforced via inner and surface" strategy. Firstly, based on tanning theory, polyhedral oligomeric silsesquioxane based fluorinated copolymer composite (POSS/FPs) was first synthesized using vinyl cage sesquisiloxane (POSS-Vi), trifluoroethyl methacrylate (TFEMA), and methacrylic acid (MAA) as raw materials via a radical polymerization approach. The as-prepared POSS/FPs combined with zirconium sulfate was then applied in the leather tanning process to impart tanning properties, electron-trapping properties and polarity (inner strategy). Secondly, based on the interface design, fluorine-bearing silane chains were grafted to the surface of tanned leather by chemical vapor deposition method to increase the triboelectric charge density and improve the hydrophobicity of tanned leather (outer strategy). The shrinkage temperature of the prepared leather could reach 88.6 °C, displayed an excellent electrical output (45 V) and good hydrophobic property. Interestingly, the output voltage remained stable after 4000 s of continuous operation. As such, an effective and powerful strategy is proposed to construct leather-based triboelectronegative materials based on environmentally friendly chromium-free tanning methods.

Keywords: green tanning; reinforced via inner and surface; leather based triboelectric material

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Carbon quantum dots derived from leather solid waste: s novel, efficient and sustainable masking agent for leather tanning

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Abstract: Tanning is a key industrial process in leather production and a crucial step in transforming skin (or hide) into leather. Traditional chrome tanning possesses troubling application prospects due to its pollution problem. Chrome-free metal tanning agents (such as Zr(IV) and Al(III)) are widely recognized for their strong coordination ability and environmental friendliness, which could replace chrome tanning to achieve efficient and sustainable tanning. However, the strong crosslinking reactions of these metal tanning agents with leather surface fibers could greatly weaken their uniform penetration ability inside the leather, thereby affecting their tanning performance. Therefore, the development of masking agents plays a crucial role in improving the tanning performance of these chrome-free metal tanning agents. Carbon quantum dots (CQDs), as a new type of carbon nanomaterials, have outstanding characteristics such as easy surface modification, excellent chemical stability, and biocompatibility, and have considerable application prospects in many fields. Herein, we synthesized biomass-derived functionally modified carbon quantum dots (BFM-CQDs) by the typical but simple hydrothermal method, in which the delimed cattle pelt waste (DCPW) was applied as the synthetic precursor and carboxyl/phenolic hydroxyl reagents were added to achieve functional modification of BFM-CQDs. The resulting BFM-CQDs had rich coordination groups on their surface, which could form the coordination interactions with the chrome-free metal tanning agents during the tanning process, thus weaken their crosslinking reactions with collagen fibers on the leather surface, promoting uniform penetration and efficient binding of tanning agents, and thereby enhancing the tanning effect. Results indicate that BFM-CQDs, as the masking agents, could effectively improve the shrinkage temperature of leather and modify the tanning effect of chrome-free metal tanning agents. In short, this work not only provides a new type of CQDs prepared by using the leather solid waste, which realizes the high value-added resource utilization of leather solid waste, but also contributes to a novel strategy for efficient and sustainable tanning by using the CQDs as masking agents.

Keywords: leather solid waste; carbon quantum dots; masking agent

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Reduction of carbonization and gas emissions using mechatronics based intelligent laser beam machining with machine learning for cutting leather with better environmental measures for operator health

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Abstract: Laser cutting is gaining considerable attention for leather cutting, since it can eliminate the need for certain manual procedures. The attributes of laser technology for leather cutting include adaptability, mass production, the capability to cut complicated patterns, the ease of producing tailored components, and a reduction in leather waste. Due to the thermal influence of conventional laser cutting, a slight carbonization of the cut edge occurs. In this investigation, an endeavour is proposed to design and develop a self-tuned laser diode assisted laser beam machining system using a mechatronics engineering approach to analyse the impacts of the laser diode on environmental measures such as carbonization, striations, dross, and emission formation in leather cutting. It has been inferred that only little effort was made on the laser diode assisted LBM process to reduce carbonization and gas emissions. This machining system has a wide range of Pulse Width Modulation (PWM) control, self-tuned Standoff Distance (SOD) control, effective emission filters, and Graphical User Interface (GUI) implementation with a touch display. The chrome vegetable tanned cow leather was machined under various machined conditions. The analysis of carbonization through machine vision, kerf width, Material Removal Rate (MRR), and emission rate has been analysed and recorded to obtain the optimal control loop approach and optimal parameters for leather cutting.

Keywords: laser diode; PWM; SOD; carbonization

Synthesis of isocyanate-based polymeric dye with high coloring component content and its application in the dyeing of organic chrome-free leather

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Abstract: Leather dyeing is an important step that endows the resultant leather products with the first property to be assessed by the consumer or customer for making judgments. Achieving high-performance dyeing of organic chrome-free leather is becoming one of the keys to boosting the sustainable development of the leather industry. Herein, we proposed a strategy to fabricate isocyanate-based polymeric dye (IBD) with high coloring component content (higher than 50%) and investigated its application in the dyeing of biomass-derived aldehyde-tanned leather. GPC and NMR analyses indicated the successful synthesis of IBD, and its weight average molecular weight could be controlled at around 1800 g/mol. Furthermore, the as-prepared IBD was used in the dyeing of biomass-derived aldehyde-tanned leather. The application experimental results showed that the crust leather prepared from IBD dyeing had higher color fastness than the crust leather dyed with conventional anionic dye (CAD). Besides, the IBD-dyed crust leather had better fullness than CAD-dyed crust leather. This work suggests the desirable application potential of IBD in the manufacturing of high-performance organic chrome-free leather products.

Keywords: polymeric dye; biomass-derived aldehyde; chrome-free tanning; dyeing performance; physical properties

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Synthesis and properties of novel fluoroacrylate containing rigid cyclohexane structure as a mesogenic core

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Abstract: Fluorine-containing liquid crystal polymers have excellent hydrophobic stability, so they have attracted much attention in the field of stable hydrophobic coatings. Thus, a novel fluoroacrylate monomer (FAM) containing rigid cyclohexane structure as a mesogenic core was simply synthesized to improve the hydrophobic stability of fluoropolymers using isophorone diisocyanate (IPDI), hydroxyethyl methacrylate (HEMA) and perfluorohexylethanol (S104) as raw materials. The structure, liquid crystal behavior, thermal properties, and hydrophobic properties of monomers and homopolymers were studied by Fourier transform infrared spectrometer, nuclear magnetic resonance spectrometer, X-ray diffractometer, polarizing microscope, differential scanning calorimeter, thermogravimetric analyzer, and static/dynamic water contact angle measuring instrument and dodecalofluoroheptyl methacrylate (DFMA) used as a reference substance. The results showed that the synthesized product was a fluoroacrylate containing a rigid cyclohexane structure. The monomer and homopolymer are thermotropic liquid crystals, which facilitate the dense distribution of fluorocarbon chains at the end of the homopolymer side groups and prevent surface group reconfiguration when the homopolymer comes into contact with polar liquids, resulting in better thermal stability, hydrophobicity and hydrophobic stability. Therefore, this study will find a broad application prospect in the field of stable hydrophobic coatings on flexible substrate such as leather matrix.

Keywords: fluoroacrylates; rigid side-chain liquid crystal; surface free energy; hydrophobic stability

Synthesis of bisphenol-less retanning agent using innovative technology for eco-benign leather production

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Abstract: Leather making with unique characteristics is becoming increasingly important due to regulatory restrictions in REACH, which in turn leads to a growing demand for sustainable products. The retanning process is crucial in leather production, as it significantly modifies the properties of leather, such as fullness, softness, grain tightness, and fastness. However, concerns have emerged regarding bisphenols and their derivatives due to their endocrine disrupting properties. The European Chemicals Agency (ECHA) has proposed restrictions, including limiting the concentration of BPA and BoSC (BPB, BPF, BPS, and BPAF) in leather articles and mixtures to 500 ppm. Certain bisphenols like BPA, BPS, and BPB are identified as substances of high concern (SVHC) under REACH regulations and are included in the Candidate List for authorization. These restrictions directly impact the Leather Industry Business, presenting significant challenges for tanneries and the chemical industry. However, chemical manufacturers are actively working to develop alternative products for bisphenol-based retanning agents and manufacture products with extremely low bisphenol limits.

Our R&D group has made a significant breakthrough in addressing the challenges through the development of BENITAN, an innovative range of retanning syntans. BENITAN, offers low-bisphenol and zero-formaldehyde retanning agents derived from special derivatives. These unique eco-benign products were developed using advanced technology and chemistry, resulting in high-quality leather with exceptional characteristics. The leather industry's shift towards bisphenol-free production is crucial for long-term success, fulfilling customer needs, and promoting sustainability.

Keywords: bisphenol; retanning; BENITAN

Metal-organic framework materials based chrome-free leather tanning system

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Abstract: As an essential wearable and decorative material, the demand for eco-friendly and chrome-free leather-based merchandise in human's existence has been increased. The adjustable components and abundant metal sites provide the attractiveness of metal organic framework materials (MOFs) in the realm of leather tanning. Herein, a sequence of MOFs-based materials have been utilized into leather tanning process in this study. Firstly, the shrinkage temperature (Ts) of leathers tanned by various metal based MOFs were investigated to examine the influence of metal centers on their tanning properties. Then, the metal ion doping MOFs were prepared to further enhance the tanning overall performance of MOFs-based tanning agents. The structure, morphology, and stability of MOFs-based tanning agents are characterized by using XRD, SEM, FT-IR, and TG. The results showed that MOFs have a stable structure and small size, which is conducive to infiltrate into collagen fibers. The application performance of tanned leather was investigated using Ts as the main indicator. The experimental results exhibited that MOFs could appreciably increase the Ts (> 25℃) of tanned leather when it was utilized into the tanning as a chrome-free tanning agent, indicating that MOFs could significantly improve the hydrothermal stability of leather. It is conclusive that this study can provide theoretical guidance for promoting the application of MOFs in the field of chrome-free tanning.

Keywords: metal-organic frameworks; chrome-free tanning; nano-tanning agent

Polyphenols: from leather manufacturing to engineering multifunctional materials

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Abstract: Polyphenols are abundant natural products in plants traditionally used for leather tanning. They possess unique properties that could enable new functional materials beyond leather manufacturing. Our research utilized the metal coordination and surface adhesion abilities of polyphenols to engineer nanocomplexes that rapidly self-assemble on cell surfaces, forming biohybrid Cellnex systems. Erythrocyte-nex exploited polyphenol adhesion to deliver 11-fold more therapeutic agents to the lungs versus controls. Macrophage-nex harnessed polyphenol's versatility to functionalize antibodies and double tumor suppression. We also constructed supraparticles from catechol-terminated building blocks via hierarchical polyphenol assembly. The supraparticles demonstrated tunable functions including dual pH-responsiveness, light-controlled permeability, and rapid cell fluorescence labeling. Additionally, we designed polyphenol-based membranes that extract uranium from seawater through metal coordination. Field testing of 10 L seawater showed 27.81 mg uranium extraction at 84% efficiency. We also revealed the self-assembly mechanism of polyphenols and constructed mesocrystalline anode materials by tuning metal coordination and π-π interactions, enabling advanced sodium-ion battery performance. Collectively, we have developed a polyphenol-based functional materials platform for biomedicine, environmental science, and energy storage by exploiting their unique properties. Our work demonstrates the potential of polyphenols as a versatile biomass resource for innovative materials beyond traditional leather manufacturing. We look forward to engaging in insightful discussions during the upcoming presentation.

Keywords: tannins; polyphenols; functional materials; biomedicine; water treatment; self-assembly

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Odorless reductive liming, without thiols, thioglycolates and sodium sulphide

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Abstract: This research work has been developed after frequent requests from customers to have an odorless liming process, especially during the hair removal phase, and with less use of thiols, thioglycolates and above all sodium sulphide.

Using bibliographic research on starches and sugars, studying their reducing power, we have formulated a mixture of organic and inorganic substances that can catalyze the reducing power of sugars.

The first big problem encountered was the different nature of the hair belonging to various types of skins, for example pig' s hair is very difficult to remove without sodium sulphide. For this reason, we have developed a balanced formulation that worked for every hair type in presence of only a small amount of sodium hydrogen sulfide. This quantity varies between 0,5%-0,7% for calf hair or cow hair and of 1% for bristles.

The main characteristics of this formulation are the sources found for the organic substances (from food waste or from renewable plant), the power to dissolve the hair, clean the bulbs and remove the soiled and the keratin on the surface of the skin without sulfur smell.

The data collected during our tests will be illustrated and explained during the presentation in which we' ll show the content of sulphates in the baths, the value of COD, microscopy studies of the hair degradation and the physical characteristics of the tanned leather and the crust.

Keywords: liming; renewable; hair

Construction of dendritic polyphenol-metal spiderweb-like structure and its strengthening effect on collagen fibrils by multiform crosslinking

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Abstract: Based on the large end-group functionality and strong designability of the dendrimer, a series of phenolic hydroxyl terminated dendrimer (Gx-GA) was firstly synthsized by using polyamide-amine dendrimer (Gx) as matrix and gallic acid (GA) as modifier. Then, Gx-GA complex with Al^{3+} to construst different generations of chrome-free tanning agent with polyphenol-metal network (MPN) structures (Gx-GA-Al). The results of infrared spectroscopy (FT-IR), ultraviolet-visible spectrum (UV-Vis), hydrogen nuclear magnetic resonance spectroscopy (1H-NMR), and X-ray photoelectron spectroscopy (XPS) showed that the phenolic hydroxyl and Al^{3+} both were successfully incorporated into Gx matrix. Gx-GA-Al were used in the tanning experiment of pickled sheepskin. The results showed that the properties of leather tanned by Gx-GA-Al were significantly improved compared with 8% aluminum-tanned leather. In particular, the shrinkage temperature of leather tanned with the first generation of chrome-free tanning agent (G1-GA-Al) reached to 87.2 ℃ which was higher 17.6 ℃ than that of 8% aluminum-tanned leather. Meantime, the thickening rate increased by 173.8%, the tensile strength and elongation at break increased by 26.5% and 60.8%, respectively, as well as the leather had better fullness, softness and filling. After washing 2 h, the shrinkage temperature nearly had no change, and the fastness to washing was greater than 99%. The scanning electron microscope (SEM) and ultra depth of field microscope results showed that the dispersion of the leather collagen fiber tanned by Gx-GA-Al was better. The anti-bacterial rate against *Staphylococcus aureus* and *Escherichia coli* reached 99.9% and 98.7%, respectively, which indicated that Gx-GA-Al tanned leather had excellent anti-bacterial activity. The assessment results for tannage wastewater showed that BOD_5/COD_{Cr} of Gx-GA-Al tannage wastewater was between 0.33 and 0.38 which was higher than the ratio of aluminum tanning processes, which proved that it had better biodegradability.

Keywords: dendritic polymer; polyphenol-metal network; chrome-free tanning agent; collagen fiber; hydrothermal stability

UV-induced self-healing/ hydrophobic polyacrylate latex used for leather coating

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Abstract: Polyacrylate is widely used in the textile, leather and functional coating sectors due to its excellent film formation and flexibility. However, polyacrylate-based leather coatings are susceptible to scratch and breakage damage, which can considerably reduce their lifespan. In this study, we aim to design and prepare a UV-induced self-healing/ hydrophobic polyacrylate coating material (PXD) using vinyl-modified coumarin and acrylate monomers. The effect of the vinyl-modified coumarin structure on the mechanical and self-healing properties of polyacrylate latex films was systematically evaluated. The results indicated that the healing efficiency of samples exceeds 60% after irradiation of 365nm UV for 6 hours at 90℃. In addition, the self-healing mechanism of polyacrylate coating was explained by molecular dynamics simulations. The leather samples finished by PXD exhibited prominent hydrophobicity, stain resistance and durability. Scratch of 100 μm length on the leather samples could be repaired well. The successful preparation of UV-induced self-healing/ hydrophobic polyacrylate material provides a new direction for the development of functional leather coating materials.

Keywords: polyacrylate; UV-induced self-healing; hydrophobic; leather coating

A green one-pot method for the synthesis of a novel epoxy-modified oligomeric chitosan-based chrome-free tanning agent towards sustainable processing of functional leather

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Abstract: To reduce the contamination of Cr^{6+} and dyes from tannery wastewater, a chromium-free tanning agent with rich terminal epoxy groups (COS-GTE) was synthesized using oligomeric chitosan (COS) and glycerol triglycidyl ether (GTE). The structural characteristics and application performance of prepared COS–GTE were investigated by FTIR, NMR, GPC, SEM, adsorption properties of fatliquor and dyes, and other analysis techniques. The application results indicated that the shrinkage temperature of finished leather tanned with COS–GTE can reach 83.5 °C. Compared with traditional tanning materials (F-90 and TWS), the finished leather had better mechanical properties (tear strength of 47.410 N/ mm^2) and yellowing resistance. Moreover, the natural skin modified with COS–GTE showed excellent antimicrobial properties against *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus flavus*, and *Aspergillus niger*. Especially, the finished COS-GTE tanned leather had a high absorption rate of fatliquor (69.27%) and dyes (X=93.21%), which is beneficial for reducing comprehensive wastewater pollution. The research revealed that the COS–GTE not only can be considered a new biomass material to solve the problem of chromium and dye contamination in the leather industry but also endows leathers with a unique antimicrobial function to extend product protection and service time.

Keywords: chrome-free tanning agent; oligomeric chitosan; antibacterial properties

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Preparation of anionic high solid waterborne polyurethane and its application in microfiber material impregnation

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Abstract: With isophorone diisocyanate (IPDI) and polytetrahydrofuran (PTMEG) as basic raw materials, 1,4-butanediol (BDO), 2,2-dimethylolpropionic acid (DMPA) and self-made novel hydroxyl sulfonate (SE) as chain extension agents, trimethylolpropane (TMP) as crosslinking agent, N, N- dimethylethanolamine (DMEA) as neutralizer, the sulfonic acid/carboxylic acid type high solid content waterborne polyure-thane (WPU) was synthesized. FTIR results demonstrated that WPU molecular chain contained carboxylic acid and sulfonic acid groups. The results of TGA, DSC and tensile testing indicated that WPU with high content of SE had higher thermal stability and mechanical property when the total content of hydrophilic groups was consistent. Especially when the content of SE is 2% (wt%), the solid content of the prepared polyurethane emulsion can reach 50%, and the average particle size of the emulsion is 143.7nm, which has excellent storage stability, freeze-thaw stability and alkali resistance stability. The tensile strength of PU film-forming is 14.3MPa, and corresponding elongation at break is 1380%. Further application experiments on microfiber material impregnation and alkali-decrement processes suggested that the WPU filled in the base has excellent alkali resistance. The scanning electron microscope (SEM) showed that there is still a large amount of resin filling in the fiber gap after alkali-decrement, and the obtained environmental-friendly microfiber base is soft and has good resilience property.

Keywords: high solid content; sulfonate; waterborne polyurethane; microfiber leather

Aggregation behavior of cationic amphiphilic polymers and their application in metal-free leather retanning

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Abstract: The charged nature of polymer retanning agents has a significant impact on their retanning performance. However, few studies have paid attention to the relationship between the charge properties of cationic polymer retanning agents and their aggregation behavior in aqueous solution as well as the retanning performance. Herein, a series of cationic amphiphilic acrylic polymers, Poly(SMA-co-DMAEMA)s (PSDs), with different protonation degrees (60%, 80%, 100%) were synthesized by radical polymerization. Then the PSDs were applied to retanning of metal-free leather tanned with TWS tanning agent. Dynamic light scattering and diffusing wave spectroscopy analyses demonstrated that the nanoparticles of PSD with lower protonation degree showed slower Brownian motion and larger aggregates size in aqueous solutions. The Molecular dynamics simulations showed that the electrostatic repulsion and number of hydrogen bonds formed between PSDs and water were reduced with decreased protonation degree of PSDs, which significantly promoted the aggregation of PSD and decreased the solvent (water) accessible surface area. This was consistent with the experimental findings. The PSD with protonation degree of 60% formed thicker hydrophobic films on the collagen fiber surface than the other PSDs, resulting in better static and dynamic water resistances, fiber dispersion and physical properties of leathers. Therefore, the comprehensive performance of the metal-free leather would be improved through PSD retanning.

Keywords: amphiphilic polymer; retanning; metal-free leather; protonation degree; aggregation behavior; hydrophobicity

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Eco-friendly sandwich-like structured nanocoating: construction and flame-retardant

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Abstract: Water polyurethane (WPU), one of the most promising coating materials, exhibits high flammability and fire risk. The addition of environmentally friendly flame retardants that can achieve WPU coating with efficient flame-retardant is of great significance to human life and public safety. Herein, an eco-friendly sandwich-like structured polyurethane nanocoating was developed via layer-by-layer assembly strategy. Primarily, the phytic acid (PA), as a bio-based phosphor polyols, was employed to prepare phosphorus-containing WPU (P-WPU). Then, the multimetallic layered double hydroxide with flame retardant (CoMnAl-LDHs) was combined with P-WPU and PA to obtain sandwich-like CoMnAl-LDH/P-WPU/PA nanocoating from the bottom up. The unique combination of PA and CoMnAl-LDHs has a synergistic effect to endow nanocoating with prominent flame-retardant. The limit oxygen index (LOI) and carbon residue rate of nanocoating could reach 31.5% and 28.8%, respectively. The lower PHRR (83.16 kW/m^2) and THR (1.61 MJ/m^2) of nanocoating markedly prevented the burning of the base material. This deeply originated from the shield effect of the formed polymetaphosphoric acid film and the CoMnAl-LDHs with mulitlamella-like structure. Meanwhile, the formed polymetaphosphoric acid and Co/Mn composite metal oxide played the role of catalytic carbonization to enhance the flame-retardant in the burning process. This work provides a new insight into developing flame-retardant polyurethane and extending its application on leather, textile, building, and so on.

Keywords: waterborne polyurethane; flame-retardant; phytic acid

A waterborne polyurethane coating with room-temperature, self-healing and antibacterial functions based on coordination bond and hydrogen bond

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Abstract: Waterborne polyurethane have been widely used in coating materials, but macroscopic damage or cracking by external forces during their use inevitably reduces their durability and service life. Herein, a room-temperature self-healing waterborne polyurethane (WPU-Zn-3) based on Zn^{2+}-carboxyl coordination bond and hydrogen bond was prepared by adding zinc ion buffer solution to WPU emulsion. Due to the synergistic effect of dynamic coordination bonds and hydrogen bonds, the optimized sample exhibited excellent mechanical properties (a tensile strength of 7.26 MPa, a elongation at break of 855 % and an exceptional toughness of 26.76 MJ/ m^3) and fast room-temperature self-healing capacity under ethanol induction (a high healing efficiency of 88 % within 4 h), showing a good balance between fast room temperature healing ability and excellent mechanical properties. Interestingly, this method also works for nickel ions but not for iron and aluminum ions. Due to the presence of zinc ions, the sterilization rates of the WPU-Zn-3 film samples against Escherichia coli and Staphylococcus were 97.1 % and 97.8 %, respectively. Compared with neat WPU, the WPU-Zn-3 coated leather samples exhibit better mechanical properties and self-healing ability.

Keywords: waterborne polyurethane; coordination bond; self-healing; antibacterial; leather coating

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Renewable fulvic acid as a masking agent together with aluminum to enhance the hydrothermal stability of leather

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Abstract: In metal tanning agent the aluminum is considered to be more environmentally friendly, but the penetration of aluminum ions in leather collagen fibers is uneven and the resultant leather has poor washing resistance. Therefore, in this study the biochemical fulvic acid (BFA) obtained from plants by biotechnology is used as masking agent to prepare fulvic acid-aluminum (BFA-Al) tanning agent. It can not only promote the penetration of aluminum ions, but also can crosslink with collagen fibers to realize multiform bonding. The results showed that the shrinking temperature of BFA-Al tanned leather was 81.5 °C. Compared with aluminum tanned leather, the thickening rate is increased by 49.3%, the elongation at break is increased by 13.9%, and the tear strength is increased by 20.9%. The most important was the aluminum content ingrain layer increased from 11% to 34%, which proved that BFA-Al had better penetration in leather collagen fibers due to the masking of BFA. At the same time, the absorption rate of aluminum reached 94.7%, an increase of 12.5%. The absorption rate of fulvic acid can reach 98.4%, and the absorption rate of different dyes can reach more than 90%. Moreover, the absorption rate of BFA-Al tanned leather to fatliquor was more than 95%. The environmental impact assessment showed that BOD_5/COD of BFA-Al tannage wastewater was more than 0.4, which confirmed that it had excellent biodegradability. BFA as a renewable resource provide a new alternative and it has potential application value in chrome-free tanning.

Keywords: masking agent; biochemical fulvic acid; chrome-free tanning agnet; uniform penetration of aluminum; hydrothermal stability

Anti-freezing and bacteriostatic PVA/chitosan-based organohydrogel triboelectric nanogenerator constructed by the synergistic effect of coordination crosslinking and salting-out action

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Abstract: The anion salting-out action and the cation-induced-crosslinking reaction have been reported separately for the preparation of conductive hydrogels in the past decade, but there are few studies on the synergistic effect of the two interactions. Also, how to construct flexible strain sensors with more functions is rarely reported by introducing multiple ions through the simple immersion method based on the synergistic action of two kinds of ions. Herein, a polyvinyl alcohol (PVA)/O-carboxymethyl chitosan (O-CMCS)-based composite conductive organohydrogel was designed and fabricated by replacing pure water solvent with nano-silver particles (AgNPs) solution, followed by the immersion treatment in the PG (1, 3-propylene glycol)-$ZnSO_4$ (zinc sulfate) blended solution. The triboelectric nanogenerator (TENG), constructed by this organohydrogel, exhibited considerable anti-freezing, moisturizing, antibacterial, conductive (1.5 S/m) and mechanical properties (fracture stress of 2.5 MPa), and could be used as strain sensors for the monitoring of human motions at both room and low temperatures. Owing to the synergistic action of anions and cations, this flexible strain sensor, prepared by the immersion strategy in the mixed PG-$ZnSO_4$ water solution system, demonstrated almost unchanged mechanical, electrical and sensing behaviors at low temperature and after long period of storage under room environmental condition. In summary, this work successfully constructed an organohydrogel-based TENG with the advantage of remaining good mechanical durability and applicability under harsh environmental conditions, and the fabrication strategy used provides a new idea for the construction of conductive hydrogel via ion immersion procedure.

Keywords: triboelectric nanogenerator; coordination crosslinking; salting-out effect

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Synthesis and characterization of self-healing nonionic waterborne polyurethanes

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Abstract: Waterborne polyurethanes constitute an exemplary class of synthetic polymeric materials, owing to their light weighting, favorable thermal insulation, corrosion resistance, and other superlative properties. Nonionic waterborne polyurethanes, in particular, have attained broad utilization in leather finishes, biomedical appli cations, packaging, automotive systems, sealants, and sundry other domains, consequent to their unparalleled compatibility and stability. Nevertheless, the propensity of polyurethanes to incur macroscopic or microscopic impairment and fracture upon exposure to mechanical or photonic stimulation during practical implementation circumscribes their applications substantially by abridging their service life. Consequently, the incorporation of self-healing materials into nonionic waterborne polyurethanes is of considerable moment. In accordance with the reversible chemical mechanisms of multiple hydrogen bonds and disulfide bonds, this study reports the synthesis of a nonionic waterborne polyurethane with self-healing properties. In consideration of its mechanical character, this approach not only enhances the safety of use, mitigates surface traces, actualizes the recovery of the material, and effectively curtails resource consumption. 2-Amino-4-hydroxy-6-methylpyrimidine, 4-methylumbelliferone, and 2-hydroxyethyl sulfide were introduced into nonionic waterborne polyurethane, harnessing their dynamic reversibility for self-healing. The sequence and content of their addition were explored systematically. Key functional groups were elucidated through infrared spectroscopy, and the synthesized emulsions and films were evaluated through centrifugation, tensile testing, particle size analysis, and allied techniques. The results indicate that the addition of 2-amino-4-hydroxy-6-methylpyrimidine and 4-methylumbelliferone during the chain extension phase in the synthesis of nonionic waterborne polyurethane exhibited the optimal self-healing effect without significantly impacting other properties.

Keywords: non-ionic; waterborne polyurethane; self-healing; disulfide bond; multiple hydrogen bond

Synthesis of spirooxazine compounds and their application in waterborne polyurethane systems

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Abstract: As a class of photoresponsive materials, photochromic materials have attained successful application in molecular switches, memory storage, anti-counterfeiting materials, and other domains. Among these, spirooxazines (SPOs) have been extensively utilized due to their superior fatigue resistance and photostability. Waterborne polyurethanes (WPUs), owing to their nontoxic, non-polluting, environmentally friendly, and highly compatible properties, have been widely applied in leather finishing, adhesives, and other fields. In this study, a spirooxazine compound was synthesized, and optimal conditions for its synthesis were explored. With 1,2,3,3-tetramethyl-3H-indolenine iodide as an intermediate and anhydrous ethanol as the reaction solvent, reacting at 90 °C for 12 hours yielded 52.3%. This compound was then incorporated into waterborne polyurethane through covalent polymerization, generating SPO-WPU. Its photochromic properties and mechanical performance were also investigated. The results demonstrate that incorporating SPO into WPU through covalent polymerization not only enhanced the fatigue resistance of SPO but also significantly improved the thermal stability and mechanical properties of WPU.

Keywords: spirooxazine; polyurethane; leather finishing

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Green functional nanocomposites for leather chemicals

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Abstract: Leather manufacture is a process in which animal skins can be transformed into leather by a series of physical operations and chemical modifications. Leather chemicals including tanning agents, fatliquoring agents, and finishing agents play important roles in leather manufacture. In order to promote the transformation and upgrading of leather industry, a series of green functional nanocomposite for tanning agents, fatliquoring agents, and finishing agents are designed and constructed in our research, and the relevant technologies are extended to shoe materials, smart leather product and other fields. As for tanning agents, Mannich reaction was innovately proposed to introduce cationic groups into carboxyl group and ester group α-H of vinyl polymer to obtain amphoteric vinyl polymer tanning agent, which could solve the problem of "color loss" in the leather industry. The chromium-free nanocomposite tanning agents were obtained by introducing montmorillonite (MMT), polyhedral oligomeric silsesquioxane (POSS) and layered double hydroxides (LDHs) into vinyl polymers, and the multi-point cross-linking in different levels of collagen fibers was formed through the construction of charge effect and network structure, which can facilitate the clean production of leather. In the aspect of fatliquoring agents, the vegetable oils were modified by nanomaterials with different functions such as MMT, LDH, TiO_2, ZnO, and nano Ag, the as-prepraed fatliquoring agents could be endowed with excellent flame-retardant, low atomization, yellowing resistance and mildewproof properties. Additionally, polyacrylate and casein based nanocomposite finishing agents with thermal insulation and VOCs fluorescence sensing/degradation properties were designed, which could help realize the potential applications of leather in electronics and artificial intelligence. Based on the above researches, relevant technologies were empolyed to make efficient use of collagen biomass resources thus expand its application in the fields of sensor, fluorescent anti-counterfeiting, cultural relic protection, and smart shoe materials. In the future, leather chemicals are developing in the direction of green low-carbon, functionality and intelligence.

Keywords: functional nanocomposites; Green leather chemicals; Leather cleaner production

Preparation of an antibacterial retanning agent based on styrene-maleic anhydride copolymer and its performance

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Abstract: Recently, more and more attention has been paid on functional chemicals in leather industry. In this paper, an antibacterial retanning agent (SMAE) was prepared by the esterification of styrene-maleic anhydride copolymer with borneol in the N,N-dimethylformamide (DMF) medium. The esterification kinetics was investigated by an on-line reaction infrared spectrometer. The structure of SMAE was characterized by 1H NMR and FT-IR, and the thermal stability and surface activity were studied by thermal gravimetric analyzer and contact angle test. The antibacterial activity of SMAE against gram-positive bacterium and gram-negative bacterium were investigated. It demonstrated high antibacterial properties against both gram-positive and gram-negative bacterium. SMAE was applied to the retanning of goat wet blue, which exhibited better retanning properties. The prepared antibacterial retanning agent has prospective application in leather manufacturing.

Keywords: styrene maleic anhydride copolymer; borneol; esterification; retanning agent; bacteriostatic activity

Synergistic effect of layered double hydroxide and graphene on flame retardancy and smoke suppression of bio-based leather finishes

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Abstract: As fire safety has become a major security hazard in our daily life, high-performance flame-retardant leather products with excellent smoke suppression are highly desired for applications in vehicles and furniture. In this study, to improve flame retardant and smoke suppression performance of casein-based leather finishes, layered double hydroxide-graphene (LDH-rGO) was fabricated and introduced into casein system. In detail, method was used to synthesize a hybrid of LDH-rGO, which was used as a flame retardant and introduced into the casein substrate. The composition, structure and morphology of LDH-rGO were characterized by FTIR, XRD, TEM and TGA. It was found that LDH-rGO had been successfully prepared. Further, the effects of LDH-rGO amount on flame retardancy and smoke suppression of finished leather were studied. The LOI value of finished leather was increased from 24.1% to 27.4% by using 5% of LDH-rGO. Heat release rate (THR) and smoke release rate (SPR) of finished leather were decreased dramatically. Typically, 36% and 69% reduction in PHRR and SPR were achieved with 5% LDH-rGO dosage. This dramatic reduction of fire hazard was mainly attributed to the synergistic effects of LDH and rGO, which lie in non-combustible gas released between layers of LDH. Meanwhile, MgO and Al_2O_3 generated from LDH-rGO in the combustion process helped enhance the production of char residue and raised the compactness of the char layer. This work provides a feasible pathway for preparing green and efficient flame-retardant leather finishing materials.

Keywords: LDH-rGO; flame retardancy; finished leather

A solvent-free LDH nanofluid for improving the flame retardant properties of leather

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Abstract: Leather fatliquoring agent, as one of the most widely used chemicals in the leather industry, have the functions of making leather soft, improving its mechanical properties, waterproofing properties, and supplementary tanning. However, the neutral oil easy migrate under heat lead to the inflammability of leather. It is important for human life and health to improve the flame retardancy of leather. Layered double hydroxide (LDH) has been developed rapidly in the field of flame retardancy due to the characteristic of catalytic matrix carbonization. However, high surface energy with LDH can easily cause aggregation, which is not conducive to the dispersion of LDH and thus affects the flame retardant efficiency. In this study, a solvent-free LDH nanofluid with good fluidity and high dispersion was prepared using LDH as core, silane coupling agent and polyether amine flexible long chain as shell. Solvent-free LDH nanofluid was introduced into modified castor oil (SSCOF) to prepare solvent-free LDH nanofluid/SSCOF flame retardancy fatliquoring agent. Compared with the leather treated with SSCOF, the after flame time of the leather treated with solvent-free LDH nanofluid/SSCOF was reduced from 61 s to 32 s, the limiting oxygen index was increased from 24.3% to 27.1%, the heat release rate was decreased by 43.6%, and the total smoke production was decreased by 20.8%, respectively. In addition, solvent-free LDH nanofluid improved the softness of the leather. This study provides a new idea for the research and development of flame retardant leather chemicals, which is conducive to the realization of high value utilization of leather.

Keywords: solvent-free LDH nanofluid; leather fatliquoring agent; flame retardancy

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Developments of the ecological tanning based on modified carbohydrates

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Abstract: This work is based on the application development of biopolymers derived from modified starches, as per the study "Ecological tanning based on modified carbohydrates" presented at the III IULTCS Eurocongress Vicenza 2022, taking into consideration the tanning applied on hides deriving from liming processes of a different nature:

- traditional reductive liming with the use of sodium sulphide and sodium sulphide
- reductive liming with the aid of thio-derivatives without the use of sodium sulphide and sodium sulphide
- reductive liming as per the project "Odorless reductive liming, without thiols, thioglycolates and sodium sulphide"
- oxidative liming

In the previous study, all the application tests were carried out on hides derived from reductive liming based on thio-derivatives in the complete absence of sulfides and sulphides, noting a good distribution and penetration of the tanning agent which improved performance when combined with various capping agents which included both organic substances (glutaraldehyde, oxazolidine and synthetic tannins) and inorganic substances (zeolites, silicates and non-metal free tanning agents).

This work, on the other hand, will present the developments carried out on hides from different types of liming with the aid of new capping agents and different manufacturing procedures and will also be linked to the work "Odorless reductive liming, without thiols, thioglycolates and sodium sulphide", developed partly for starch tanning to improve the final quality of the leather.

Keywords: tanning; sustainable; carbohydrates

The preparation of a noval amphoteric retanning agent and its mass transfer properties in leather

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Abstract: In recent years, with the rise of chromium-free tanning technology, amphoteric retanning materials have been paid more and more attention. In this paper, first, a series of poly (N-vinylformamide-co-acrylic acid) copolymers were synthesized by free radical copolymerization reaction initiated by azodiisobutylamidine hydrochloride. Then the amphoteric retanning agent (Am-PVAm) was obtained by the hydrolysis of poly (N-vinylformamide-co-acrylic acid) copolymers. Their structures were characterized by FTIR and ^{1}H NMR, and their isoelectric points were determined by colloid charge titration. To evaluate the effect of the molecular weight of Am-PVAm on its penetration and mass transfer in leather, a fluorescent tracer (FAm-PVAm) was prepared by using fluorescein 5-isothiocyanate reacted with Am-PVAm. It was found that Am-PVAm penetrated mainly from the flesh side into the crust. The Am-PVAm could distribute evenly in the leather in 60 min. However, when the dosage was not enough, it distributed mainly on the flesh side of the leather. When its dosage was above 15%, the retanning agent could distribute uniformly in the collagen fibers.

Keywords: amphoteric polyvinylamine; retanning agent; mass transfer

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Acrylic resin coating agent modified by cellulose nanofibers

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Abstract: Acrylic resin is commonly used in leather finishing process, but it has some problems such as poor mechanical properties. Cellulose nanofibers are a kind of biomass material with excellent mechanical properties and are often used as reinforcement materials. In this paper, high strength acrylic resin coating agent was prepared by cellulose nanofibers and acrylic resin. The micro morphology and properties of acrylic resin before and after modification were characterized by scanning electron microscope, tensile testing machine, rotary viscometer, etc. The use performance of finished leather coated with acrylic resin was evaluated by fabric moisture permeability tester, and rubbing color fastness tester, and the effects of different modification conditions and cellulose nanofiber content on the performance of acrylic resin finishing agent were explored. The results showed that when 0.3% cellulose nanofiber was added, the mechanical properties of acrylic resin finishing agent were greatly improved. The tensile strength was up to 7.43 N/ mm^2, increased by 111.68%. The tear intensity was 17.61 N/ mm and the elongation at break was 653%. Compared with the unmodified acrylic resin, the tear strength and elongation at break were increased by 32.61% and 31.92%. In addition, the modified acrylic resin was used as a finishing material to improve the performance of finished leather.

Keywords: cellulose nanofiber; acrylic resin; mechanical property

Green synthesis of TiO_2 nanoparticles with quebracho extract and their photocatalytic activities

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Abstract: Titanium dioxide (TiO_2) has been extensively applied due to its high photocatalytic activity, non-toxicity and biocompatible properties. There are various synthesis techniques in the preparation TiO_2 nanoparticles, including hydrothermal method, sol-gel method, etc. In this study, anatase TiO_2 nanoparticles were synthesized by green chemical method using tetrabutyl titanate (TBOT) as precursor and chestnut wood extract as the template. The obtained TiO_2 were characterized by X-ray diffraction (XRD), dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FTIR), UV-vis spectroscopy (UV-vis), and scanning electron microscope (SEM). It was indicated that titanium dioxide with anatase structure was successfully synthesized. The effects of the content of chestnut wood extract on the structure and properties of TiO_2 were analyzed. The addition of chestnut wood extract could effectively improve the homogenization of morphology and size of TiO_2, while the addition of excessive chestnut extract will affect its antibacterial and photocatalytic properties. The antibacterial activity of TiO_2 was tested with ultraviolet light irradiation, and an antibacterial effect on both Gram-positive bacteria (*S.aureus*) and Gram-negative bacteria (*E.coli*) was found. In addition, the study on adsorption and photocatalytic properties of TiO_2 for methylene blue suggested that TiO_2 has great potential application in leather artifact protection and tannery wastewater treatment.

Keywords: TiO_2; green synthesis; photocatalysis

Ionic modification of graphene nanosheets to prepare high performance organosilicon composite coatings

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Abstract: Composite coatings were fabricated using quaternized silicone oil modified graphene oxide (M-GO) and silicone polymer. Quaternized silicone oil was successfully synthesized through copolymerization of octamethyl cyclotetrasiloxane (D4), chloropropylsilane and triethylamine. The M-GO could be dispersed without aggregation in some organic solvents, and the concentration of M-GO could be up to 3 mg mL^{-1}. The M-GO-reinforced silicone composites exhibited obvious improvements in thermal stability, mechanical properties and especially anticorrosive properties with the highest Ecorr (−121 mV) , and the protection efficiency of the matrix could reach 99.97%. This work provides a ready strategy for modification of GO and fabrication of high performance graphene-based silicone composite materials.

Keywords: silicone; modified graphene; composite

Synthesis and application of an polymer auxiliary with silicon

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Abstract: In order to reduce the density of the finished leather and the amount of fat-liquor during the production of leather-making, an polymer auxiliary with silicon is synthesized by radical co-polymerization of acrylic acid, meth-acrylic acid and polyvinyl silicone oil, etc. The polymers were applied to the re-tanning process of sheepskin. Comparing the viscosity and applied properties of the polymer auxiliary with silicon, the mol ratio of acrylic acid, meth-acrylic acid used was confirmed to be 0.5:0.2, the consumption of polyvinyl silicone oil, ammonium persulfate the reactive temperature and time is 5%, 1.5%, 80-85 °C, 120-180 min, respectively. Infrared spectroscopy shows that the structure of the polymer auxiliary contains -Si-O- bond. The thickening rate, softness of the treated leather is 23.1%, 6.0 and the consumption of fat-liquoring agent after re-tanning can be reduced to 4%~8% when the optimum consumption of the an polymer auxiliary is 8%~10%, The retreated leather is fine, soft, hydrophobic and the density is 0.457 g/cm^3.

Keywords: acrylic acid; polyvinylsilicone oil; acrylic decanter; itaconic acid; v softness

Interaction of Clostridium collagenases with compounds of carboxylate and hydroxamates by multi-spectroscopy

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Abstract: Collagens are important component of extracellular matrix in mammalian tissues, whose primary function is to provide stability, elasticity and support to cells and tissues. They are also involved in regulating cell signalling, differentiation and migration. Collagenase plays a critical role in metabolizing of collagens. The over-expression of collagenase may cause abnormal degradation of collagen thus bring the risk to collagen metabolism related diseases. Therefore, it is of great significance to inhibit collagenases. In this study, the inhibitory effects of compounds such as carboxylates and hydroxamates on Clostridium collagenase were investigated. The results showed that sodium salicylate and acetohydroxamic acid had the best inhibitory effect under the experimental conditions, with the inhibition rates at 82.7% and 54.2%, respectively. The interaction of sodium salicylate and acetohydroxamic acid inhibitors with Clostridium collagenase were demonstrated by multi-spectroscopic approaches. UV-Vis spectra showed that Clostridium collagenase had an absorption peak at 260 nm, which will be affected by the addition of two inhibitors, the sodium salicylate led to a blue shift, while acetohydroxamic acid caused a red shift. The fluorescence spectroscopy shows that when the excitation wavelength is at 280 nm, the fluorescence absorption peak of Clostridium collagenase is at 410 nm, which will be quenched by the increase of sodium salicylate. The structure of Clostridium collagenase changed dramatically while binding with sodium salicylate and acetohydroxamic acid, while the activity of Clostridium collagenase is inhibited. These findings provide insights for the screening and development of novel collagenase inhibitors.

Keywords: Clostridium collagenase; inhibitor; multi-spectroscopy

Research on aromatic syntans without restricted bisphenols

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Abstract: Bisphenol A and its substitutes, such as bisphenol S, are widely used to produce polycarbonate, epoxy resin and other chemical materials. In leather industry, bisphenol S and bisphenol F can be easily found in aryl synthetic tannins derived from phenols. ECHA and the Member States have assessed a group of 148 bisphenols and recommended that more than 30 bisphenols need to be restricted due to their potential hormonal or reprotoxic effects. In this paper, the current situation of bisphenols content especially the bisphenol F and bisphenol S in aryl synthetic tannins and in the leather is studied by using HPLC and the formation mechanism of bisphenol F and bisphenol S will also be discussed. At the same time, suitable hydrophilic aromatic sulfonic acids and hydrophobic aromatic monomers are chosen to condense with formaldehyde under optimized conditions to form a series of aryl synthetic tannins without the 148 bisphenols announced by ECHA. The new synthetic tanning agents have good performances in leather application and the resultant leathers have good physical properties.

Keywords: aromatic syntans; restricted bisphenols; good performances in leather application

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Topic IV Innovations in leather chemicals

Structure design and application performance study of retanning fatliquor based on solid state lubrication technology

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Abstract: To address issues such as poor yellowing resistance, strong odor, and high hexavalent chromium content when using natural oils and their unsaturated bond-rich modifiers as leather fatliquors, research is conducted a study on polymer molecular structures with low unsaturation that are suitable for leather fatliquoring, and also develop a new polymer materials as alternatives to traditional fatliquors. The side chains of new polymer materials contain numerous carboxyl groups and long hydrophobic chains of natural biopolymers. This structure combines the characteristics of retanning and fatliquoring due to the effective binding of carboxyl groups to chrome-tanned leather and the positive effects of lubrication and dispersion by long chain hydrophobic groups on leather fibers. The findings of the study reveal that a higher degree of hydrophobicity in the polymer leads to improved softness of the leather upon application. However, once the hydrophobicity reaches a certain threshold, the impact on softness becomes less pronounced. Additionally, the molecular weight (M_w) of the polymer ranges from 5000 to 13000, and it is observed that as the molecular weight decreases, the softness of the leather improves. The application verification of the synthesized polymer material has demonstrated its remarkable capability to soften leather fibers and exhibit excellent filling properties. As a result, it has the potential to partially or even entirely substitute conventional retanning agents and fatliquors. Furthermore, it offers additional advantages, including resistance to oxidation and water washing, low fogging value, and high tear strength.

Keywords: solid state lubrication; retanning fatliquor; hydrophobicity

Understanding the mechanism of leather biodegradability: insights into collagen structure, tanning agents, biodegradation tests, and compostability

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Abstract: The leather industry faces the imperative of effectively managing its solid and liquid waste streams, driven by escalating costs due to legislative requirements. To address this challenge, it is crucial to explore cost□effective methods for handling leather industry waste. Biodegradation and composting have emerged as efficient and acceptable waste management options in this context. However, the biodegradation process can be influenced by various factors, including temperature, moisture, and microbial activity. Furthermore, the chemistry of tanning agents and finishes used in leather production often correlates with their ability to inhibit biodegradation. This talk will focus on understanding leather biodegradability and composting by examining the intricate relationship between collagen structure, tanning chemistries, and finishes, elucidating their impact on the biodegradation and composability of leather waste. Additionally, the utilization of earthworms as bioindicators of compost quality will also be discussed.

Keywords: biodegrability; crosslinking mechanisms; collagen structure

Preparation and properties of tea polyphenol modified collagen edible films from dried bovine-limed hide fibers

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Abstract: Dried bovine-limed hide fibers were rewetted, acid-swollen and ground to obtain a homogeneous collagen syrup. Different concentrations of tea polyphenols (0.2 wt%, 1.0 wt% and 1.8 wt%) and glycerol (30 wt%, all based on dry collagen fibers) were orderly added into the above collagen syrup and fully dispersed to form the film-forming solutions. Finally a series of collagen composite films (CCF) were prepared by solution casting method. The structure, thermal properties, hydrophilicity, microstructure and mechanical properties of CCF were studied by Fourier transform infrared spectrometer (FT-IR), X-ray diffrotometer (XRD), differential scanning calorimetry (DSC), water contact Angle meter, scanning electron microscope (SEM) and tensile testing machine. Results showed that with the increase of the amount of tea polyphenols (TP), thermal stability of CCF film increased. Scanning electron microscopy (SEM) results showed that the control film surface without TP was not smooth with some cavities, and the film cross-section was not compact. With the increase of the TP amount, the voids on the CCF surface disappeared and the number of particles gradually increased, and the compactness of the film section increased. The static water contact Angle of the film surface increased from 93.4° to 124.3°, indicating the increased hydrophobicity. The tensile strength of the film increased from 5.17Mpa to 9.78Mpa, and the elongation decreased from 6.1% to 2.5%. Therefore, this study can bring a new opportunity for the resource utilization of dried bovine-limed hide fibers.

Keywords: dried bovine-limed hide fibers; tea polyphenols; composite films; thermal stability

Hydrophobic lipophilic modified leather shavings for oil absorption

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Abstract: Leather shavings are one of the main solid wastes in leather processing. In this paper, a biodegradable superhydrophobic and lipophilic porous material was prepared by introducing low surface energy hydrophobic groups of polysiloxane on the surface of leather shavings through simple impregnation modification. The surface structure was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). After hydrophobic modification, the hydrophobicity and oil absorption performance of leather shavings are significantly improved; the oil absorption rate of modified leather shavings is fast, the water contact angle is >142°, and the oil absorption rates of dichloromethane, n-hexane, and rapeseed oil are all > 400%. The leather shavings can be recycled again by simple extrusion; in addition, the modified leather shavings as a filter material show a good effect on the continuous separation of oil-water mixtures and the adsorption separation of oil-in-water emulsions.

Keywords: leather shaving; biomaterials; super hydrophobic

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Fast biodegradation of organic tanned sheepskins waste

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Abstract: The fate of leather articles after the end of their life cycle as well as of the tanned leather waste is a matter of serious concern due to the limited available solutions. In this regard, the prevention of environmental pollution by processing leathers with improved biodegradability represents a challenge of finding the best balance between durability and biodegradability. Previous studies showed that the retanning materials can highly influence the biodegradability of chromium-free tanned leathers[1]. Other reported investigations revealed that some organic tanned leathers such as glutaraldehyde tanned wet-white leathers have lower biodegradability as compared to chromium leathers[2]. Our previous research investigated the potential of new composites based on renewable raw materials such as collagen or keratin hydrolysate, whey, and vegetable tanning extracts[3] as alternatives for chromium tanning. Sheepskin leathers processed with new composites showed good properties for children' s shoes and luxury handbag manufacturing. The impact of the new organic sheepskin leather waste was evaluated by using a composting method based on microbes released by extremophilic bacteria, of the acidophilic type, that act at pH=3.5-6.5 and temperatures of 50-70℃ with the ability to reduce the volume of organic waste by 90% and generate a pre-compost in 24 hours. The analyses of the pre-compost showed non-phytotoxic properties for plant nutrition. The results are promising for the further development of fast composting processes of leather industry waste.

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Keywords: biodegradable leathers; leather waste composting; fast composting

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Comprehensive utilization of leather waste

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Abstract: This work reviews the sources, hazards, output and domestic and foreign measures for the management of leather solid wastes such as leather hair waste, chromium-containing waste, tanning sludge and tanning wastewater generated during the leather production process. It summarizes the progress in the recycling and utilization of hair waste and chromium-containing leather scraps produced in the hair removal and chromium tanning processes at home and abroad. This mainly includes the extraction and application of keratin from hair, the indirect application of collagen and chromium extracted by oxidation, acid hydrolysis, alkali hydrolysis, enzymatic hydrolysis, etc. from chromium-containing leather scraps, and the direct application without chromium removal. Finally, it summarizes and prospects the existing problems in the recycling and utilization of solid wastes from leather making.

Keywords: leather waste; resource utilization; keratin; collagen; chromium

High-efficiency and high added-value of waste animal hairs into carbon quantum dots and activated carbon-like materials for environmental and analytical applications

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Abstract: The preparation of carbon materials from biomass, including waste ones, has aroused considerable research interest, which could enable their high-efficiency and high added-value utilization. Animal (e,g, pig, cattle, goat, sheep, etc.) hairs, a common but unmanageable leather solid waste, are a kind of cheap, substantial, biocompatible and environmentally friendly animal biomass waste, and are expected to be applied as raw material to make fluorescent carbon quantum dots (CQDs) and activated carbon-like materials (ACM) owing to the presence of abundant carbon, nitrogen and oxygen elements in them. Here, cattle and goat hairs, produced in the hair-saving dehairing procedure of leather-making, were used as precursors, following a highly efficient, green, eco-friendly, sustainable one-step hydrothermal method, to achieve the complete transformation of them into CQDs and ACM. Results indicate that the resulting CQDs possessed stable optical and chemical properties and low cytotoxicity. Further, we successfully realized the applications of these hair-derived CQDs in the sensitive and selective detection of Cr^{6+} ion, the construction of fluorescent anti-counterfeiting ink and cell imaging. Interestingly, the ACM obtained at the same time, as the by-product of hydrothermal carbonization reaction of hairs, had rich surface functional groups and exhibited good and persistent adsorption ability to methylene blue (MB) in water. Thus, this work provides a universal route, in which the simple but efficient hydrothermal method could completely transform waste animal hairs into two functional carbon materials in one step, and at the same time, the present strategy is economical, sustainable and low-carbon high-value conversion of leather solid wastes, which is helpful way in the field of leather industry to achieve a "carbon peak and carbon neutrality" policy.

Keywords: waste animal hairs; carbon quantum dots; activated carbon-like materials

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Application of chromium-containing wastewater as Cr-doped hydrotalcite nanomaterials in post-tanning wet processing

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Abstract: With the concept of "zero discharge" of wastewater and the gradual improvement of environmental regulations, the control of heavy metal ion concentration in wastewater has become more and more strict. At present, 90% of the tanneries in the world still use chrome tanning method, which generates a large amount of chromium-containing wastewater, causing harm to the environment and is not conducive to the sustainable and healthy development of the leather industry. In this study, a layered double hydroxide (Zn-Cr LDHs) with good crystalline structure was prepared from chromium-containing wastewater, chromium nitrate and zinc nitrate, which was used for leather tanning. The binding fastness of the tanning agent to leather, the compatibility between crust nd various retanning agents, and the effects of cycle times on the crystal structure and tanning performance of hydrotalcite were studied. The results showed that in different leather processes, except for washing out some filled Zn-Cr LDHs or organic substances in the washing process, other processes have no significant impact on the bonding fastness between hydrotalcite and leather; Zn-Cr LDHs nano tanning agent has good compatibility with BN, BOS, and SS retanning agents, but poor compatibility with ARE and RMD. After 5 cycles of tanning wastewater, hydrotalcite with good crystal structure and excellent tanning performance can still be successfully prepared. This system circulation puts forward an ecological and economic method for chromium recycling and utilization, which reduces environmental pollution.

Keywords: hydrotalcite; compatibility; chromium resource recycling

Novel bio-based filler derived from waste cattle hair and its application in PU coating -- a closed cycle strategy of solid waste

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Abstract: In the process of leather making, the hair-preserved unhairing methods plays a particularly important role. In this paper, the waste cattle hair produced in this process was recovered, and after ball milling treatment, the bio-based filler was obtained. The filler was applied in the surface PU coating of the film transfer finished leather to improve its hygienic performance.The effects of filler amount, curing bath temperature, DMF concentration and polyurethane resin modulus on the properties of PU film were studied. SEM, the universal tensile machine, water contact angle measuring instrument and water vapor permeability tester were used to analyze the PU film properties. The experimental results showed that the pore distribution of PU film with bio-based fillers was more uniform, which had a better thickening effect. When the amount of filler is 1.5%, the mechanical properties of PU film are better, and the tensile strength is 6.35 MPa. With the increase of DMF concentration, the water droplet pore content in PU film cross section increased because the curing rate slowed down. Compared with the PU films which used the lignin and light calcium as fillers, the PU film prepared by the bio-based filler have uniform distribution of cross-sectional pores, and have better elasticity, fullness and moisture permeability.

Keywords: hair persevere method; waste cattle hair; PU film; bio-bass; filler

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Preparation of magnetic cattle hair powder adsorbent and its adsorptive property toward acid dye

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Abstract: In this paper, waste cattle hair is collected and milled to obtain the original adsorbing material. In order to solve the difficulty of adsorbing material separation process, the magnetic cattle hair powder was prepared. The structure and properties of pristine and magnetic adsorbing material were characterized by FT-IR, SEM-EDS, BET, TG-DTG. The prepared was used to adsorb the solution prepared with acid dyes, and the most suitable dosage, pH and time for dye adsorption, as well as the influence of the initial concentration of dye solution on adsorption, were explored. The results showed that the adsorption capacity of pristine cattle hair powder for acid dye increased with the decrease of pH value. The optimal adsorption conditions of 500 mg/L acid dye solution are as follows: the dosage of 200 mesh cattle hair powder was 0.5 g, pH value was 3, time was 60 min, the adsorption capacity and removal rate were 487.57 mg/g and 98.65% at 35 ℃. After magnetic, the separation process was much easier compared with the pristine one. The research provides a new direction for the recycling of waste cow hair.

Keywords: waste cattle hair; dye adsorption; magnetic

Collagen peptide improves bioethanol yield in the fermentation process of *Saccharomyces cerevisiae*

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Abstract: Bioethanol is a sustainable and clean bioenergy. However, *Saccharomyces cerevisiae* is subjected to severely challenge by ethanol stress in high gravity (HG) ethanol fermentation. Proline (Pro) is a common stress protectant, but the endogenous ability of Pro biosynthesis is limited for *S. cerevisiae*, and the exogenous feeding of pure Pro is costly for large-scale bioethanol fermentation. Here, collagen peptide (CP), as a Pro-rich biomass, remarkably improved the cell survival rate against ethanol stress. The cells morphology was seriously damaged by ethanol stress, while the integrity and stability of cells were greatly maintained under the protection of CP, suggesting that CP endows *S. cerevisiae* with a robust resistance to ethanol stress. Interestingly, the enrichment analysis of differential expression genes indicated that CP obviously affected the Pro metabolism of *S. cerevisiae*. Meanwhile, CP can effectively improve the intracellular glycine (Gly), Pro and hydroxyproline (Hyp) contents. Accordingly, the supplementation of Pro, Gly and Hyp all improved the tolerance against ethanol stress. Moreover, CP could not only promote glucose utilization and enhance ethanol production, but also reduce fermentation period and improve fermentation efficiency. CP can increase intracellular Pro, Gly and Hyp contents of *S. cerevisiae* at the early stage of ethanol fermentation. Hence, the promotion function of CP in HG fermentation was closely related to its specific amino acid composition. These results revealed that CP is effective for improving bioethanol yield in the fermentation process of *S. cerevisiae*.

Keywords: collagen peptide; bioethanol; fermentation; *Saccharomyces cerevisiae*; stress

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Effect of dyes on the pyrolysis kinetics, thermodynamics and volatile products of chrome-tanned leather shavings

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Abstract: The industrial tanning of leather produces considerable amounts of solid wastes, such as chrome-tanned leather shavings (CTLS), and liquid effluents, such as dyes, making the treatment and recycle intractable. That will pose a serious threat to the environment and human health if they are not well treated. In this work, three different kinds of dyes were adsorbed by CTLS and the adsorption ability were evaluated by UV-vis spectrophotometry. The pyrolysis process was carried out through thermogravimetric analysis under nitrogen atmosphere from 30 to 600 ℃ at different heating rates of 10, 30, and 50 ℃/min, respectively. And the evolved gaseous products were analyzed by thermogravimetric analyzer coupled with Fourier transform infrared spectrometry and mass spectrometry (TGA-FTIR-MS) analysis. The Flynn-Wall-Ozawa (FWO) method was used to calculate the kinetic parameters, and the average activation energy of CTLS adsorption on Acid Red 18 was as low as 325.5 kJ/mol. The pre-exponential factors (A) of the CTLS before and after dye adsorption were on the order from 1024 to 1038. The wide range of A implies that complex chemical reactions occurred during the pyrolysis process. The kinetics and thermodynamics results provide essential information for optimization of pyrolysis process of dye-containing chrome-tanned leather shavings, and are helpful for the development of clean technology for the disposal of leather solid wastes.

Keywords: chrome-tanned leather shavings; dyes; pyrolysis; kinetics; thermodynamics

An eco-friendly sand-fixing material based on waste bovine hair for potential desertification control application

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Abstract: An eco-friendly copolymer based on solid waste bovine hair was synthesized as sand fixing material to improve the efficacy of sand fixing and solve the retention problem of sand-fixing agent, at a reduced cost compared to traditional sand fixing materials. In this study, the synthesis starts from the extraction of keratin from waste bovine hair by alkali oxidation, followed by copolymerization with calcium lignosulfonate (CL), acrylic acid (AA) and N, N-methyldiacrylamide (MBA) to obtain the copolymer K-g-PAA-CL. The structure and morphology of the copolymer were characterized by FT-IR, TG-DTG and SEM, and later its sand-fixing properties were investigated. The results demonstrated that K-g-PAA-CL had good stability and environmental friendliness. When applied to sand, K-g-PAA-CL can combine with sand grains to form a consolidation layer, which shows good water retention, high compressive strength, as well as strong resistance to wind and water erosion. When the mass fraction of K-g-PAA-CL was 1%, the compressive strength reached 1.19Mpa, meeting the basic requirements of sand fixation. This work provided an effective strategy to utilize waste bovine hair for the improvement of desert ecological environment.

Keywords: waste bovine hair; resource utilization; eco-friendly; sand fixation

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Zero chemical treatment of leather waste for highly performing, circular and sustainable finishings

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Abstract: Many strategies have been adopted, in recent years, in order to minimize the impact of tannery waste, mainly made up of solid waste, such as sewage sludge, shavings, trimmings, splits and more. On the other hand, tanning waste recovery processes already identified are a virtuous application case of the circular bioeconomy for the use of waste tanning biomass, as secondary raw materials in the production of other industrial sectors. Currently, the main challenges are focalized on finding solutions for the transformation and valorization of tanned waste, characterized by a significant and variable chemical complexity; moreover, the growing use of innovative tanning systems, makes the search for solutions for the treatment of waste more challenging. In the present work, which originates from a Research and Development Project, co-financed by the Italian Ministry of Economic Development, the use of mechanical pre-treatments using ball milling technologies has been identified as a particularly sustainable, promising and transversal approach, for obtaining leather micro and nano-fibers, to be used as a reinforcement and replacement component in finishing, through conservative processes of the collagen structure, according to the PMW (Principle Minimal Wrecking) and PMS (principle of massive separation) principles. The obtained micro and nano-fibers have been finely characterized, by multiple techniques including X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Attenuated Total Reflection infrared spectroscopy (ATR-IR); then, water dispersions of the fibers have been used in finishing formulations, in addiction or substitution of polyurethane and polyacrylate based chemicals. The obtained films have been applied on leather samples, both on laboratorial and industrial scale.

The performances of the obtained films and of the treated leather samples have been tested in terms of mechanical, chemical-physical properties, mereological features and sustainability impact, through multiple techniques, including Thermogravimetric/Derivative Thermogravimetric analysis (TG/DTG), Attenuated Total Reflection infrared spectroscopy (ATR-IR); Gas chromatography–mass spectrometry (GC-MS) - Purge & Trap equipped. Finally, the studies carried out allowed to verify the applicability of the strategy to different sectors, with reference to the production of leather for footwear, leather goods and the automotive industry, determining the impacts in terms of economic and environmental impacts, which highlighted the feasibility of the approach for obtaining finishes with increased performance, biodegradability and sustainability.

Keywords: leather Waste; zero chemical; mechanical treatments; ball Milling; nanotechnologies; circular finishing

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Novel PLA and TPU bio-composites from leather wastes for fused filament fabrication additive manufacturing technologies

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Abstract: The new industrial revolution in the of sustainability and circularity direction driven by brands of fashion and automotive sectors, finds its motivations in the ecological transition where production can no longer be disconnected from ethical, social and environmental assessments. Leather production is a complex process which produces liquid, gaseous and solid wastes. In particular, solid wastes represent the 31% of the total and are made up of wastes from splitting, shaving, finishing and trimming residues that produces a big impact on the environment. In this project sustainability and circularity paradigms have been approached by the key enabling technology (KET) of Additive Manufacturing (AM) for the research of new printable bio-composite from leather wastes. With a view to circularity, shavings residues have been used as reinforcement of PLA and TPU polymeric matrices to produce bio-composite as suitable material for Additive Manufacturing Fused Filament Fabrication (FFF) applications. In this study polymer matrixes have been reinforced using tanned collagen from wet-state leather shavings grinded in three different sizes. Wastes have been preliminary characterized from a chemical and eco-toxicological point of view and subsequently the grinded material has been morphologically analyzed to determine the particle size distribution for determining its effects on material properties. Thermal and mechanical performances of the bio-composites have been assessed considering three different fillers contents and three different grinding sizes. The bio-composites have been subsequently tested in FFF devices as novel 3D printable materials.

Keywords: leather; leather waste; shavings; additive manufacturing; FFF; filament fused fabrication; sustainability; circularity; reuse; 3D printing; PLA; TPU; particle size distribution; PSD

Preparation of cow hair waste biochar loaded Prussian blue analogs and its effect on Cs(I) adsorption

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Abstract: Radioactive isotope cesium is one of the major pollutants in high-level radioactive waste. Prussian blue analogs (PBAs) exhibit strong affinity and high selectivity of Cs(I). However, the application of PBAs is limited due to low stability in alkaline environments and in seawater, which can easily decompose into highly toxic cyanide ions. To solve these issues, biochar (BC) was prepared from leather solid waste and used as the precursor for the synthesis of PBAs/BC composite material, which was used for cesium adsorption. The material was characterized using FTIR and SEM techniques, and the effects of environmental factors such as pH, adsorbent dosage, reaction time and temperature, and water quality on the cesium adsorption capacity were investigated. The results showed that the PBAs/BC exhibited excellent selectivity and ion resistance, and could safely enrich Cs(I) from the environment, the equilibrium adsorption capacity was as high as 401.82 mg/g. This study provides a new pathway for the resource utilization of leather solid waste.

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Keywords: cow hair waste biochar; cesium; adsorption

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Montmorillonite/gelatin composite aerogel with slit-shaped pores: removal of methylene blue from wastewater

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Abstract: A superior porous structure cellulose aerogel material was prepared using cellulose, gelatin, and clay as raw materials. The microporous structure of the porous gel was achieved via design and regulation of the synthetic process. The structure of composite hydrogel was characterized using XRD, SEM, TG, and FTIR techniques, and adsorption on methylene blue (MB) dye was studied. It is revealed that an initial concentration of 100 mg/L MB, a pH of 7, an adsorbent dosage of 4.3 g/L, an adsorption temperature of 30 ℃, and an adsorption time of 90 min led to an absorption amount of 20.91 mg/g. The thermodynamics and kinetics of adsorption demonstrated that the pseudo-second-order kinetic model was in accordance with the research findings, and the adsorption isotherm met the Langmuir model, displaying good regeneration performance.

Keywords: gelatin composite aerogel; slit-shaped pores; adsorption

Approaches of amidoxime functionalized keratin fibers for uranium extraction from seawater

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Abstract: Keratin fibers from mammalian animal wool and hairs are a recyclable biomass resource with good physical and mechanical properties and excellent textile performance. Keratin, the main component of wool and hairs, is rich in active groups such as disulfide bonds, amino groups, carboxyl groups and hydroxyl groups, which could be feasible modification chemically. We have prepared a series of amidoxime groups functionalized keratin fibers and applied for uranium extraction from seawater. Firstly, amidoxime functionalized wool fibers were prepared by introducing polyacrylonitrile on the surface of wool fiber using potassium permanganate/oxalic acid initiator system, and then reacting with hydroxylamine. The results showed that the feasibility of the surface grafting of wool fiber with amidoxime group. The adsorption capacity of the amidoxime functionalized wool fibers can reach 78.19 mg/ g. Secondly, amidoxime functionalized wool fibers loaded with inorganic nanoparticle antibacterial particles were prepared by radiation-induced grafting polymerization and in situ coprecipitation method to solve the problem that uranium extraction materials in seawater are not resistant to biofouling. The adsorption capacity of nano titanium dioxide amidoxime modified wool fiber adsorbent prepared by this method can reach 113.1 mg/ g on uranyl ions, and the antibacterial rate against *Escherichia coli (E. coli)* is 90%, and the antibacterial rate against *Staphylococcus aureus (S. aureus)* is 95.2%. The adsorption capacity for uranyl ions of the prepared nano zinc oxide amidoxime modified wool fiber adsorbent is at 96.2 mg/ g, with an antibacterial rate of 99.9% for *E. coli* and 99.9% for *S. aureus*. Thirdly, the modification strategy of thiol-ene click reaction was proposed since the characteristic of disulfide bonds rich in keratins. The disulfide bond was reduced by L-cysteine to release of free sulfhydryl groups, and then reacted with acrylonitrile by thiol-ene click reaction to obtain amidoxime-modified wool fibers. The prepared amidoxime functionalized wool fibers show an adsorption capacity of 169.3 mg/g for uranyl ions. By loading nano antibacterial particles, such as TiO_2 nanoparticles, Ag nanoparticles and Cu_2O nanoparticles, the material can also be endowed with excellent anti-microorganism properties. This work provides not only a way for green utilization of animal wool and hairs but also an effective strategy for preparation of adsorbents for extracting uranium from seawater.

Keywords: keratin fiber; amidoxime group; uranium extraction from seawater; adsorption; antibacterial

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Fabrication of leather shavings/polylactic acid biocomposite with anti-stress relaxation, high toughness, and flame retardancy

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Abstract: Millions of tons of leather shavings (LSs) are produced globally each year, which will cause serious waste of resources and environmental pollution if not properly disposed. Polylactic acid (PLA) is a biodegradable polymer, but its widespread application has been limited due to the stress relaxation phenomenon, brittleness, and flammability. Here, a sustainable strategy to improve the anti-stress relaxation, toughness, and flame retardancy of PLA was proposed by blending PLA with LSs-based fillers (LSFs). The LSFs were prepared by hydrophobic modification of chrome-free LSs with epoxidized soybean oil, and scanning electron micrographs showed that LSF/PLA biocomposites were homogeneously blended without any gaps. Comparing LSF/PLA with pure PLA and LS/PLA showed that LSF/PLA had the highest stress (8.49 MPa) and modulus (532.0 MPa) under long-term deformation, which indicated that the introduction of LSF greatly improved the anti-stress relaxation of PLA. The toughness of PLA was also improved because LSF inhibited the microcrack growth of PLA matrix during material failure. Moreover, LSF/ PLA exhibited the longest ignition time as well as gentle exotherm and oxygen consumption, which meant that this biocomposite has a flame retardancy. This work provides insights into the resource utilization of LSs and the development of PLA biocomposites with excellent comprehensive properties.

Keywords: leather shavings; polylactic acid; epoxidized soybean oil; anti-stress relaxation; toughness; flame retardancy

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Sustainable porous activated carbon as a potential electrode material for flexible supercapacitor application

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Abstract: Developing value-add material from waste generated from the leather industry is pertinent to enable sustainability in the leather industry. This study explored the possibility of using chrome shaving wastes from the leather industry for supercapacitor applications. Chrome shaving waste was carbonized, followed by chemical activation, then utilized as electrode materials, and gel polymer was used as an electrolyte (GPE) for the supercapacitor. GPE has been used instead of liquid electrolytes in symmetric two-electrode setups to deal with leakage and corrosion problems. In the three-electrode mode, chrome shaving waste-derived porous carbon electrodes exhibited a high specific capacitance of 245 F/g at 0.5 A/g. Further, the porous carbon was tested for a symmetric two-electrode setup in a GPE medium. The flexible symmetric capacitor exhibited a high energy density of 14.7 Wh kg^{-1} at a current density of 0.5 A g^{-1} and a power density of 8000 W kg^{-1} at a current density of 4 A g^{-1}, respectively. Also, we fabricated a prototype pouch cell supercapacitor (3*3 cm^{-2}) for real-time supercapacitor application. The fabricated device has been investigated in a serially connected device that can light up the LEDs. This research provides a simple, cost-effective approach to utilizing porous carbon materials for flexible supercapacitor applications and the circular economy.

Keywords: porous activated carbon; surface area; supercapacitor; gel polymer electrolyte; pouch cell

Cryogenic delamination of finished leather as a tool for circular economy

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Abstract: Finished tanned leather are usually covered by a thin polymeric layer. This layer has the scope to change the morphological aspect of the finished leather as well as to improve the impermeabilization properties. Many times the finished product is refused by the final client and then the tannery has to store significant amount of materials in the hope of a new destination or, in the worst case, to destroy it as waste product. It is then very important to remove this finishing polymeric layer to recover the tanned leather and to reprocess it towards a new finishing. The bonding between the polymeric film and the leather is so strong that today only a blade shaving process is able to perform this separation at the expenses of a reduction of the leather thickness. Here, using the significant difference in the dilation properties between the tanned hide and the polymeric film, a cryogenic process is developed. The use of cryogenic fluids, like liquid nitrogen or solid carbon dioxide, is able to freeze the polymeric layer under the glass transition temperature and then inducing a brittle behavior. The result is an easy separation without the alteration of the tanned leather layer. Thus the here developed process allows the reuse of the tanned leather towards a new life in the respect of the circular economy principles.

Keywords: finished leather; recycle; circular economy

Comparative analysis of volatile compounds in leather using solvent-assisted flavor evaporation and solid-phase microextraction

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Abstract: The leather volatile component is a mixed various compound. The leather odor analysis has been performed mainly using a gas chromatography-mass spectrometry (GC/MS). Pretreatment is required before introduction of sample to GC. Solid-phase microextraction (SPME) is a solvent-free sample preparation method using coated fibers to extract analytes from samples prior to GC. The SPME method is a simple method, but the adsorbed compounds depend on the type of fiber. Quantitative analysis is difficult because the gas phase is injected into the GC. To understand the totality of the volatile compounds of leather, we need to look at solvent extraction. High-vacuum distillation using a solvent-assisted flavour evaporation (SAFE) is known as a method of distilling volatile compounds with high boiling points at high yields. In connection with a high vacuum pump (5×10^{-3} Pa), contaminants can be removed by high vacuum distillation. The optimized water bath temperature was 30 °C and condenser temperature was 30 °C. In this study, volatile compounds in leather were extracted using two different pretreatment methods, SAFE method and SPME method. Then identification of the volatile compounds was achieved using GC/MS. Comparison of extraction techniques showed that the SAFE method had a higher recovery for chemicals for finishing.

Keywords: solvent-assisted flavour evaporation; solid-phase microextraction; gas chromatography-mass spectrometry

Review progress of assessing and preliminary research of certified reference material on odour of leather

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Abstract: As the main material for shoes and leather goods, leather is widely used and recognized by consumers because of its good sensory and performance characteristics. Nowadays consumers pay more and more attention to the health and environmental protection of the products they used. The odour of leather goods and the raw material used has gradually attracted the attention of consumers and quality supervisors. However, at present, the subjective evaluation method is the main method for the detection of different odour of leather, and there is no relevant certified reference material. In this paper, the main sources of leather odour, influencing factors and research progress of detection methods were summarized, and the preliminary proposal of certified reference material on odour of leather was presented, which provides suggestions for odour detection of leather, shoes and other field.

Keywords: leather; certified reference material; odour; rare delicacy; detection and assessing

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Magnetic multi-template molecularly imprinted materials: synthesis, characterization and selective adsorption for chlorophenols

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Abstract: Magnetic multi-template molecularly imprinted materials (M-mt-MIMs) were synthesized by multi-template imprinting strategy and surface imprinting technology. Magnetic iron oxide nanoparticle-multiwalled carbon nanotube (M-MWCNTs) composites were firstly prepared by one-step solvothermal method and polydopamine (PDA) coating was formed on the surface of M-MWCNTs by the oxidative self-polymerization of dopamine. The PDA coated M-MWCNTs were used as supporting materials for the preparation of imprinted materials, with the mixture solution of 2-chlorophenol, 4-chlorophenol, 2,6-dichlorophen, 2,4-dichlorophen and 2,4,6-trichlorophenol as templates, methacrylic acid (MAA), ethylene glycol dimethacrylate, acetonitrileas functional monomer, cross-linker and porogens, respectively. To select the optimized functional monomers, the binding energy between templates and different kinds of functional monomers (MAA, 4-vinylpyridine and acrylamide) was simulated calculated by Gaussian. The morphology, structure, functional group thermal stability and magnetic property of prepared M-mt-MIMs were characterized by SEM, TEM, XRD, FT-IR, TGA and VSM. The statistic adsorption experiments were performed to obtain the adsorption capacity of 32.59- 89.92 mg/g for five kinds of chlorophenols (CPs) and the adsorption isotherm was well fitted with the Langmuir isotherm model. The kinetic adsorption data could be well described by the pseudo-second-order and showed rapid transfer rate. Compared with non-imprinted materials, M-mt-MIMs showed better adsorption selectivity and could be reused at least 5 times without prominent degradation of performance. Moreover, tannery wastewater and the hydrolysate of wet blue and crust leather spiked with different concentration level of five CPs were further evaluate the adsorption property of the as-prepared M-mt-MIMs, showing satisfactory selectivity.

Keywords: magnetic molecularly imprinted materials; multi-template imprinting strategy; chlorophenols

Membrane protected micro-solid-phase extraction based on multi-template imprinted materials for HPLC determination of chlorophenols in leather

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Abstract: In order to rapid and high selective analysis chlorophenols in complicated leather matrix, multi-template imprinted materials (mt-MIMs) were prepared by surface imprinting technology and packed into porous nylon membrane as micro-solid-phase extraction (μ-SPE) unit, coupled with HPLC-DAD to simultaneously enrich and determine five kinds of typical chlorophenols in leather matrix. Mesoporous silica modified multiwalled carbon nanotubes (MWCNTs@mSi) was firstly prepared as supporting materials, the mixture solution of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol as template, and the imprinted layer containing recognition site of template were formed on the surface of MWCNTs@mSi by free radical polymerization. The as-prepared imprinted materials were characterized by SEM, TEM, FT-IR, TGA and BET and the adsorption properties were investigated by static adsorption, dynamic adsorption and selective adsorption experiments, showing high adsorption capacity of 25.64~58.61 mg/g and rapid transfer rate of 30 min. The parameters affecting the extraction efficiency were optimized, including the amount of adsorbent, sample pH, the type and volume of desorption solvent, vortex time, salt effect and reusage. The established mt-MIMs-μSPE-HPLC method showed satisfactory linearity, high accuracy and sensitivity, with the linearity range of 2.00~200.00 μg/L, LODs and LOQs of 0.36~1.29 μg/L and 1.18~3.86 μg/L, intra-day and intra-day precision of 1.05%~3.64% and 1.88%~4.77%, respectively. The method was successfully applied to analyze chlorophenols in leather samples, with the recoveries of 81.65%~106.46% and RSD of 0.72%~2.84%. This study provides a reliable analytical method for the determination of trace level of chlorophenols in leather matrix.

Keywords: multi-template imprinted materials; membrane protected micro-solid-phase extraction; chlorophenols

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Key odorants of polyurethane materials used in steering wheel

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Abstract: Polyurethane (PU) is the main component of wrapping materials of steering wheel in the car, but suffered the volatilization of volatile organic compounds (VOCs) and especially malodorous substances. Herein, steering wheels made of three PU materials (W-PU, B-PU, and B-PU-p) were evaluated by the sensory method VDA 270 and Quantitative Descriptive Sensory Analysis combined with chemo-analytical characterization using the thermal desorption system coupled to gas chromatography-mass spectrometry-olfactometry (TDS-GC-MS/O), and the key odor substances of steering wheel PU are selected by calculating OAVs. The results indicated that three PU materials possessed medium-high odor intensities rated from 3.5 to 5.0 (scale 1-6). Furthermore, panelists showed a general dislike of the odor with hedonic ratings from 3 to 5.5 (scale 0-10). Compared to the W-PU, the overall odor intensity of B-PU and B-PU-p showed an increasing trend and the stink, pungent and fruity odor intensity increased significantly, indicating that colorants (B-PU) and paints (B-PU-p) were the main sources of steering wheel PU odor. In total, 144 volatile compounds were identified, and 48 compounds with odor characteristics. Among them, aldehydes, esters and aromatic hydrocarbons contribute the most. Hexanal, heptanal, octanal, nonanal, butyl acetate, toluene, and phenol were the key odorants in the sample of B-PU-p.

Keywords: odorants; polyurethane; TDS-GC-MS/O

Tannin identification and pyrolysis behavior of vegetable-tanned leather

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Abstract: Leather cultural relics are important carrier for human civilization, which might witness the development of culture, science, and technology. Therefore, the research on the identification and aging mechanism of ancient leather artifacts is of great significance. In this work, with both tara- and quebracho-tanned leathers as cultural relic models, the pyrolysis characteristics, kinetics, and products of the samples were investigated using thermogravimetric (TG) analysis, TG coupled with Fourier-transform infrared spectroscopy, and mass spectrometry (TGA-FTIR-MS) analysis. The results showed that the gaseous products mainly consist of CH_4, NH_3, H_2O, CO, HNCO, CO_2, and pyrrole. The presence of CO and the intensity changes of CH_4 and NH_3 could provide secure and reliable identification of tannin types. Additionally, the modified Kissinger-Akahira-Sunose (MKAS) and Friedman (FR) methods were used to investigate the pyrolysis kinetics, providing insight into the aging mechanisms of ancient leather samples. As a non-destructive approach, FTIR analysis has been proved useful in tannin identification. This study might provide a theoretical basis for the conservation and restoration of collagen-based cultural relics, practical guidance for cultural heritage conservationists, as well as identification and preservation of cultural relics of vegetable-tanned leather.

Keywords: leather; cultural relics; aging mechanism

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Influence of high temperature and humidity on the leather tanned with betel nut extract

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Abstract: Leather artifacts, mainly composed of collagen and tanning agents, possess significant historical importance. However, external factors could lead to the aging of such artifacts during preservation. Therefore, it is crucial to examine the impact of various factors on leather aging. In order to mimic the effects of high temperature and humidity conditions on the aging changes of leather artifacts, the traditional vegetable tanning with betel nut tanning agent was used to tan the pickled sheepskins. The leather artifact model samples were aged for 0, 5, 10, 20, and 30 days at 80 °C and 65% RH, and their structural and morphological changes were analyzed using Fourier transform infrared spectroscopy (FTIR), chromatography, ultra-deep microscopy, and scanning electron microscope (SEM). The thermal degradation of the samples before and after tanning with betel nut was analyzed using a thermogravimetric analyzer (TGA). Both methods of Friedman (FR) and Flynn-Wall-Wzawa (FWO) were employed to calculate the activation energy and thermodynamic parameters, respectively, by which the thermal degradation activation energy of samples before and after betel nut tanning were obtained. Furthermore, the tensile performance of the samples was investigated at different aging stages. By the present study, valuable insights into the stability of leather artifacts during long-term storage, the optimization of storage conditions, and guidance for the restoration and preservation of leather artifacts might be provided.

Keywords: leather; temperature and humidity; influence

The chemical degradation of vegetable tanned sheepskin leather under acidic condition

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Abstract: The production and use of leather products have a long history, and are still one of the most important materials in the daily life. However, because leather is a natural polymer material, with the main component collagen, it is extremely easy to deteriorate due to the changes of environmental conditions. Acid aging is one of the main causes of serious damage to leather. Low pH in humid environment, soil acidification, air pollution, organic acid produced by fungi and excessive use of acid in leather making might lead to the acid aging of leather products. In the present work, the properties of vegetable tanned sheepskin leather before and after artificial acid aging is studied, the modern analytical techniques were used to characterize and analyze the acid aging mechanism of the leather samples. The changes in morphology, color, and structure were analyzed by ultra-depth three-dimensional microscope, high precision colorimeter and Fourier transform infrared spectroscopy (FTIR). It was found that leather samples tanned by different types of vegetable tanning agents have different deterioration behaviors. The research is of great significance to prevent leather products from acid deterioration, by which a theoretical basis for the repairing of leather artifacts that have been acid deterioration might be provided.

Keywords: vegetable-tanned leather; degradation; acid aging

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Innovative method for the determination of hydrothermal stability of leathers using DMA techniques

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Abstract: Shrinkage temperature (Tg) represents the hydrothermal stability of leather. At specific temperature and in wet conditions leather undergoes an irreversible degradation of the triple helix structure of collagen to a random coil network; from a macroscopic point of view, this solid-solid transition manifests itself in a reduction in a dimensional reduction of the material (shrinkage). The shrinkage temperature depends on the state of the skin and on the efficiency of the crosslinking by tanning agents; while raw hides/skin could only resist up to 60 °C, vegetable tanned leathers have a shrinkage temperature of about 70 °C, glutaraldehyde tanned leathers resist up to about 80 °C and chrome tanned leather present the higher value of hydrothermal stability that is about 105-110 °C. From a processing point of view, shrinkage temperature is assessed to qualify the quality and the efficiency of the tanning process from raw hide to tanned leather. It is usually determined according to ISO 3380:2015 | IULTCS/IUP 16 that provides the immersion of a rectangular sample in a vessel fixed in iso-strain conditions in a specimen holder at a specific temperature ramp. When shrinkage occurs, the correspondent temperature is noted as the hydrothermal resistance of leather. This test method presents some operative issues that can complicate the measurement. From the one hand, if there is not an automatic mean to assess the temperature when contraction occurs, there could be problems in the precise definition of hydrothermal stability and a loss of time of operators that carry out the test; on the other hand, many commercial devices have problems to maintain constant the rate of heating in the tolerances indicated in the standard. In this study, shrinkage temperature has been assessed using DMA techniques. Different tanned samples have been fixed in tensile clamps equipped with a washer and iso-strain conditions at ISO 3380 temperature

ramp and the stress correspondent to the solid-solid transition have been measured instrumentally. The results have been compared with those from the traditional device and the validation of the test method provides an innovative instrumental method for the determination of the hydrothermal resistance of leathers.

Keywords: shrinkage temperature; hydrothermal stability; dynamic mechanical analysis; DMA; ISO 3380; degradation; hydrolysis

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Insights on the estimation of particle size distribution (PSD) of grinded leather particulate using a digital image processing method (DIP)

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Abstract: In tanning industry, the use of solid waste as a polymer filler/reinforcement to produce new circular materials is widespread. Leather fibers have been successfully employed in furniture as upholstery textiles consisting in shaving powder (generally chrome-tanned) incorporated in a polymeric matter. In order to respond to the need of circular and sustainable processes, numerous studies on composites with polymeric matrix filled with particulate reinforcement or tanned leather fibers have been carried out. These studies focus mainly on characterization of mechanical properties of the final product containing different concentration of the filler. However, to improve the effectiveness of the use of such organic waste there is the need to assess the shape and size of grinded scraps. In literature, only in a few cases the particle size distribution (PSD) of fibers/particles (that is the dimensional distribution curve of the size of the particulate) has been characterized. The PSD is very important because it affects the interface surface between the filler and the matrix, so at the same concentration of reinforcement, the final product will have different mechanical properties depending on their dimensional distribution. The dimensional quantification is conventionally performed by optical microscopy by considering linear estimation of milled leather fibers. Nevertheless, linear measurements are not adequate for the experimental evaluation of the PSD, since the milling process does not produce linear fibers but agglomerates of different density linked by fibrous elements. Aim of this study is to propose a procedure for the identification of the PSD by means of the acquisition of images using optical microscope and their post-processing with an open-source digital image processing software (DIP) able to quantify the area of the particle.

Keywords: particle size distribution; PSD; digital image processing; DPI; leather waste; grinded leather

Research and implementation of leather shrinkage temperature detection method

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Abstract: The constant tension of 3 grams and the further improvement of detection accuracy have always been two major challenges in the leather shrinkage temperature (Ts) testing device. Relying on the advantages of leather specialization in the school, and after more than ten years of exploratory research based on the MSW-YD4 first-generation machine, the second-generation machine with independent intellectual property rights, TMAF-YD4 collagen fiber thermal deformation analyzer, has finally overcome this technological bottleneck by using a non-contact displacement sensor based on visual technology and combining the natural balance method effectively. For the first time, it not only fully meets all the testing conditions in domestic and foreign Ts testing standards such as "QB/T2713--2005" but also significantly improves the accuracy of shrinkage deformation detection (0.01mm). In addition, overall optimization and improvement measures have been taken in terms of the uniformity of the heating medium temperature field, the setting of the optimal temperature acquisition point, the fixing method of the sample hanging hole, and the corresponding standard sampler, which have effectively improved the accuracy and credibility of the testing data. The abundant data, various real-time display methods, and output in the host interface, as well as other modern processing methods, provide strong technical support for further professional research and analysis. The second-generation machine, together with the first-generation and other series products, covers the different levels of needs of users including universities, institutions, and enterprises. The prototype has been tested for one year with good results, and its application has been extended to biomedical engineering fields such as heart valves.

Keywords: collagen fibers; Ts; detections condition; accuracy; hanginger sample fixation; data processing

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Emission characteristics and probabilistic health risk of volatile organic compounds from leather sofa

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Abstract: Furniture is identified as a vital volatile organic compound (VOC) emission source in the indoor environment. Leather has become the most common raw and auxiliary fabric material for upholstered furniture, particularly with extensive consumption in sofas, due to its abundant resources and efficient functions. Despite being widely traded across the world, little research has been conducted on the VOCs released by leather materials and their health risk assessment in the indoor environment. Accordingly, this study investigated the VOC emissions of leather with different grades and the health risk of the inhalation exposure. Based on the ultra-fast gas phase electronic nose (EN) and GC-FID/Qtof, the substantial emissions of aliphatic aldehyde ketones (Aks), particularly hexanal, appear to be the cause of off-flavor in medium and low grade (MG and LG) sofa leathers. The health risk assessment indicated that leather materials barely pose non-carcinogenic and carcinogenic effects to residents. Given the abundance of VOC sources and the accumulation of health risks in the indoor environment, more stringent specifications concerning qualitative and quantitative content should be extended to provide VOC treatment basic for the manufacturing industry and obtain better indoor air quality.

Keywords: indoor environment; leather; volatile organic compounds (VOCs); health risk assessment

Insights into the key odorants in automotive interior leather by application of the sensomics approach

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Abstract: The automotive interior leather with a specific odor characteristic is the primary factor to influence the interior odor in car. However, its key odorants are still unknown. Meanwhile, the complexity process of the leather bring the odor diversity. In this study, the effect of the process on the key odorants in automotive leather has been investigated in detail. The odor type of the automotive interior leather can be divided into senven ones including sweet, fruity, green, woody, leather-like, pungent and stench using VDA 270. 34 odorants were analyzed by thermal desorption system-gas chromatography-mass spectrometry-olfactory (TDS-GC-MS-O). In particular, 19 key odorants (OAV ≥ 1) were screened by calculating the odor activity value (OAV), while 13 key variables (VIP > 1) were used for screening by calculating the variable importance in prediction (VIP). Furthermore, odorants with OAV and VIP greater than 1 (hexaldehyde, heptanaldehyde, D-limonene, N, N-dimethylformamide, nonaldehyde, butyldiglycol) were confirmed as key variable odorants of leather by odor recombination and omission experiments. The knowledge of key odorants obtained showed potential for removing the off-odor of the automotive interior leather.

Keywords: odor of the automotive interior leather; odor activity values; odor recombinate; omission tests

Collagen extraction and hydrolysis from sheepskins: advancing value and eco-friendly practices

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Abstract: Sheepskins, traditionally processed as pelts, face challenges due to their low value proposition in the leather industry. To overcome this limitation, innovative approaches are required to unlock their potential and create high-value opportunities. This study focuses on the extraction and hydrolysis of collagen from sheepskins, a promising avenue for value enhancement.

Collagen extraction involves the removal of wool fibers from the skins, which can hinder the process. Conventional dewooling methods rely on harsh sulfide paint, known for its detrimental environmental impact. In contrast, this study proposes acetic acid depilation as a cost-effective and eco-friendly alternative. Acetic acid effectively separates wool fibers from fresh skins, providing a sustainable solution for collagen extraction. The aim of this research is to comprehensively characterize the process of collagen extraction and hydrolysis from raw sheepskins. Key parameters such as the efficiency of acetic acid depilation, collagen yield, and quality are investigated. Optimization of hydrolysis conditions is also explored to ensure the production of high-quality collagen. Through detailed characterization, the physical, chemical, and structural properties of the extracted collagen are evaluated. This includes assessing molecular weight distribution, amino acid composition, and functional properties. Potential applications in industries such as cosmetics, food, and biomedical sectors are explored, considering properties like physicochemical characteristics, solubility, and film-forming capabilities. Moreover, the environmental impact and sustainability of the collagen extraction and hydrolysis process are analyzed. A comparison between acetic acid depilation and conventional sulfide-based methods is conducted to evaluate the eco-friendliness and cost-effectiveness of the proposed approach. This analysis provides valuable insights for implementing sustainable practices in the leather industry. The outcomes of this study contribute to the advancement of sheepskin utilization by transforming them into high-value collagen-based materials. Optimal extraction and hydrolysis processes result in collagen with desirable properties for various applications. Additionally, the adoption of the environmentally friendly acetic acid depilation method represents a significant step towards sustainable and responsible leather processing.

Keywords: sheepskin; collagen extraction; hydrolysis; acid depilation; sulfide depilation

The application of recombinant *WB600/KerT protease* with low collagenolytic activity in unhairing system

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Abstract: In order to mitigate the pollutants generated in traditional unhairing process such as sulfide and waste hairs, the application of recominant *WB600/KerT protease* has been proposed in an advanced unhairing system for hair removal and the extraction of regenerated protein from waste hairs. By genetically modifying the producing strain, the recombinant *WB600/KerT protease* exhibits superior keratinase ability while minimizing collagen degradation, thereby preserving the surface grain of hide in the enzyme unhairing process. The mechanism of recombinant *WB600/KerT protease* unhairing are investigated in this research, while its continuous influences on subsequent processes including liming and deliming are evaluated. In addition, the wastewater generated during unhairing-liming and deliming stages was analyzed for assessing the environmental impact. Afterwards, the effects of the *WB600/KerT protease* unhairing system are examined for the production of goat skin and cow hide, in conjunction with Cr-tanning and aldehyde-vegetable combination tanning. The waste cow hairs produced from enzyme unhairing process are collected and the regenerated protein is extracted utilizing the recominant *WB600/KerT protease* treatment. The properties of the regenerated protein are analyzed for the potential future applications. This research develops an industrial enzyme unhairing system that facilitates cleaner production in the leather production, while simultaneously enabling the efficient utilization of waste protein sources.

Keywords: unhairing; recombinant *WB600/KerT protease*; grain surface integrity; regenerated protein; environmental assessment

LCA analysis of a novel polymeric fatliquor

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Abstract: The Corichem company has recently developed and patented a new class of polymeric fatliquors based on the combination of polymeric glycols and functionalized fatty substances. This new class is characterized by excellent flexibility, improvement of fixations and reduction of COD and high performance of the obtained leather, in particular for that intended for the automotive industry. In the development of these new products, particular attention was paid to the analysis of their life cycle through the use of the LCA tool. This tool has provided us with support on the choice of raw materials, on the opportunities for reducing environmental impacts and has allowed us to compare the various products developed to optimize their long-term sustainability. In this work we intend to present a case-history, illustrating the environmental impact assessment of a specific polymeric fatliquor for automotive wet-white leather, produced from raw materials from renewable sources. We will present the initial data collection process, their evaluation and their optimization, their processing through the use of models. Finally, we will illustrate the data obtained by expressing them in terms of acidification, eutrophication, photochemical oxidation and global warming. The results obtained are beneficial for the improvement of the company strategy, of knowledge of the processes and are a starting point for further evolutions of the products range of company by the Research and Development laboratory.

Keywords: LCA; polymeric fatliquor; sustainability

The mechanical analysis and application effect evalution of chromium-tanned mycelium leather

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Abstract: Ganoderma applanatum is one of the most popular medicinal mushrooms due to the rich content of biologically active ingredients. In recent years, the substitutive leather has been attempted to make from mycelium of ganoderma applanatum, which is expected to be more environmentally friendly and fully biodegradable. However, the mechanism of tanning of mycelium leather has not yet been explored. In this study, the reaction mechanism of chromium tanning used for producing mycelium leather was explored. The helical conformation and spatial structure of chromium-tanned mycelium leather were studied using UV spectrum and scanning electron microscopy. Additionally, molecular analysis was conducted using infrared and nuclear magnetic resonance spectroscopy to reveal the effects of chromic sulfate and its pretreatment on the structure of Ganoderma lucidum mycelia. The results indicate that the main components of Ganoderma lucidum mycelium are polysaccharides and a small amount of amino acid groups, and chrome agent can crosslink with the hydroxyl groups of Ganoderma lucidum mycelium. This research systematically elucidates the structural characteristics of chromium-tanned mycelium, enriches the structural information of chromium-tanned mycelium, and lays the foundation for the development and application of mycelium leather.

Keywords: chromium-tanning; mycelium leather; ganoderma applanatum; mechanistic study; leather alternatives

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Bioremediation of leather using laccase for the degradation of phenolic compounds

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Abstract: Chlorophenols and bisphenol compounds are commonly found in industrial wastewater and they have harmful effects on human health and the environment. They are toxic, carcinogenic and endocrine-disrupting, and can cause a range of health problems. Our study investigated the degradation of chlorophenols and bisphenol compounds in leather and its wastewater by laccase. The laccase was used to degrade a range of these compounds, including 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, bisphenol A and bisphenol B. The results showed that the laccase was effective in degrading these compounds, with degradation efficiencies ranging from 60% to 95%. We also investigated the effects of pH, temperature, and laccase concentration on the degradation efficiency. A temperature of 45 °C and a pH of 4.5 are the conditions under which laccase is most efficient in degrading these compounds. Our findings show the potential of laccase as a bioremediation agent in the treatment of leather contaminated with chlorophenols and bisphenol compounds. This is a promising approach to reduce the negative environmental impact of leather.

Keywords: laccase; chlorophenols; chlorophenol pollutants; bisphenol pollutants

Development of a non-alkaline pH unhairing process based on the partial oxidation of the disulfide bond, followed by a sulfitolytic treatment

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Abstract: Also in the tanning industry, in recent years, the emphasis has been particularly placed on the various environmental problems that any industrial sector is forced to consider. Along the leather production process, one of the phases particularly placed in the spotlight, due to its polluting nature, is the liming-unhairing process. In order to find a way to avoid these environmental problems we have try to develop a new oxidative pathway for the unhairing of the hide. To avoid the production of heat during the treatment, the oxidation of cystine residue is stopped to the partial oxidation products cystine thiolsulfinate and cystine thiolsulfonate, obtained respectively through a single and a double oxygen transfer. The partial oxidation is obtained at slightly acidic pH using a Titanium peroxocomplex as catalyst. These products of partial oxidation are more prone to undergo a nucleophilic displacement attack by inorganic anion that we have operate with the use of sodium bisulfite near to neutral pH, resulting in a room temperature sulfitolytic scission of the oxidized R-S-S-R bond. The hair result to be loose and partially degraded and the unhairing can be ultimate using a very gentle protease treatment at the same pH of the sulfisolysis. The outcome is to obtain an oxidative hair-saving unhairing process without the development of heat and that work at near neutral pH, avoiding the uses of bases and sodium chloride.

Keywords: unhairing; oxidation; sulfitolysis

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Understanding the bisphenol content of leather: a study of the influence of chemical type and processing method

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Abstract: Bisphenol A (BPA) has been identified as an endocrine disruptor[1]. The endocrine system covers multiple functions within the body through a series of feedback loops that help with the regulation of organs through the secretion of hormones. As such, any chemicals which are endocrine disrupting can have widespread impact within the body or the natural environment. Despite this over 1,000,000 tonnes/annum of BPA are produced, imported, and used within the EU[2]. Also of concern are substances related to BPA, in particular Bisphenol S (BPS) and Bisphenol F (BPF) which, while less evidence exists, have had endocrine disrupting properties identified in Zebra fish, rats, mice and humans [3]. Both BPS and BPF are often found in leather, in the case of BPS as the starting material from which sulphone replacements syntans are produced, and in the case of BPF as a byproduct in the production of phenolic syntans. Due to the environmental concerns, the European Union is proposing restrictions in total bisphenol content in leather of 10 mg/kg, with a temporary higher limit of 500 mg/kg between 2025 and 2030 making the presence of bisphenol compounds in leather a compliance as well as an environmental issues[2]. Despite the proximity of these new regulations in the EU, there is little information in the public domain related to their presence in leather chemicals and their transference into leather. There is an urgent need for research in this area. Here we have applied high performance liquid chromatography (HPLC) to study bisphenol content in sulphone and phenolic syntans and their incorporation into leather. Interestingly, significant variations in BPS and BPF content were observed. Sulphones contained between 207 and 41,200 mg/kg BPS, though most had concentrations above 6,000 mg/kg. Phenolic syntans contained between 240 and 563 mg/kg. Some products contained both BPS and BPF. In all cases bisphenol contents were higher in belly areas compared with those measured at the official sampling position (OSP), typically by 12 – 14%. This questions the suitability of the OSP as a sampling position to ensure compliance with the proposed EU regulations. Additionally, a comparative trial of 4 separate approaches to leather processing was undertaken, where it was demonstrated that final leather BPS and BPF concentration can vary significantly depending on the point of application of the replacement syntan, and other variations, with up to 25 – 35% reduction of final leather bisphenol content achievable.

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Keywords: bisphenol; restrictions; syntans

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Exploring biodegradability in leather: impact of tanning and finishing processes

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Abstract: As environmental sustainability becomes increasingly important, the biodegradability of materials plays a crucial role in reducing their impact on the environment. Leather, composed mainly of collagen, is a popular and inherently biodegradable material. However, the chemical processes involved in its production can influence its biodegradability. This study investigates the biodegradability of leather produced through tanning, retanning, and finishing processes, with a specific focus on chromium and zeolite tanning. Our findings reveal that chromium-tanned leather exhibits exceptionally low biodegradability, while zeolite tanning demonstrates higher biodegradability, although reduced when combined with retanning and fatliquoring products. Furthermore, we demonstrate that the biodegradability of zeolite-tanned leathers can be enhanced by incorporating sustainable products. However, chrome-tanned leathers maintain their persistently low biodegradability. Regarding finishing, our results suggest that although the process has some influence on the final outcome, it has minimal impact on leather biodegradability and does not prevent degradation. The type of crust appears to be a more influential factor since, as even when using finishing products with limited biodegradability, the overall biodegradability of the leather remains relatively unaffected. These results highlight the urgent need for adopting sustainable and environmentally friendly practices within the leather industry to mitigate its environmental impact. By optimizing tanning processes, favoring zeolite tanning over chromium tanning, and incorporating sustainable approaches during retanning and finishing, it is possible to improve the biodegradability of leather. This research contributes to the goal of fostering a more sustainable and eco-conscious leather production industry.

Keywords: biodegradability; finishing; retanning; sustainability

Preparation of a mussel-inspired bio-adhesive composed of polylysine modified gelatin and 3,4-dihydroxybenzaldehyde

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Abstract: Bio-adhesion has been wildly used in various biomedical applications, such as orthopedics, surgery, drug delivery systems, etc. While preparation of bio-based adhesives with high strength and biocompatibility is still a major problem. Gelatin is a promising material for bio-adhesive due to protein's abundance, its excellent biocompatibility, resorbability and typically low immunogenicity. However, its high permeability to water and its relatively poor adhesion strength limits its applications. Inspired by the mechanism of bio-adhesive proteins such as mussels and oysters, we used a two-step process to develop a gelatin-based adhesive. First, polylysine (ε-PL) was introduced into gelatin chains catalyzed by microbial transglutaminase (MTG) to improve the number of amino groups available for the next reaction. Second, 3,4-dihydroxybenzaldehyde (DHBA) was intercalated to form a gelatin-polylysine-benzaldehyde (Gel-PL-DB) adhesive. The as-prepared adhesives were characterized by ultraviolet-visible spectroscopy (UV), infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA/DTA). The results of UV-visible spectroscopy showed that ε-PL was successfully grafted onto gelatin molecules, and FTIR test results indicated that DHBA was successfully polymerized into Gel-PL. TGA/DTA curves showed that the thermal degradation of Gel-PL-DB began at 200 °C and had high thermal stability. Adhesive strengths were evaluated using fresh porcine skin as a model system, which was lapped under constant temperature and humidity for 9 h. The highest adhesion strength was 47.26 ± 14.40 Kpa, which was 10 times that of Gel-PL. The biocompatibility of the adhesive was evaluated by MTT assay. The relative proliferation rate of cells cultured with the extract for 48 h was more than 85%. In summary, the bio-based tissue adhesives synthesized in this study have good biocompatibility, high adhesion properties, and has good application potential in the biomedical applications.

Keywords: gelatin-based adhesive; mussel-inspired; high adhesion properties

Development of leather-like materials with glutaraldehyde processing of mycelium

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Abstract: As the demand for environmentally friendly materials continues to rise, sustainable mycelium leather derived from mushrooms has been considered as a promising alternative to traditional animal leather. In this study, we focused on exploring the physicochemical and mechanical properties of mycelium after treatment with glutaraldehyde. The interactions between glutaraldehyde and mycelium were characterized using NMR and FTIR analysis, elucidating the underlying chemical crosslinking reaction. Furthermore, the structural changes of mycelial fibers were observed with SEM observation. Subsequently, the tanned mycelium was treated following the post-tanning process of traditional leather manufacturing such as fatliquoring and dyeing. The resulting mycelium leather was evaluated for key characteristics including tensile strength, elongation at break, thickness, density, and shrinkage temperature (Ts). The results show that the mycelium leather exhibited a shrinkage temperature exceeding 150 °C and possessed an average thickness of approximately 0.8 mm, which is half the average thickness of conventional goat leather. The corresponding tensile strength was determined to be around 5.3 MPa. Importantly, the growth time and density of mycelium were found to significantly influence the thickness and tensile strength of the resulting mycelium leather. This study demonstrates the feasibility of treating mycelial materials, providing valuable insights for the development of leather-like materials. The physicochemical and mechanical characterization presented the potential application of mycelial leather as a viable alternative eco-friendly material.

Keywords: mycelium Leather; glutaraldehyde; leather-like material

For a sustainable leather industry: environmental effects of tanning fish skins with beverage residues

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Abstract: In recent years, various research on the possibilities of using fish skins, which are a by-product of the fish processing industry in many areas have started to gain intensity. One of these possibilities is the processing of fish skins as finished leather in order to add value. Studies on the tanning of fish skins, which are considered exotic leathers, have focused on the physical and chemical properties of the leathers obtained. In this study, rainbow trout fish skins were tanned by being used alone or in combination with tannins obtained from used tea and coffee residues, and also peels and seeds of the pomegranate unused in the production of pomegranate juice. The wastewater pollution parameters such as chemical oxygen demand (COD), biological oxygen demand (BOI), total suspended solids (TSS), chloride, and total nitrogen in wastewaters of soaking, liming, tanning, and post-tanning processes. The obtained results were compared with the values obtained in chrome leather production.

Keywords: fish skin; coffee; tea; pomegranate; process wastewater

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Leather manufacturing: what is indeed AI chatbot capable of

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Abstract: As one of the most advanced AI language models, CHATGPT became popular in very short days, breaking many Internet records. Later on, other AI chatbots have emerged. Now AI language models had became a productive tool. The application fields were covered IT, e-commerce, intelligent customer service, games, education, medical, media, entertainment and others. It was also be applied in many traditional manufacturing cases. Within today's rapid development of artificial intelligence, sustainability of modern leather-making will need all the tanner' s contribution. However, as a tanner what benefits can get by the using of CHATBOT. The application in practical of how to using a CHATBOT in proper way, when you are a tanner, it will be quite necessary for you to know how to ask the robot the question, when you want a specific answer.The author summarizes some skills in the application of the most popular AI language model regarding the leather making issues.

AI Robots that involve language models that can be manipulated are: OPEN AI: CHATGPT

GOOGLE: BARD

MICROSOFT: NEW BING

BAIDU: WEN-XIN-YI-YAN and 360: WISDOM-BRAIN this two domestic AI models have not yet been tested because they are still in internal testing.

Keywords: CHATGPT; leather manufacturing; AI; CHATBOT; artificial intelligence

Synergia effect of keratinase and protease on the soaking-unhairing process in leather production

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Abstract: Proteases are effectively used in the unhairing process, and the synergistic application with keratinases is considered to improve the efficiency of unhairing action. In the soaking process, to investigate the effect of keratinase on the epidermal removal, the suitable keratinases are initially screened by keratinase activity assay. Subsequently, the effect of keratinase application in soaking process on the unhairing efficiency of protease (P-LKT-N) is investigated. The results showed that alkaline protease (P-2709-B) acted strongly on collagen fibers, when P-2709-B, P-SP450-K, P-TK-K, and P-AKT-K were used in soaking process. The soaking effect of keratinase showed that P-TK-K removed the epidermis the fastest, while P-AKT-K was the least effective in removing the epidermis, which was completely removed only after 18 h of soaking. In addition, the results of the synergistic effect of soaking and unhairing enzymes showed that, the keratinase used in soaking process significantly reduced the unhairing time, especially with P-TK-K. Compared with the effect of alkaline protease, the P-TK-K has a comparable epidermal removal rate, but the content of hydroxyproline produced in its waste solution is greatly reduced. This research confirmed that the keratinase application in soaking process can effectively shorten the time of enzymatic unhairing, which in turn reduces the hydrolysis of collagen fibers by protease, and greatly reduces the application risk of unhairing enzyme. It provides a reference for the safe application of enzymes in unhairing, and further promotes the clean enzyme application in leather processing.

Keywords: keratinase; protease; synergistic effect

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Trioctylamine extraction and back-extraction of acid lake blue dye in solution

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Abstract: A large amount of dyeing wastewater is generated during the leather and textile dyeing process. In this paper, the extraction and back-extraction rules of trioctylamine on the anionic dye Lagoon indigo were studied by solvent extraction method. During the extraction and back-extraction process, the optimal environmental conditions were screened out by a single-factor experiment. The influence of five parameters, such as water phase, extractant concentration, reaction temperature, reaction time, and oil-liquid ratio, on the extraction effect was explored. Experiments show that under the conditions of water phase pH of 2, a reaction time of 90 min, an extraction agent concentration of 0.162 g/L, a reaction temperature of 25 °C, and the oil-liquid ratio of 1:1, the maximum single extraction rate can reach 99.99%. During the stripping process, the effects of NaOH concentration, reaction temperature, and oil-liquid ratio on the stripping effect were investigated. Experiments show that the stripping effect reaches the maximum under the conditions of NaOH concentration of 0.05 mol/L, an oil-to-liquid ratio of 1:1, and a stripping temperature of 25 °C. Extraction combined with backextraction can realize the extraction and enrichment of dyes in the solution, which has a certain guiding significance for solving the pollution of dyeing wastewater in tanning and printing, and dyeing industries.

Keywords: solvent extraction; trioctylamine; anionic dye

Product environmental footprint of tanning industry: a case of study

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Abstract: The tanning industry is a fundamental sector in Italy: it represents respectively 23% and 65% of the global and European production, reusing, and valorising the by-product of the food industry: raw animal skin from slaughter. The leather industry faces global challenges regarding sustainability and transparency of its supply chain. The strategies and communication on enhancing its sustainability are also strongly influencing the market, which is increasingly looking for objective, verifiable, and non-misleading data on the performance of products, processes, or services, not only in terms of material performances but also from the point of view of environmental footprint. It is well-known that this sector contributes to the consumption of energy, material natural resources and pollution, causing environmental impacts: that means that it is required a complex and extended environmental assessment to manage these challenges effectively. The Product Environmental Footprint (PEF) is a useful tool to measure the environmental performance of products throughout their life cycle based on internationally agreed scientifically sound assessment methodology. PEF studies mainly face the following objectives: the identification of the materials and the processes that contribute most to the environmental impact, the development of improved solutions to reduce the environmental footprint of leather, the editing of a document that can be used as a basis for communicating the PEF profile. A PEF product certification defines a clear ID for the environmental impact of the production and allows to quantify of possible improvements in terms of sustainability. In this study, the impacts of different finished leather products (automotive interiors, furniture upholstery, and upper footwear) have been assessed. The scope analyze and the comparison of the environmental impactindicators of three different tanning systems to provide information to enable leather tanning companies to calculate environmental performance to support more sustainable production practices.

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As finished leather is an intermediate product, downstream processes such as distribution, further manufacturing into finished consumer products, distribution to customers, use phase, and end-of-life treatment of used products are out of scope.

The PEF study was carried out in compliance with PEFCR-2018 for leather (Product Environmental Footprint Category Rules) and it includes the PEF scope, the declaration of boundaries, the measure of the most relevant impact categories, the interpretation of results, the major gaps of research, and the future perspectives.

Keywords: environmental footprint; PEF; LCA; sustainability; PCR

Sustainability challenges of tanning industry in Ethiopia

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Abstract: Since developing countries have huge livestock resource potential and they must utilize available raw materials in order to eradicate poverty by generating the required revenue and create employment opportunity for their citizens. Life as usual way of industrialization that is "take-make-use-dispose" scenario is not recommended for sustainability of the leather sector. In order to mitigate environmental challenges, the leather industries need to implement RECP, waste recycling and reuse technologies in order to comply with the existing environmental discharge norms of the country as well as to ensure the social cohesion among the community, it is critical to establish the common effluent treatment facility having the state of art technologies that enable the tanneries to comply with the global environmental and social compliance requirements such as ZDHS, ZLD and LWG. To establish eco industrial park, regional government, land administration bureau' s and relevant government and non-government organizations must work closely in order to manage the waste generated. In addition to that the availability of raw hide and skin resource is not by itself guaranty to develop the leather sector, there should be development of related industries such as chemical industries, agro processing industries, mining sector, energy sector, agricultural sector and furniture industries and so on is important for sustainable development of the leather and leather product industries.

Keywords: sustainability; resource efficiency; environmental challenges

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Sustainable chemicals fitting the future leather trends

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Abstract: Implementing sustainable products will be a necessity in the upcoming years. The world population is growing and if we continue as before the global oil demand will continue to rise. It' s necessary to develop a second scenario, the "Sustainable Development " scenario. Europe and EEUU are implementing sustainable goals based on public policy like the "European Green Deal" and "Green New Deal" to mitigate the Climate Change and the Global Warming. In 2021, UNDP China convened several policy dialogues and published a number of policy and issue briefs analyzing newly released policy documents including China's 14th Five-Year Plan, which will shape China's green development for years to come.

Trumpler is producing a new generation of biobased chemicals used as sustainable retanning agents for leather. Those chemicals are based on renewable raw materials coming from wastes of the tanning industry. They are highly biobased, with good biodegradability and low environmental impact.

The biobased carbon content of a material describes the percentage of carbon with "natural" origin compared to carbon with "synthetic" origin (petrochemical). Another important concept to develop sustainable products for leather is the biodegradability. Leather, as bio-based, biodegradable, and compostable material is an alternative to many fossil-based, non-biodegradable materials. Compostability is one end-of-life option for biodegradable leathers in a future circular economy. The impact of various tanning technologies, retanning chemicals, as well as finishing products on the compatibility and the biodegradability of leather is examined and evaluated.

To be able to accurately quantify the environmental impact of artificial materials, including leather, will be necessary and perhaps mandatory soon. Before long, the demand for detailed LCA (life cycle assessment) data across the entire supply chain is expected to grow exponentially. This type of data will help to calculate and certificate the total environmental impact values for sustainable leathers in a transparent way. Transparency combined with its unique and convincing properties will finally support the strong reputation of leather.

Keywords: sustainable chemicals; biobased; biodegradability; compostability; life cycle assessment

Soil burial degradation of leather tanned by different methods

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Abstract: As a crucial part of the recycling of animal biomass resources, the leather industry can convert the by-products of slaughtering and meat processing industry, raw hide, into high value-added leather products, which is in accordance with the national strategic targets, "carbon neutrality" and "sustainable development" . However, the impacts of discarded leather products on the environment and whether they can be derived from nature and back to nature remain unknown. Thus, the biodegradability of leather is one of the most crucial indicators in evaluating whether they are sustainable. The soil burial method usually can be measured the biodegradability of leather. Compared with conventional chrome tanned leather, the biodegradability of chrome-free tanned leather may have advantages. The paper aims to study the biodegradability of various chrome-free/chrome tanned leathers and crust leathers in terms of appearance, weight remaining, shrinkage temperature and thermogravimetry of leather, and metal content, C/N content, microbial density, pH and microbial community diversity of soil after being buried for a certain period of time.The results showed that, microorganisms grew and reproduced rapidly within 6 months of soil burial. After 6 months, the growth of microorganisms moved into a stabilization period, and the degradation rate of leather was also slowed down. During the 1-year soil burial degradation process, the biodegradability of chrome-free tanned leather tanned by TWLZ, OSA, or TWS was significantly higher than that of chrome tanned leather, and was similar to that of depickled hide, TWLZ, OSA, TWS tanned leather and depickled hide all had mass residuals between 40% and 50%, while chrome-tanned leathers hada higher mass residual of 78.4%. In terms of appearance, chrome-free tanned leather tanned by TWLZ, OSA, TWS, and depickled hide gradually discolored and moldy, finally, breaking into small pieces under the effect of microorganisms. In contrast, the appearance of chrome tanned leather did not change significantly. Also, burial led to an increase in soil organic carbon and total nitrogen content and a constant decrease in pH. In addition, metal-tanned leather can lead to the release of metal ions into the soil. As for chrome tanned leather, the total chromium content of the soil increased from 55.4 mg/kg to 137.9 mg/kg from the beginning and end of degradation. The analysis of soil microbial diversity also showed that the differences in microbial species between soils buried with OSA tanned leathers and TWS tanned leathers were small, but in soil buried with other leathers were significant. In addition, pot experiments were conducted to investigate the effect of burial of different types of leather on the growth of cherry radish, the results showed that the addition of depickled hide significantly promoted the accumulation of dry matter in cherry radish by 86.4% compared to the blank, followed by TWLZ(46.3%), TWS(23.5%), OSA(21.7%), and Cr(-5.8%) tanned leather. Based on the soil burial test, a comprehensive method for evaluation of leather biodegradability with wide dimensions and diverse indices was built. This method is suitable for in-depth investigation of the biodegradation behavior of leather in the laboratory.

Keywords: leather; biodegradation; chrome-free tanning; soil burial test

Controllable oxidation and degradation of lignin: from biomass into tanning and retanning agents for sustainable eco-leather manufacturing

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Abstract: Chrome-free and formaldehyde-free eco-leather manufacture is one of the major focuses of leather industry. Herein, lignin-based tanning and retanning agents (LTA and LRA) were controllably prepared by regulating the oxidation conditions, and their application mecahnism and environmental benefits in tanning and retanning were investigated. Oxidation broke the aliphatic side-chain β-O-4′ , β-5′ , and β-β′ linkages of lignin, transformed the adjacent phenolic hydroxyl group and methoxy group on the benzene ring into carboxyl group, and reduced the colority of LTA and LRA. When LTA was combined with aluminum–zirconium salts (AZ) for leather tanning, the LTA with appropriate Mw (1,498 g/mol), carboxyl (6.27 mmol/g), and phenolic hydroxyl (0.18 mmo/g) content improved the penetration uniformity of LTA–AZ complexes in leather and imparted leather with a shrinkage temperature close to 90 °C. When LRA was applied for Cr-tanned leather retanning, the phenolic hydroxyl and carboxyl groups in LRA coordinated with Cr(III) to form a robust macromolecular cross-linking network structure and endowed leather with satisfactroy physical and organoleptic properties. Life cycle assessment demonstrated that both LTA tanning and LRA retanning systems were more sustainable than conventional chrome tanning and aromatic syntan retanning systems due to their low environmental impacts on resource consumption and climate change. This work provids practical approaches to utilize biomass resources and promote the sustainability of leather industry.

Keywords: lignin; oxidation; chrome-free tanning; formaldehyde-free retanning; eco-leather; life cycle assessment

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Design and preparation of fish collagen membranes for guided bone regeneration

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Abstract: Guided bone regeneration (GBR) has been proved to be an effective treatment for alveolar bone defects, and the key of GBR is a barrier membrane placed between soft tissue and bone defect. An ideal GBR membrane requires sufficient mechanical strength, suitable degradation rate matching with bone regeneration, and porous structure to maintain essential transport of nutrients. Collagen is the most frequently used raw material to fabricate such a degradable GBR membrane due to its significant biocompatibility and biodegradability. However, the current mammalian collagen-based GBR membranes exhibit limitations such as relatively poor mechanical properties and rapid biodegradation, as well as potential risks of disease transmission. In this study, a series of fish collagen membranes were fabricated for GBR application based on different strategies. Two types of building blocks (collagen molecules and self-assembled collagen fibrils) were used, while the adipic acid-N-hydroxysuccinimide ester and metal organic polyhedral (MOP) were introduced to cross-link and enhance the membrane performance desired by GBR. The surface topography, mechanical strength, water vapor permeability, degradation and thermal stability of the membranes were determined. Compared with the membranes made of collagen molecules, those made of self-assembled collagen fibrils exhibited better properties in all aspects. Furthermore, the cross-linking and organic-inorganic hybridization endowed the membranes with considerable increase in structural stability and permeability. Overall, this study provides a promising mode for the sustainable utilization of fish skin and the prepared novel collagen membranes may have potential application in biomedicine.

Keywords: guided bone regeneration; fish skin collagen; collagen barrier membrane; cross-linking

Application of ozone in reduction of pollutional load and removal of colour-innovative technologies

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Abstract: The tanneries in India and most of the Asian countries use large amount of poor-quality chemicals in semi-finishing and finishing operations. In wet finishing operations different types of fat liquors, dyes and non-degradable chemicals are used and the residual chemicals discharged as waste in the effluent. The effluent from semi-finish to finishing operations contains pH in the range of 4-5, COD in the range of 4000-5000 mg/L, color in the range of 1500-2000 in Platinum-Cobalt Color Scale (Pt-Co). These discharge causes occupational health and safety issues, corrosion in the pipeline, increase in emission of H_2S when it mixed with effluent from beamhouse operation such as sulfide liming and deliming. The conventional physiochemical and biological treatment process could not achieve discharge parameters such as COD, colour in the treated effluent.

With a view to address the challenges of odour emission of non-degradable COD, colour, etc. in the effluent and to meet new discharge standards and guidelines an advanced oxidation system with ozone has been developed and adopted in a tannery cluster of 120 units and in a Common Effluent Treatment Plant (CETP) with a capacity of 3000 m³/day. This unique and first of its kind system started its successful oper-ation in India. The advance oxidation system is developed in such a way that the treated effluent meet all discharge parameters (i.e. BOD-20 mg/L, COD-250 mg/L & SS-50 mg/L) except Total Dissolved Solids (TDS). The sequence of the new treatment process is: Preaeration with ozone treatment in dye bath effluent → Mixing with other sectional streams → Primary treatment for removal of suspended matters and sludge → Secondary biological treatment → Tertiary treatment → High-rate advance oxidation for reduction of colour and non-degradable COD.

For the development of high-rate advance oxidation system, two stage process is followed. The first stage is generation of oxygen from atmospheric air using oxygen generator with a ratio of 100:5 (i.e. Atmospheric air → Oxygen in m³/hr). The oxygen is stored in a separate container and ozone is generated from oxygen using ozone generator at a ratio of 100:15 (Oxygen → Ozone in m³/hr).

The ozone is distributed through diffusers in advance oxidation treatment with a detention time of about 90 minutes. The reduction in COD is from 400 mg/L to <250 mg/L and colour is reduced from >500 Pt-Co to less than 200 Pt-Co units & the ozone treated effluent looks like a clear water. The dissolved oxygen level in the final treated effluent is increased to 5-7 ppm and creates a pleasant & safety atmosphere in the tannery cluster & treatment plant. The view of full-scale advance oxidation system with ozone treatment implemented with a capacity of 3000 m³/day is shown in Fig.2 (see full paper). The advance oxidation system designed and implemented for a capacity of 150 m³/hr is fully operational with onsite generation of oxygen and ozone. The oxygen generation plant supplies 2000 m³/hr of oxygen at 93% purity and ozone is generated for a capacity of 30 kg/hr in two modules each of 15 kg/hr. The application of advance oxidation system for colour removal and non-degradable COD is first of its kind in terms of technological development. There is scope of replicability in many of the industrial effluent treatment plants which are planning to recover and reuse of water.

Keywords: advance oxidation; ozone treatment; colour removal

Novel bottom-up biomimetic collagen-based membranes for corneal repair with mechanical self-reinforced through slide-crosslinking

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Abstract: Corneal transplantation is the most effective treatment for corneal blindness. However, in the context of the global shortage of donor corneas, the development of artificial corneas has quickly become a research hotspot. Collagen, known for its superior biocompatibility, is considered an excellent substitute for corneal repair but the current collagen materials used for corneal repair are limited by their insufficient mechanical properties. Therefore, in this study, we developed a novel biocompatible collagen-based corneal repair material with phenomenal mechanical properties and self-reinforcing effect enhanced by utilizing the sliding crosslinking effect between collagen and carboxymethyl-β-cyclodextrin-pseudopolyrotaxanes. The fourier transform infrared spectroscopy confirmed that collagen and pseudopolyrotaxanes in sample COL(P0.5) were cross-linked by amide bonds. Scanning electron microscopy revealed that COL(P0.5) possessed an organized layered sectional structure. Uniaxial tensile tests demonstrated that COL(P0.5) could withstand cutting force of the suture with a tensile fracture stress of 1.98 MPa. Small and wide angle X-ray scattering analysis indicated that COL(P0.5) displayed an axial orientation degree of 81%, signifying anisotropic characteristics. In vivo rabbit lamellar keratoplasty models showed epithelialization was completed by approximately 14 days post-transplantation, with corneal transparency restored within 30 days. No evidence of inflammation, neovascularization, corneal rejection, or keratoconus were observed. Hematoxylin and eosin staining and Masson's trichrome staining at 30 and 90 days after surgery suggested that COL(P0.5) effectively facilitated the reconstruction of corneal epithelial and stromal layers. Moreover, corneal biomechanical testing and confocal laser microscopy at 180 post-surgery demonstrated that COL(P0.5) restored the corneal curvature and mechanicalttt

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properties of the treated cornea to the level found in a normal eye. The proliferation, consistency, and density of both epithelial and stromal cells were satisfactory, with no abnormality such as hyperplasia observed. In conclusion, COL(P0.5) shows considerable potential for application in corneal tissue engineering, offering new possibilities to address the global issue of donor cornea shortage.

Keywords: collagen; pseudopolyrotaxanes; self-reinforcement; slide-crosslinking; cornea repair

Notes for sustainable leather products from analysis of product complaints database

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Abstract: In order to sustainably expand sales of leather products, recycling-oriented sustainable manufacturing and appealing superiority over competing materials are essential. In other words, we need to make more use of upcycling and reuse, so it is very important to learn what kind of quality problems there are in aging products. While we are establishing quality standards at Japanese department stores, we are constantly in contact with product complaints. Product complaints are difficult to resolve individually and are often handled confidentially, but when aggregated into statistical data, they clearly reflect customer wishes and disappointments. Furthermore, by comparing competing materials in the same way, we would like to draw out the problems faced by leather products and their superiority over competing materials. In this survey, products that have been sold for more than 3 years are defined as aged products, and compared with products that have been sold for less than 3 years (mostly less than 1 year). As a result, the composition ratio of synthetic leather, etc., has increased in aging products, while the composition ratio of natural leather has decreased. This reflects the fact that in hot and humid climates such as Asia, polyurethane is hydrolyzed, and its strength is likely to drop significantly. In addition, there were cases where stains occurred on the leather near the areas where the adhesive was used. From the above results, we have reached the following conclusions. Synthetic leather products are not durable, so it is recommended to wear them as soon as possible rather than storing them for a long time. Since natural leather products are durable, they can be used for a long time by replacing consumables such as metal fittings and fasteners. This report discusses these issues while presenting the basis for product complaints, such as the composition ratio and typical examples.

Keywords: leather product; consumer complaint; quality magement

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Fabrication of flame retardant casein-based microcapsule as leather finishes

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Abstract: Modern leather industry is trending towards green, functional and intelligent development, thus leather finishing materials must adapt to this development trend of leather industry. As the most common film-forming agent in leather finishing agent, casein shows good market competitiveness and broad application prospects in leather finishing because of its strong adhesive force and hygienic property. However, leather is flammable, and burning will release toxic gases and smoke, so flame retardant leather technology has become one of the industry's focus of attention. The modification of leather with flame retardant function has become a hot research topic nowadays. Moreover, the pristine casein film is hard, brittle, and intolerant to heat. Therefore, in this study, in order to overcome the disadvantage that casein is intolerant to heat, and to endow the leather a flame retardant function, flame retardant microcapsule leather finishing agent (APP@CA-CPL) was prepared by using casein as the shell and ammonium polyphosphate (APP, n>1500) as the core, which shows good flame retardant properties. The structure and morphology of the composite material were characterized by Fourier transform infrared spectroscopy (FT-IR), energy dispersion spectroscopy (EDS), scanning electron microscope (SEM), transmission electron microscope (TEM), etc., as well as the flame retardant properties of the finishing materials were investigated. The results showed that microcapsules with size of about 300 nm were successfully prepared. When the concentration of APP was 0.05 g/mL, the finished leather showed good flame retardant properties, since the total heat release (THR) of leather samples was 10.482 MJ/m^2, which was 41% lower than that of unfinished leather; the limiting oxygen index (LOI) of finished leather samples was 31.4%, which was about 22% higher than that of untreated leather, indicating that leather finished by the as-obtained microcapsule was hard to burn. This research will provide significant theoretical guidance for the development and utilization of green bio-based functional leather finishing materials.

Keywords: casein; ammonium polyphosphate; flame retardant; finishing agent; microcapsule

Influence of heel type and height on plantar pressure and gait stability with professional shoes

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Abstract:

Introduction: Leather shoes have good permeable air performance and hygienic performance, forming a good air circulation in the shoe chamber. Professional high heel shoes are indispensable leather products for women on formal occasions. However, high heels with different types and heights will make a difference on the health and balance of women's lower limbs.

Methods: The participants included 18 female adult volunteers (age 23.0 ± 2.0 years, height 162.0 ± 2.3 cm, weight 52.0 ± 3.0 kg, and BMI 18.9 ± 2.5 kg/m2). Four pair of test leather shoes with 2 heel types (stiletto vs. Wedge) and 2 heel heights (3 cm vs. 7 cm) were custom-made by the same shoe last and materials. Plantar pressure of the participants were collected by Pedar-X inshoe plantar pressure measurement system when they were walking in the test shoes. The participants wore the shoes in a random order. A two-way 2×2 repeated measures ANOVA analysis was applied to investigate the effects of two intra-subject factors on plantar pressure and balnce.

Results: When the heel height is 3 cm, the pressure in the M1 of the participants with wedge heels is slightly higher than that of the participants with the stiletto heels. When the heel height is 7cm, the pressure generated by the stiletto heels in M1 is significantly higher than that of the wedge heels. At the same time, this value is also significantly higher than that of 3 cm high heels, while the wedge heels do not show a trend of pressure increasing with heel height.

When the height is the same, the MaxF and FTI in M23 of the participants with wedge heels are higher than those of the stiletto shoes, and the difference in FTI is significant. The MaxF and FTI in M45 and HM of the participants with wedge heels were lower than those of stiletto heels, and the difference in MaxF is significant.

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When the center of pressureis at M1, the gait cycle is at the end of the single support period or the early swing period, and the contralateral foot is at the end of the swing period or the initial landing period. When the participants with stiletto heels make the initial contact, the contact point between the shoes and the ground was too small, resulting in poor stability of the contralateral foot. In order to maintain sufficient stability, the wearer would automatically change the load-bearing strategy and shift more load to the contralateral foot, resulting in an increase in the peak pressure of the forefoot of the foot.

Considering that impulse is the accumulation of force to time, this result indicates that the contact time of in the M23, M45 and HM regions becomes longer when wearing wedge heels compared with stiletto heels. The contact time of the forefoot and heel is mainly related to the initial contact period (ICP), forefoot contact period (FFCP), and flat foot contact period (FFP) of the gait cycle. The functions in the three periods are slowing down the impact speed, maintaining load-bearing stability. It also provide the capacity of lower-limb motion control. The prolonged period shows that wedge heels make more contribution to dynamic stability compared with stiletto heels. The hollow structure of the outsole of the stiletto heel leads to a smaller heel axis. To retain the posture balance, the participants would subconsciously shorten the contact time of ICP, which leads to a faster contact on the ground.

Conclusion: It can be seen that compared to the stiletto heel, the wedge heel has better gait stability. However, the greater cumulative effect of the medial forefoot stress could result in an increased risk of stress fracture in this area. Attention should be paid to the cushioning design of the front heel in the functional and structural footwear design.

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Keywords: leather shoes; high heels; plantar pressure; posture balance

Research on the influence of heel structure on the stability of high-heeled shoes during treadmill walking

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Abstract:

Background: Leather is perceived as the most important material for footwear which has excellent biocompatibility and breath-ability. Especially, Leather high heel is a daily necessity for professional women on formal occasion. It can manifest women's profession and personal character. However, prolonged wearing of high heels can result in decreased postural stability and increased risk of lower extremity injuries. Therefore this study aimed to investigate the differences in the center of pressure (COP) characteristics of young women wearing different heel heights and heel types, informing women's daily footwear choices.

Methods: Fifteen healthy young women were recruited as subjects for this study. They were asked to walk on the treadmill at a fixed speed (3.0 km/h). Nine pairs of high-heeled shoes with three different heel heights (3cm, 5cm, and 7cm) and three different heel types(slope, thin and thick) were evaluated. The temporal gait and COP parameters were measured using the Pedar-X insole system. Temporal gait parameters were analyzed by one-way analysis of variance ANOVA and Bonferroni post-hoc test. The main parameters of COP in the medial-lateral and anterior-posterior direction, including displacement(COP_X, COP_Y) and velocity(COP_{VX}, COP_{VY}), were analyzed by one-way repeated measures ANOVA and Bonferroni post-hoc test during initial contact phase(ICP), forefoot contact phase(FFCP), foot flat phase(FFP) and forefoot push-off phase(FFPOP).

Results: Drawing inferences from the data, it was found that the percentage of stance period for slope heels was significantly greater than thin heels when heel height was 7 cm($p=0.019$). More percentage of the stance period for slope heels indicates a decrease in stability. Dynamic stability during walking is maintained mainly during FFCP and FFP. The COP parameters of this study showed significant differences mainly during FFCP. In the FFCP, the COPY of slope heels was significantly greater compared to thick heels with 5 cm($p < 0.001$) and 7 cm($p < 0.001$) high heels. Additionally, the COP_{VY} of 7 cm high heels was significantly greater compared to 3 cm($p < 0.001$) and 5 cm($p < 0.001$) high heels in the case of slope heels during FFCP.

Conclusion: The results from this study indicate that there are differences in COP characteristics between different heel structures. A loss of stability in walking with the heel lifts. The slope high-heeled shoes show worse stability than others, which may be related to the construction of solid support in the mid-foot area. The issue of stability with different heel types warrants further consideration.

Keywords: high heels; center of pressure; stability; heel structure

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Investigation of the relationship between structure and function of acrylic polymer retanning agents and their mass transfer behavior

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Abstract: Acrylic polymer retanning agents are widely used in the production of various types of leathers because of their advantages such as high selective filler properties. However, we do not understand the relationship between the structure and application properties of these acrylic polymer retanning agents. As a result, this leads to the use of large amounts of acrylic polymer retanning agents added, with little absorption of these acrylic polymer retanning agents by the leather thus leading to waste, resulting in high COD/TOC content inside the waste stream and also greatly increasing the cost of acrylic polymer retanning. In this paper, we discussed the properties of acrylic polymers with different molecular weight and structure, such as viscosity, acid resistance, chromium resistance, particle size and surface charge, and their effects on the thickening rate, compressibility and absorption rate of acrylic polymers after retanning, as well as their penetration and distribution in the leather by Nile blue staining. The results showed that the lower the viscosity of the acrylic polymer, the better the resistance to chromium, the better its penetration in the leather, but its filling performance becomes worse; the better the acid resistance, the higher the thickening rate. As the pH decreases, the particle size and the negative charge on the surface of the polymer decrease, and the penetration performance in the leather is better, and the absorption rate, the compressibility and the filler property of the leather are greatly improved. The results have certain guiding significance for the future synthesis of acrylic polymer tanning agent, which greatly reduces the waste of acrylic polymer tanning agent, responds to the national policy of carbon neutral and carbon peak, and promotes the green and sustainable development of leather industry.

Keywords: acrylic acid polymer; molecular weight; structure; permeation; surface charge; particle size

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Application of functional footwear comprehensive scene simulation laboratory

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Abstract: Jihua 3515 Leather and leather Shoes Co., Ltd. was founded in 1951, located in NO. 197 RENMIN Dong road, shaoling district, Luohe, He'nan province. Now it is belong to Jihua Group Co., Ltd. — second grade company of Xinxing Jihua Group— one of world's 500 large central enterprises and under the supervision of State Council and the SASAC. The company is an excellent backbone of JihuaGroup Co., Ltd., is the demonstration unit for promote the national scientific and technological achievements. The company and Sichuan University jointly launched and established the Chengjihua Scene Simulation Laboratory project. The real simulation laboratory will focus on realizing the human body real-time data acquisition, shoe boots embedded exoskeleton structure, terrain information sensing the integration of artificial intelligence technology, with a higher dimension of information technology conditions as the guidance, the development of different application scenarios, form the leading global high-tech shoe technology chain.They main focused on closely around the high performance boots material research and application, function shoes physical and chemical performance testing, biomechanical performance testing, and footwear comfort quantitative standard and performance evaluation and other major research and development areas, obtain a number of leading domestic, the international first-class research and development, develop a number of national and industry standards, achieve the ability and level of leading the industry.

Keywords: functional footwear; sensing collection; real simulation laboratory