Special Review: Collagen Modification Using Nanotechnologies: A Review

by

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Abstract

The essence of leather industry is modified collagen fibers. With more challenges facing traditional chemicals used for leather making, along with the development of higher living standards, great demand is imposed on the leather industry. Therefore more researchers are paying attention to collagen modification using nanotechnologies for tin leather industry. In this review, we present a critical discussion of collagen modified by nano-size emulsion, clay minerals, nano silicon dioxide, or nanosilver. In the end, we conclude this review with some perspectives on the future research and development of collagen modified by nanotechnology.

Introduction

Animal hides or skins predominantly contain collagen and are commercially important as natural frameworks largely utilized in medical, food, and leather industries. The leather making protein collagen is the most abundant protein and a major component of connective tissue. "Hierarchy" of collagen structure is a feature of the properties of collagen and it has "layers" of structure, which combine to allow the formation of fibers.[1-2] Collagen consisting of tropocollagen molecules has lengths of L≈280 nm and diameters of ≈1.5 nm.[3-5] Collagen fibers are intertwined to form a fiber bundle having a diameter of 20 to 150 μm, and fibril bundles come together to create fibers. Stabilization of collagen, thus being endowed with mechanical stability and retardation of biodegradation, is an important requisite for industrial application. Actually, the leather manufacturing process is a modified process of collagen fibers. Generally, the modifiers include metal ions, vegetable, glutaraldehyde, polyphenols, epoxides and so on. Multiple-way crosslinkers are known to result in development of collagen materials exhibiting novel properties. Traditional chemicals used for leather are facing more and more challenges. With environmental safety coming under intense legislative, political and press scrutiny, governments have implemented many stringent regulations to restrict the reckless expansion of the leather industry. Moreover, with the improvement of living standards, more demands are being placed on leather products aside from its protection function, for example, demands out of comfortable, aesthetic, antibacterial, or hydrophobic consideration.

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This Review received January 12, 2013, accepted for publication March 21, 2013

Nanotechnology is the manipulation of matter on an atomic and molecular scale. Generally, nanotechnology works with materials, devices, and other structures with at least one dimension sized from 1 to 100 nanometres. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale. Nanotechnology has matured significantly during the last decade as it has transformed from bench-top science to applied technology. Presently, nanomaterials, are used in a wide variety of fields such as electronic components,[6-7] textile industry [8-9] biomedical applications[10] and so on.

The collagen fibers have a complex spatial structure. To obtain the modified collagen fibers, the material is first to meet a certain size, to penetrate into the skin, gap of fibrils and then collagen, and with collagen on the micro-scale and nano-scale. On the basis of the properties of nano material, Qi Wu[11] proposed potential prospects of nanotechnology in the leather industry. In the past decades, many researchers introduced different nanomaterials in different leather processes, and mainly concentrated on collagen modification, the finishing of the leather surface and effluent treatment. Considering the rapidly expanding body of literature on nanotechnology in the leather industry, we will mainly focus on collagen modified by nanotechnology. First, representative works are selected from the literature available and critical discussions about collagen modified by nano-size emulsion, clay minerals, nano silicon dioxide, and nanosilver are offered. Lastly, we conclude this review with some perspectives on the future research and development of collagen modified by nanotechnology.

Nano-size Emulsions

The term microemulsion was first used by T. P. Hoar and J. H. Shulman, professors of chemistry at Cambridge University in 1943. Microemulsions are clear, thermodynamically stable, isotropic liquid mixtures of oil, water, and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salt(s) and/or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons and olefins. The three basic types of microemulsions are direct (oil dispersed in water, o/w), reversed (water dispersed in oil, w/o) and bicontinuous.

The microemulsion easily penetrates into the collagen fibers of the leather and complex with the peptide chain of collagen. For wet blue leather, microemulsions also can be in ligand combination with Cr^{3+}. It makes the fiber cross-link together to play the role of the auxiliary cross-linked fibers in the main tanning agent, thus enhancing the strength and firmness of the leather.[12]

G Mallikarjun et al[13] synthesized tercopolymer microemulsion by using methyl methacrylate, n-butyl acrylate and methacrylic acid, with particle size smaller than 100nm. The microemulsion was employed in retanning chrome-tanned goatskins. The result showed marked improvement in properties, such as tensile strength, tearing strength and bursting strength. The shrinkage temperature of the retanned wet blue goat skins could increase up to 118°C. However, it could cause to some extent the denaturation of the retanned leather with large quantity of emulsifiers in the emulsion. To overcome this disadvantage, X.C. Wang et al[14] prepared 25% solid contents acrylic resin latex with particle size about 20nm. The amount of emulsifiers in the emulsion was decreased to 4%. The tensile strength increased by 68%, and the tearing strength incresed by 44% after the drop splits of pigs were retanned by 2% acrylic nanosize latex. Fu Changqing et al[15] synthesized core-shell structure acrylate micro-emulsion by pre-emulsification and semi-continuous seed-emulsion polymerization methods with acrylate monomers as main raw materials, anionic emulsifier F-20 and reactive nonionic emulsifier X-03 as anionic/nonionic composite emulsifier. The filling properties of micro-emulsion with core -shell structure were better than those with monolayer structure.

E.H.A. Nashy[16] et al prepared two nano-emulsions of styrene/butyl acrylate/acrylic acid copolymers (copolymer A) and styrene/butyl acrylate/methacrylic acid copolymers(copolymer B) using seed emulsion polymerization technique. The prepared polymer emulsions were applied as retanning agents for chrome-tanned leather. The mechanical properties of chrome-tanned leather improved when it was retanned with two prepared copolymer emulsions. Copolymer B improved the tensile strength, elongation at break and tear strength of the leather when compared with copolymer A. The improvement can be attributed to the smaller particle size of copolymer B (see Figure1) and the better lubricating effect of copolymer B that has higher ratio of the soft butyl acrylate monomer than styrene. The fullness and tightness of leather grain obtained was due to the filling action of the copolymer nano-particles.

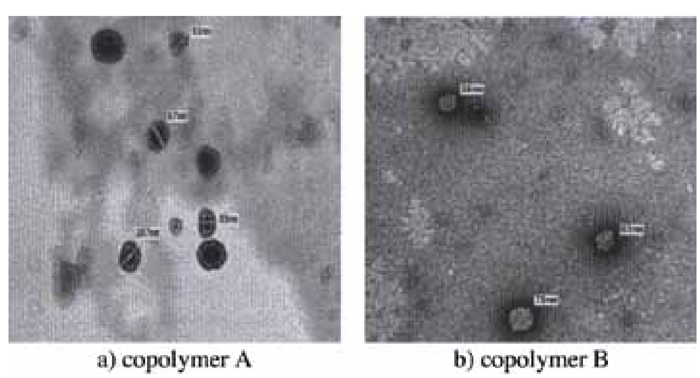


Figure 1. TEM images for co-polymer emulsion.[16]

CLAY MINERALS

The collagen modification (tanning) aims at the stabilization of the hide or skin against wet heat, enzymatic attack and thermomechanical stress. The development of chrome tanning can be traced back to Knapp's treatise on tanning of 1858. The use of chromium salts is currently the commonest method of tanning and perhaps 90% of the world's output of leather is tanned in this way.[1] Chrome tannage gives the performance of leather good, while is absorbed only by 60-70%, and the rest of the unabsorbed chromium powder is discharged into water.[17] However, the conventional chrome employed for tanning leads to significant material loss and serious environmental concern.[18] Traditional chromium tanning in leather processing is being challenged nowadays from environmental perspectives. Moreover, the chrome used in tanning is almost all imported because of the shortage of chrome resources. In recent years, there is a great need for chromium in defense industries and some of the high-tech industries, resulting in years of rising prices of chrome ore. Hence, tanners are looking for new product-process innovations towards low-waste and high exhaust chrome tanning.

Clay minerals have long attracted attention for their wide scale of application in industry and for the possibility of modifying their layered structure by intercalation. The general structure of the montmorillonite (MMT) that is widely used for nanocomposites is shown in Figure 2. They are naturally occurring 2:1 phyllosilicate, which has the same layered and crystalline structure as talc and mica but a different layer charge. The MMT crystal lattice consists of 1nm thin layers with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets, in such a way that oxygen from the octahedral sheet also belongs to the silica tetrahedral. Isomorphic substitution of Al^{3+} for Mg^{2+} or for Fe^{2+}, or of Mg^{2+} for Li^{+} within the layers generates negative charges that are counterbalanced by cations (for example Na^{+},Ca^{2+},Li^{+}) situated in the gallery. Pure MMT is a hydrophilic phyllosilicate and is only miscible with hydrophilic polymers. It is necessary to exchange alkali counterions with cationic organic surfactants in order to improve the compatibility of MMT with organic monomer or polymers.

Montmorillonite is the most commonly used layered silicate because it is inexpensive. It plays a significant role in the field of nanocomposites.[20] Polymer/montmorillonite has become an importance part in organic/inorganic nanocomposites. By virtue of the layered montmorillonite, these nanocomposites show many desirable properties, such as improved modulus and strength, higher heat distortion temperature, enhanced barrier characteristics and reduced gas permeability. The dispersion of montmorillonite in polymer matrix can result in the formation of three types of composite materials:[21]

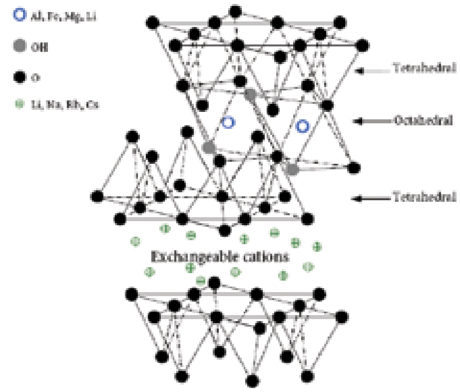


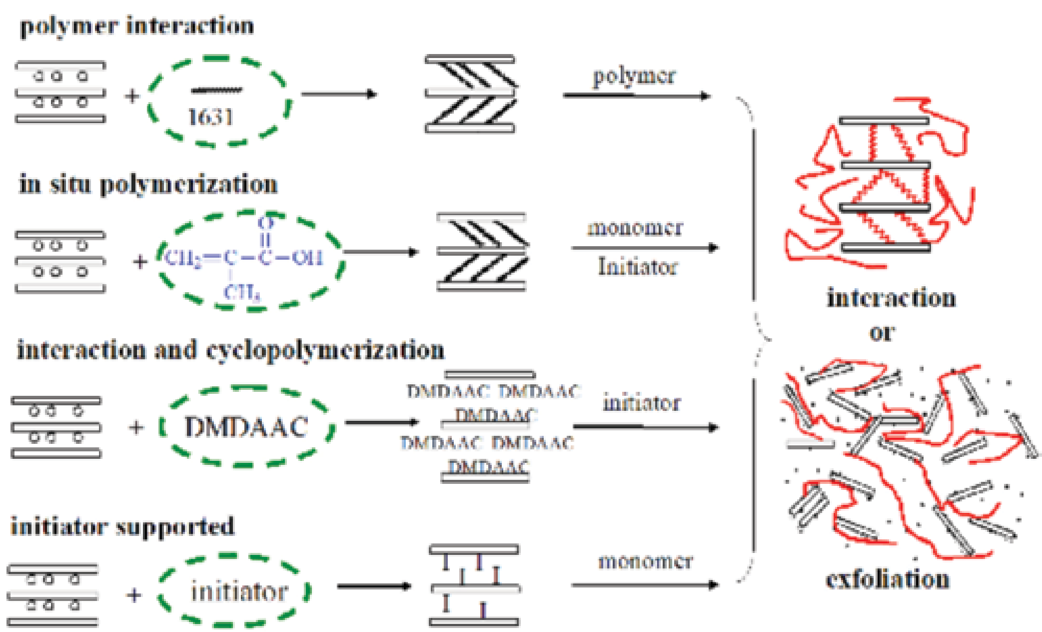
Figure 2. Structure of 2:1 phyllosilicates.[19]

aggregation, exfoliation, or intercalation. In the exfoliated nanocomposites, the distance between two clay layers is very large and the ordered lamellar structure of the montmorillonite is destroyed, while in the intercalated polymer/montmorillonite nanocomposites the lamellar structure of the clay is retained though the polymer inserts into the nanogalleries of the clay.

Lakshminarayana[22-24] found montmorillonite with small molecular size and excellent physical and chemical properties, and synthesized montmorillonite-acrylic acid graft copolymer, given leather fullness that cannot reduce the othe excellent performance.

Our group[25-27] has researched on acrylic tanning agent, including its composition, type, characteristics, synthesis, and interaction mechanism with collagen. On the basis of acrylic tanning agent, we prepared exfoliation or intercalation vinyl polymer/montmorillonite nanocomposites (see Scheme 1) by polymer interaction,[28,29] interaction and cyclopolymerization,[30-32] in situ polymerization in the presence of monomer[33,34] or initiator supported into the clay galleries.[35,36] We expected to introduce vinyl polymer and nano-scale montmorillonte to the skin collagen fibers properly, which could replace chrome tannage. If it came true, chrome-free tannage could be invented. The results indicated that active groups in the nanocomposites could crosslink with the collagen fiber reactive groups to strengthen and toughen the collagen fibers. The carboxyl and carbonyl groups in vinyl polymer could form electrovalent bond, hydrogen bond and covalent bond with various reactive groups of collagen, while nano MMT primarily served as hydrogen bond and filling between fiber bundles (see Figure 4). Leather tanned by vinyl polymer/montmorillonite nanocomposite tanning agent associated with 2% chrome could increase the shrinkage temperature above 90°C.

In our study, we found that such polymer/MMT nanocomposite could not completely replace 8% chromium powder, but its associated with 2% chromium powder was able to meet the



Scheme 1. Synthesis routes of vinyl polymer/montmorillonte nanocomposite.

Figure 3. TEM micrographs of nanocomposite.[28]

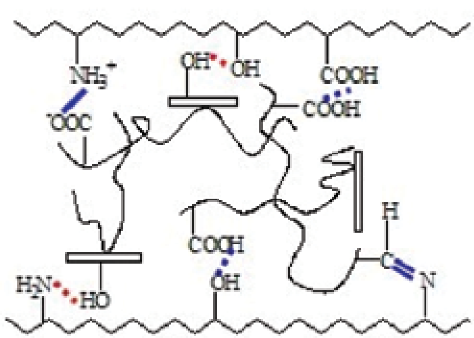


Figure 4. Possible mechanism model of nanocomposites with collagen.

requirements, and had a good absorption of chromium powder. Therefore, a novel high exhaustion chrome tanning nanocomposite auxiliary (CTA) was synthesized which had a variety of different functional groups and created montmorillonite with nanoscale dispersion.[37] Different to similar products in the market, it can be applied to either pickling or pickling-free tanning process. An attempt has been made to tan goatskins and bovine hide, along with a control test of traditional chrome tanning process. The shrinkage temperature of the resultant leather tanned by 5% CTA combined with 3% chromate was similar to that of chrome tanning using 7% chromate while the amount of Cr_2O_3 in wastewater was decreased from 2440mg/L to at least 20mg/L, and the absorption rate of Cr_2O_3 was higher than 99.0% (See Figure 5). The experimental leather exhibited clear grain appearances, porosity and good dispersion of the collagen fibers. In addition, the experimental leather had better physical properties and fullness than the leather in the control test. It can be considered as one of the most effective chrome tanning exhausted auxiliaries, which could have a potential significance for leather tanning.

NANO SILICON DIOXIDE

Silicon dioxide and sodium silicate are used for manufacturing wet-white leather. Silica tannage provides leather with softness and fluffiness because of the gelling nature of silica[38] However, the drawbacks associated with the solo tanning with silica are lack of desired shrinkage temperature and strength properties of the leather.[39] Nano-SiO_2 has been used to increase strength, flexibility and aging resistance of polymers.[40] It is reported that nano-SiO_2 is introduced into fibers of the hide by two methods: producing nano-SiO_2 between fibers of the hide by in-situ method; graft copolymerization on the surface of nano-SiO_2.

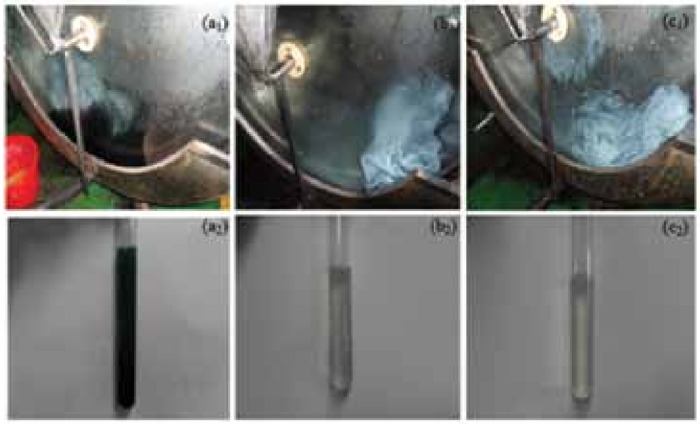


Figure 5. Photos of wastewater from tanning process.

(a_1, a_2) tradition chrome tanning using 7% chromate, (b_1,b_2) 5% CTA combined with 3% chromate tanning, (c_1,c_2) pickling-free, 5% CTA combined with 3% chromate tanning.

Producing Nano-SiO_2 Between Fibers of Hide by In-situ Method

In 2002, Fan, H. J. *etal*[41] proposed application possibility of nano-particles in tanning because of their small size, abundance of un-paired atoms and high combination ability with polymer substrates. Following in time, their group introduced a precursor containing nano-particles (such as nano-SiO_2 or nano-TiO_2) carried by polymer or modified-oil as dispersion supporter into fibers of the hide. The precursor in fibers of the hide could in-situ produce nano-SiO_2 under a special triggering condition such as radiation, heat, hydrolysis or gas reaction etc, and then a protein-SiO_2 organic-inorganic nano-hybrid with a strong interaction between the organic and inorganic phases was obtained due to the high surface activity and high surface energy of nano-particles. The collagen fiber has played the role of controlling the nano-particle size and inhibiting their agglutination, acts as organic phase; nano-SiO_2 distributed evenly in the collagen fiber acts as inorganic phase.[42-45] The result showed that the mechanical properties and hydrothermal stability of collagen treated with nano-SiO_2 could be obviously enhanced due to the strong bonding between the organic and inorganic phases.

Graft Copolymerization Method

Nano-SiO_2 particles without surface modification is easy to reunite during storing process, causing precipitation in composite tanning agent, result in decreasing of hydrothermal stability of tanned leather. In order to improve the dispersion of nanoparticles in the medium, Zhijun Zhang and his co-workers[46,47]prepared surface modification of nano-SiO_2 particles with different functional groups by in situ method, to effectively control the particle size and improve its dispersion and chemical stability in the medium. They then introduced these nano-SiO_2 particles into acrylic polymer[48] and styene-maleic anhydride polymer[49] to prepare for the nanotannage, such as surface modification of double bond,[50-51] amino group,[52] alkyl group[53] and so on.[54] The surface of SiO_2 nanoparticles was grafted with monomer reactive group to obtain homogenously dispersed nanoparticles in polymer. Therefore, nano SiO_2 was not only filled between the fibers, but also contributed to the hydrothermal stability of tanned leather.

Nano Dichromium Trioxide

The tanning industry can perhaps draw similarities and clues from the biomedical applications of collagen in developing new tanning agents that are benign and provide higher atom

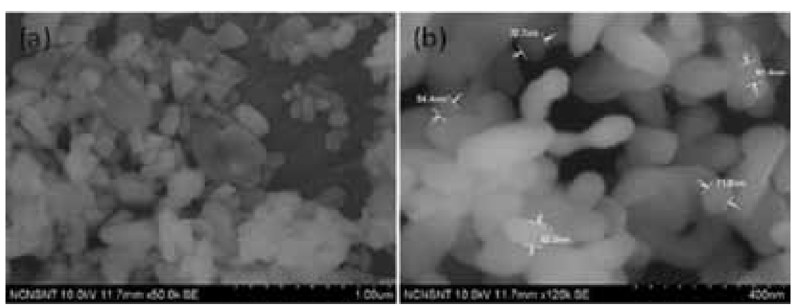


Figure 6. SEM images of Cr_2O_3 nanoparticles at two different magnifications.[55]

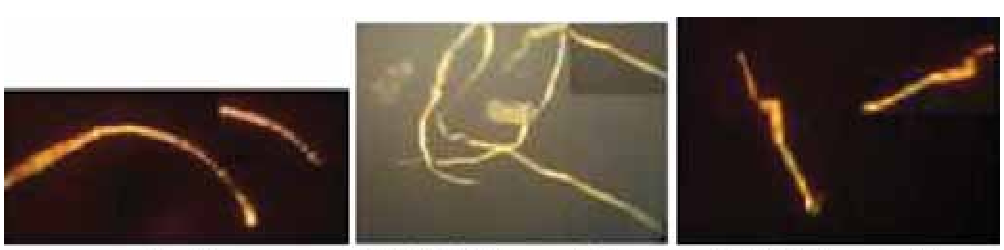


Figure 7. Polarizing optical micrographs of native fibers treated with PS-b-PAA and Cr-PS-PAA.[55]

economy through better diffusion and fixation. Kalarical Janardhanan Sreeram et al[55] synthesized nanoparticles of chromium (III) oxide with an average size ranging from 50 to 72nm (see Figure 6), functionalizing it with polymers capable of interacting with the collagen side chains and bringing about a higher degree of stability to the collagen. Native and PS-b-PAA and Cr-PS-b-PAA crosslinked collagen fibrils were characterized by polarizing optical microscopy (see Figure 7). Texture of collagen fibrils crosslinked with PS-b-PAA or Cr-PS-b-PAA did not present any major change when compared with the native fibers. However, the Cr-PS-b-PAA treated fibers were shorter in length and the extent of stability needs further improvement.

NANOSILVER

Leather and sheepskins for medical use are natural materials based on collagen and keratin, and are well known for preventive and curative properties, suitable for treatment of orthopedic, diabetic or bedsore diseases. The medical use of sheepskin has been successful since the early 1960's.[56] The microbiological resistance of leather for medical use is an important characteristic.

Silver nanoparticles have attracted considerable interest from the chemical industry and medical field due to their unique properties, such as high electric conductivity, high catalytic effect and high antibacterial activity. The biological safety of silver nanoparticles has been widely proved by much research.[57,58] Recently, silver nanoparticles as an alternative antimicrobial agent were used to leather. Carmen Gaidar et al[58,59] reported that colloidal silver solutions (CSS) obtained with electrochemical and chemical methods, with and without TiO_2 and also using chemical methods, combining with polyhydroxiurethanes were used to interact with collagen or keratin from medical leather and sheepskins to induce bioresistance properties at fungi or microbes action. Leather treated by immersion presented a good antibacterial action, even at lower Ag concentration (see Figure 8).

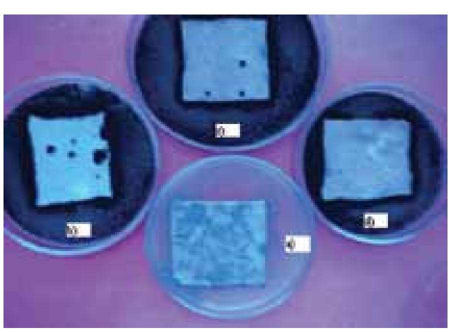


Figure 8. Fungitoxic effect on leather support expressed by mould growth: a) witness, b) 32 ppm Ag CSS, c) Ag/ TiO_2 CSS with 10 g/l TiO_2, d) Ag/ TiO_2 CSS with 50 g/l TiO_2, after 7 days.[59]

Carmen Gaidau et al[60] prepared nano-Ag based colloidal solutions and Ag/TiO_2 dispersed solutions using an efficient and simple electrochemical method. Leather treated with Ag/TiO_2 solutions had a very strong antifungal activity up to 28 days of fungi exposure, rated by 0 mark and an inhibition zone up to 25mm in the case of wet blue leather and rated by 1 mark, without inhibition zone for metal-free leather, respectively (see Figure 9 and 10). Wet blue and metal-free leather, treated with disperse systems of nano-Ag and nano-Ag/TiO_2 had exhibited inhibitory activity for Pseudomonas aeruginosa(ATTCC 9027) or Staphylococcus aureus(ATCC 6538) bacteria.

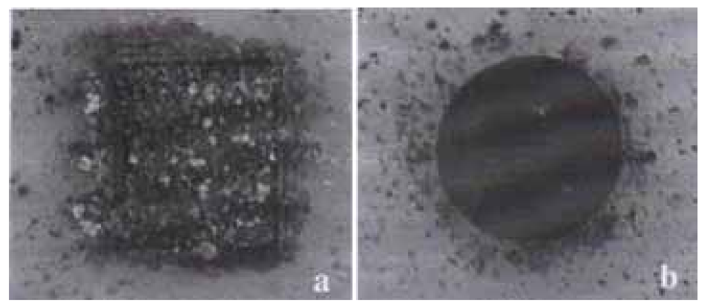


Figure 9. a) Wet blue untreated leather and b) wet blue leather treated with Ag/TiQ_2 dispersed solution after 28 days of exposure to mold colony.[60]

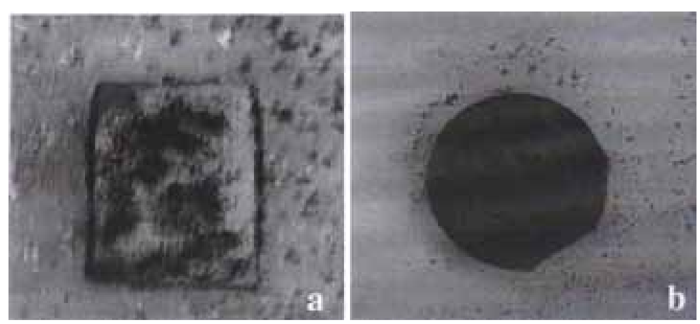


Figure 10. a) Metal-free untreated leather and b) Metal-free leather treated with Ag/TiQ_2 dispersed solution after 28 days of exposure to mold colony.[60]

A novel way to prepare antibacterial sheepskin with silver nanoparticles as an antibacterial agent was reported by Chen Wuyong et al.[61] The antibacterial study showed that the treated sheepskin had an antibacterial inhibition of 99.9% against Escherichia coli and Staphylococcus aureus, even after 6 cycles of perspiration treatment, and the sheepskin still exhibited a durable antibacterial effect with the inhibition above 79.4% and 67.1% respective to the leather and the wool (see Table 1).

TABLE I
Antibacterial inhibition (%) of the sheepskin treated with sliver nanoparticles after different cycles of perspiration treatment.[61]

Sample	Perspiration Treatment	Bacterial Strains	
Wool	0 Cycles	99.9	99.9
	3 Cycles	88.1	74.7
	6 Cycles	83.2	67.1
Leather	0 Cycles	99.9	99.9
	3 Cycles	90.6	81.3
	6 Cycles	87.5	79.4

OUTLOOKS

As can be seen from this review, extensive studies have been carried out on collagen modified by nanotechnology and some results have been obtained. Nanomaterials were applied in modifying leather collagen in mainly two aspects: as tannage and antibacterial agents. As a new tannage, the relative advances are reflected by controlling latex particles and introducing some special nanoparticles in polymer matrix; such as clay minerals, nano silicon dioxide and dichromium trioxide. There has been research on antibacterial sheepskin with silver nanoparticles as an antibacterial agent.

Although many methods have been proposed over the past ten years, none of them are perfect. This in turn provides us with more research opportunities. In particular, we believe that the following aspects should be paid more attention to in the future research and development of leather nanotechnology:

(a) For the mature cognition on nanoparticles, introducing nanoparticles into collagen modification will imparts more excellent performance to resultant leather.

(b) Complex mechanism of action between nanomaterials and collagen fibers is still not yet explained clearly. For further development of collagen modified with nanomaterials, thorough and systematic research on mechanism must be conducted.

(c) The collagen being modified will be used in conjunction with a lot of chemical materials. Although the synthesis and properties of nanocomposite have been widely studied, the investigations on optimal condition of nanocomposite and other chemical materials are relatively few. Research in this area should be strengthened, and the success of the modified collagen fiber is essential.

(d) Due to the tremendous pressure and the need of the people, modification of collagen fibers using nanotechnology was proposed, which led the leather industry to be high efficient, low-cost and environmentally friendly. Thus, toxicity and biodegradability of nano material used in collagen modification need to be further studied.

We hope that the progress in collagen modification using nanotechnologies and our personal opinions in this review can provide readers with useful information for the further development of leather industry. We believe that nanotechnology will certainly bring about a revolution in the leather industry.

ACKNOWLEDGEMENTS

This work was supported by the National Basic Research Program of China (2011CB612309), National Science Foundation of China (21104042), Excellent Youth Scholars of Ministry of Education of China (20106125120003), Science and Technology Research and Development Program of Shaanxi (2012KJXX-31) and Academic Personnel Training Projects of Shaanxi University of Science and Technology (XS11-04).

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