

NANOTECHNOLOGIES FOR LEATHER MANUFACTURING: A REVIEW

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ABSTRACT

Recently, increasing interests have been directed towards incorporating nanotechnologies into leather manufacturing, which offer cost-effective improvements in leather performances, as well as enabling the industry to meet stricter legislation regarding environmental safety. In order to guide the leather technologists and chemists worldwide, this article reviews state of the art related to existing nanotechnologies in leather manufacturing processes, including tanning, finishing and effluent treatment, over the past decade. The emphasis is placed on the mechanism by which nanotechnologies improve conventional processes, impressive performances of the resultant leather and possible obstacles that cloud technical development in this field. In the end, potential health and environment risks associated with the incorporation of nanotechnologies, which are particularly important for daily necessities such as leather but have been basically overlooked by many researchers involved, are also addressed.

RESUMEN

Últimamente ha habido un gran interés por introducir nanotecnologías a la curtición del cuero. Estas tecnologías ofrecen mejoras en el desempeño del cuero a costos favorables, así como permiten a la industria el cumplimiento de normas legales más estrictas en la seguridad medio-ambiental. Para poder guiar a los tecnólogos y químicos del cuero mundialmente, este artículo pasa revista al estado más avanzado en relación a nanotecnologías ya existentes en los procesos de fabricación, incluyendo el curtido, acabado, y el tratamiento de efluentes durante la última década. El énfasis es dirigido hacia el mecanismo por medio del cual nanotecnologías mejoran los procesos convencionales, los impresionantes logros alcanzados en el desempeño del cuero en que resulta, así como los posibles obstáculos que opacan los desarrollos técnicos en el ramo. Finalmente, los riesgos medioambientales y potenciales a la salud, asociados con la incorporación de nanotecnologías, son particularmente importantes para cumplir con las necesidades cotidianas, tal como lo es el cuero, pero han sido básicamente ignoradas por los muchos investigadores involucrados, también son examinados.

INTRODUCTION

Derived from the Greek word “nano”, meaning dwarf, nanotechnology involves the understanding, manipulation and utilization of matter that ranges from approximately 1 to 100 nanometers in at least one dimension (1 nanometer is one millionth of a millimeter).¹⁻³ The top and bottom of the nanoscale are actually hard to define sharply, but are chosen to exclude individual atoms on the lower end and things you might see with a very good optical microscope on the upper end. Since its official birth, which is usually attributed to the pivotal talk of physicist Richard P. Feynman in 1959, “There’s Plenty of Room at the Bottom”,⁴ nanotechnology has been demonstrated by many that unusual chemical, electrical, magnetic, mechanical and optical properties can emerge in materials at the nanoscale, which differ in important ways from bulk materials and single atoms or molecules.⁵⁻⁸ For example, ceramics that are normally brittle can be deformable when their grain size is reduced to the low nanometer range.⁹ In its natural bulk form, gold is famously inert, but once broken down into small clusters of atoms (particle size of 2-5nm) it becomes highly reactive.¹⁰ Until now, these unique nano phenomena have been attracting increasingly extensive attention for both fundamental research and practical applications, which bring incredible changes to various facets of human life. Inorganic nano titanium dioxide and silver oxide are coated to the interiors of Hong Kong subway trains, which exhibit self-cleaning capability by killing most of the airborne bacteria and viruses they come into contact with.¹¹ Pharmaceutical products are reformulated with magnetic nanoparticles to ferry therapeutics or diagnostic agents to specific sites in the body, allowing highly targeted treatments that minimize serious side effects.¹² With the advent of nanostructured catalysts, some companies are even on the verge of breaking through the hydrocarbon age and transforming how we imagine energy and fuel for domestic as well as industrial purposes.¹³ Not only does nanotechnology create numerous new materials and devices with a vast range of applications, it also offers great potential for industries to re-engineer many existing materials and to design novel products with unprecedented function. A good example of such re-engineering is organic-inorganic polymer nanocomposites. Combining the desirable mechanical/processing/low weight attributes of organic polymer and the

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unique characteristics of inorganic nanoparticles, polymer nanocomposites usually exhibit significantly improved properties relative to conventional composites.¹⁴⁻¹⁶ As for some more traditional light industries, such as food, paper, textile and leather manufacturing, process or product re-engineering with advanced techniques seems much more necessary and urgent. This is because on a global scale of severe competition, there is a general recognition that producing ordinary light industrial products may no longer be sufficient to sustain a viable business, so manufacturers have to move towards innovative and high-quality products in order to differentiate themselves and compete. Under such circumstance, transformation by adopting novel techniques such as nanotechnology becomes the only way out for the survival of these traditional industries in the future.

Obviously, the old leather industry has recognized the unlimited opportunities associated with nanotechnology. Since the Stone Age 2.5 million years ago, when cavemen only used raw hides or skins for protection, man has mastered the complicated leather manufacturing techniques, to chisel raw hides or skins into high-quality leather shoes, jackets, furniture and so many more necessities. During this long course, numerous novel chemicals, processing techniques and machines emerged,^{17,18} and many epoch-making theories were established,¹⁹ leading the leather industry towards contemporary prosperity. However, fast forward to the new millennium, despite all the latest techniques and an increasingly globalized market, the leather industry is still facing severe pressure from multiple sources. First, as the living standards rise, traditional leather products may no longer meet the rigorous expectations of end customers for appearance, quality and even function.^{20,21} Second, considering the scarcity of raw hides and growing ethical concern over animal rights during the last decade, competitive pressures from leather substitutes, such as polyvinyl chloride, polyurethane and microfiber materials, are becoming tougher than ever, which are racing to capture more market share.^{22,23} Furthermore, even now many processes for leather manufacturing are still known as environmentally-unfriendly.²⁴⁻²⁶ 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. In order to overcome these frustrations, leather technologists and chemists have to break out of their conventional thought process, exploring how to revitalize this old industry through multidisciplinary, interdisciplinary and transdisciplinary approaches for sustainable development in the future. An important direction of these extensive efforts involves the utilization of novel nanotechnology. In fact, the role of nanotechnology in leather manufacturing has accelerated with a positive momentum over recent years. Companies and research institutes have been spending large numbers of manpower, financial resources and materials in this field, in order to re-engineer and add

innovations to the leather products. From environmentally-friendly nano-SiO₂ tannage,²⁷⁻³¹ through self-cleaning leather coating containing nano photocatalyst,³² to high-efficient treatment of tannery effluents using nanofiltration membrane,³³ some of these technologies have even fundamentally changed the way leather is normally produced. In view of the current popularity and promise of nanotechnology in leather manufacturing, the present article addresses a comprehensive review on the state-of-the-art development of this subject, which is expected to provide guide to leather technologists and chemists worldwide. At the end of this review, a special emphasis is placed on the possible health and environment risks associated with the commercialization of nanotechnology. This part is undoubtedly important when evaluating the potential of nanotechnology in leather and other industries that produce daily necessities on a large scale, but has been basically overlooked by many researchers devoted in this field.

Nano Tannage

Tanning involves a process that introduces crosslink between collagen chains to permanently alter their structure so that they can be preserved and irreversibly converted into useful leather. Until now, there have been quite a few different methods for tanning hides, such as chrome tannage, aluminium tannage, vegetable tannage, aldehyde tannage, oil tannage, synthetic organic tannage, etc. Among these techniques, chrome tannage rapidly took its place in the commercial world shortly after its discovery in 1858 and became the predominating tanning method in global leather industry.^{34,35} However, despite many technical advantages associated with this tanning method, traditional chrome tannage is being challenged nowadays from environmental perspectives, including a global shortage of chrome source, potential carcinogenicity of hexavalent chrome and a low combination ratio of chrome in the tanned leather.³⁶⁻⁴⁰ Over the past decades therefore, there has been a huge surge of interests in seeking alternatives that are environmentally sound while retaining the versatility of chrome tannage. A burgeoning option for such purpose lies in the utilization of various nanomaterials as tanning agents. For example, G. Mallikarjun et al.⁴¹ successfully synthesized acrylic retanning emulsion from methyl methacrylate (MMA), *n*-butyl acrylate (BA) and methacrylic acid (MAA), with colloidal particle size smaller than 100nm via microemulsion polymerization. Compared with conventional emulsions, nano-sized colloidal particles were so small that they could penetrate more easily inside the leather to fill the interfibrillar spaces (see Figure 1). Meanwhile, due to the tremendous surface area of the colloidal nanoparticles, there were significantly more proton donors available in the emulsion to complex either with the polypeptide chain of collagen or the chrome of chrome-tanned leather. In this way, the shrinkage temperature of the retanned wet blue goat skins could be increased up to 118°C. Unfortunately, large quantity of emulsifiers present in the

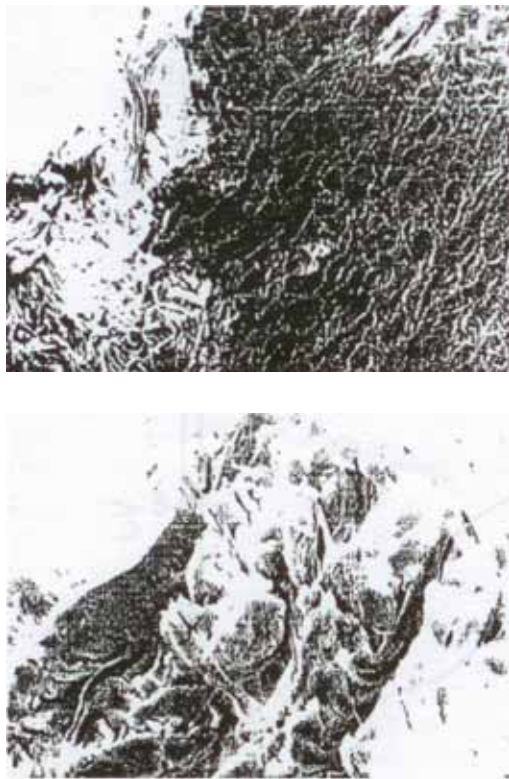


Figure 1: Scanning electron microscope (SEM) micrograph of acrylic microemulsion retanned wet blue goat skins.⁴¹

emulsion caused to some extent the denaturing of the retanned leather, which compromised the retanning contribution to the burst strength. X.C. Wang et al.^{42,43} solved this disadvantage by employing semi-continuous microemulsion copolymerization to prepare similar acrylic retanning emulsion with colloidal particle size between 16nm and 64nm. The emulsifier content in the product was only 4% while the total solid content was as high as 25%. With only 2% dosage of the retanning emulsion prepared, the retanned pig bottom splits exhibited 68% and 44% improvements in tensile strength and tear strength, respectively. On the other hand, vinyl polymer modified with intercalated or exfoliated nano montmorillonite (MMT) was also demonstrated as an efficient tanning agent.⁴⁴⁻⁴⁸ MMT is a 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 1-nm-thin layers, with a central octahedral sheet of alumina sandwiched between two external silica tetrahedral sheets. Isomorphic substitution within the layers (e.g., Al^{3+} replaced by Mg^{2+} or Fe^{2+}) generates a negative charge and for MMT is typically 0.9-1.2mequiv/g depending on the mineral origin. These layers organize themselves in a parallel fashion to form stacks with a regular van der Waals gap between them, called interlayer or gallery. In pristine MMT, the excessive negative charge is balanced by cations, usually Na^+ , which exist hydrated in the interlayer.⁴⁹⁻⁵¹ When foreign objects such as polymer chains diffuse into the interlayer, the MMT layers



Figure 2: Transmission electron microscope (TEM) micrograph of vinyl polymer/C-MMT nanocomposite (darker lines: C-MMT).⁵²

may be intercalated or exfoliated to form stable nanocomposites (see Figure 2). However, one important consequence of charged nature of MMT lies in that it is generally highly hydrophilic and therefore naturally incompatible with a wide range of polymer types such as vinyl polymer. A necessary prerequisite for successful formation of vinyl polymer/MMT nanocomposites is therefore alteration of the MMT polarity to make it organophilic. This can be made by ion exchange reaction. Na^+ ions residing in the interlayers can be replaced by organic cations such as cetyl trimethylammonium ions, which makes organosilicates compatible to polymers.⁵² When such vinyl polymer/MMT nanocomposites penetrate into the hides, synergistic tanning effects of the two components worked. The carboxyl and carbonyl groups in vinyl polymer could form electrovalent bond, hydrogen bond and covalent bond with various reactive groups of collagen, while the nano MMT primarily served as filling agent between fiber bundles (see Figure 3). Associated with only 2% chrome, such nanocomposite tanning agent could enhance the shrinkage temperature of the tanned sheepskin above 90°C, and achieve comparable strength properties and greater incrustation rates relative to conventional chrome tannage. Similar vinyl polymer-based nanocomposite tanning agent could also be prepared by employing SiO_2 nanoparticles with mean diameter around 10nm as dispersed phase.⁵³ In order to prevent organic-inorganic phase separation, the surfaces of the SiO_2 nanoparticles were grafted with vinyl groups by using *r*-methacryloxy propyltrimethoxysilane (MPTMS) as coupling agent. These grafted vinyl groups could polymerize with other vinyl monomers, such as styrene (ST) and maleic anhydride (MA), to obtain homogeneously dispersed nanoparticles in the polymer. In this case, the SiO_2 nanoparticles not only filled the interfibrillar spaces, but also contributed to the hydrothermal

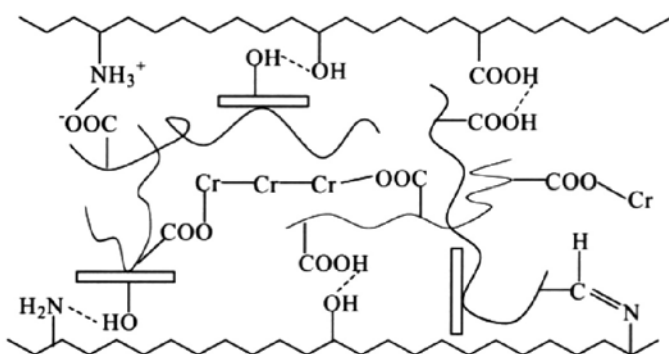


Figure 3: Possible tanning mechanism model of P(MAA-AL)/MMT nano-composite combined with chrome tanning agent.⁴⁸

stability of the tanned leather by (1) providing abundant surface hydroxyl groups to form hydrogen bonds with reactive groups of collagen; (2) crosslinking the vinyl polymer chains to intensify interactions with collagen.

The aforementioned examples demonstrate a few effective ways to improve traditional organic tanning agents with nanotechnology. As a matter of fact, single tanning using specific nanomaterials such SiO₂ or TiO₂ nanoparticles is also considered feasible, and some pioneering researches have been carried out.^{27-31,54} The theoretical foundation of such consideration is derived from the fact that nanoparticles may exhibit high combination potential with polymer substrates due to their small size and abundance of surface un-paired atoms.^{27,28} Usually, commercial nanoparticles are chemically fused together, resulting in large agglomerates that are hard to penetrate into the hides.²⁷⁻³¹ Meanwhile, compared with primary nanoparticles, significantly lower specific surface area of agglomerates also compromises their combination potential with collagen. In order to overcome these practical obstacles associated with employing commercial nanoparticles, a technical route called *in-situ* nano hybridization has been established to facilitate the introduction of nanoparticles into the targeted hides for effective tanning effects.²⁷⁻³¹ In this technique, nano precursor (tetraethoxy silane or tetrabutyl titanate) is first dispersed into a polymer- or oil-based supporter, which can easily penetrate into the raw hides. Under a specific triggering condition, such as radiation, heat or change of pH value, the nano precursor hydrolyzes and condensates within organic collagen matrix, *in-situ* generating inorganic particles. As long as the triggering condition is properly controlled, nano-scaled SiO₂ or TiO₂ particles (particle size: 80-90nm), which disperse homogenously inside the hides, can be obtained (see Figure 4). These *in-situ* generated nanoparticles are highly reactive, exhibiting strong combination potential with specific groups of collagen. Preliminary Fourier transform infrared spectroscopy (FTIR) results demonstrated that the Si-OH groups produced from the hydrolysis of tetraethoxy silane could probably (1) react with the pendant groups of arginine, histidine and tryptophane

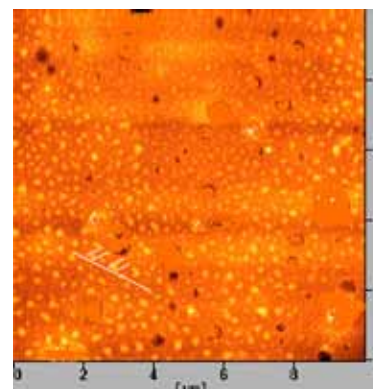


Figure 4: Atomic force microscope (AFM) micrograph concerning the size and distribution of *in-situ* generated nano-SiO₂ in protein.²⁸

to form -Si-C- bond; (2) condense with the pendant hydroxyl groups of collagen; (3) form hydrogen bond with C=O and N-H groups of collagen.^{27-29,55} Due to these multiple interactions, the shrinkage temperature of the tanned leather could be raised up to approximately 95°C. Other advantages of such nano tannage include omitted pickling process,^{27,28,30} simultaneous tanning and fatliquoring,^{27,28,30} washability/UV-shielding property/antifungal activity of the resultant leather and access to high-quality gelatin from shavings.²⁸⁻³¹ However, although such nano tannage has been proved as a promising alternative to traditional chrome tannage, there are still some technical aspects to be investigated. For example, still no solution has been found as how to introduce moisture-sensitive tetrabutyl titanate, which is expected to show stronger tanning effects than tetraethoxy silane, into the raw hides without partial hydrolysis before triggering. Furthermore, developments of compatible post-tanning processes such as retanning, dyeing and finishing are needed to facilitate the industrialization of nano tannage.

As a brand new tannage, the tanning chemistries between nanomaterials and collagen are complicated and still not fully understood thus far. In order to achieve versatile tanning effects as chrome tannage in the future, it is necessary therefore to establish a broad understanding about the fundamentals of nano tannage. By knowing how hydrothermal stability is generated from nano tanning processes, optimization can be predicted and the materials can be targeted more accurately.

Finishing with Polymer Nanocomposites

In order to modify the shade/gloss/handle, improve its physical properties (such as light/rub fastness and resistance to water/solvent/abrasion), and hide any defects or irregular appearance, leather must be finished. In general, the finishing processes include a series of mechanical operations and, normally, the application of a polymer coating to the leather surface. Among various alternatives in the market, acrylic and urethane resins have currently become the most commonly used coating-forming polymers for leather finishing due to their leather-like

appearance, handle and mechanical properties.^{17,56-59} These advantages are definitely indispensable as for ordinary leather products, but far not enough to meet the increasingly higher requirements of customers for product quality and function, such as appearance, durability, flame retardancy, wear comfort and hygienic property. In order to upgrade the inherent performances of polymer leather coating or even impart extra functions, leather technologists and chemists begin to seek technical supports from other possible approaches.

With the combination of existing materials and novel nanotechnology, polymer nanocomposites have been established as an exciting new class of materials which are particle-filled, with at least one dimension of the dispersed particles being in nanometer range. Nowadays, polymer nanocomposites are attracting wide interests in many application fields, because the addition of inorganic nanoparticles to polymer can remarkably enhance conductivity,^{60,61} mechanical toughness,⁶² optical activity^{63,64} and catalytic activity,⁶⁵ relative to conventional micrometer scale composites. As for leather finishing, such characteristics offer new possibilities for producing polymer nanocomposite coating with unprecedented performances. For example, S. Zhou et al.⁶⁶ modified acrylic-based polyurethane with nano-silica particles (mean diameter around 20nm) via physical blending or *in-situ* polymerization respectively. For *in-situ* polymerization, nano-silica was first dispersed in monomer mixture by ultrasonic irradiation, followed by polymerization according to conventional process. It was found that, compared with micro-silica, the presence of nano-silica could simultaneously improve the hardness, abrasion resistance, scratch resistance, tensile strength, Young's modulus and weatherability of the nanocomposite coating. These reinforced mechanical properties could be ascribed to (1) the reaction of isocyanate with hydroxyl groups on the surfaces of nano-silica that increased the crosslinking degree of the polymer matrix; (2) the exceptionally high specific surface area of nanoparticles, which resulted in huge interfacial interaction between polymer and nano-silica. Other researchers⁶⁷⁻⁷¹ also employed physical blending to prepare acrylic resin/nano-SiO₂ composite for leather finishing. In their studies, the nano-SiO₂ particles were synthesized via sol-gel method using tetraethoxysilane (TEOS) catalyzed with acid or alkali. Except reinforced mechanical properties, water resistance of the nanocomposite coating was significantly improved by 56% compared with control and the solvent resistance by 55%, respectively.⁶⁹ The former was attributed to the combination of nano-SiO₂ particles and polar groups in the acrylic resin, which remarkably decreased the hydrophilicity of the nanocomposite, and the latter resulted from increased crosslinking degree of acrylic matrix in the presence of nano-SiO₂ particles. When finished on leather crust, nano-SiO₂ particles could also serve as bonding agent between polar groups of acrylic resin and leather fibers, which resulted in increased finish adhesion by 10%.⁶⁹ Meanwhile, with much

smaller size than acrylic colloidal particles (approximately 100nm), nano-SiO₂ particles (approximately 20nm) could fill and level up small craters on the crust surface that acrylic colloidal particles could not access, improving the smoothness of the finished leather.⁶⁷ Thermal properties of leather coating can also be improved via nanotechnology. For example, it was reported that the presence of only 3% SiO₂ nanoparticles could significantly enhance the melting temperature of polyurethane leather coating by nearly 20°C.⁷² This result indicated that the addition of inorganic nanoparticles was potential of broadening the temperature range over which polymer leather coating could be used.

Modification with nanomaterials not only upgrades the inherent performances of the polymer leather coating, but also introduces many novel functions that are absent in unmodified one. In certain cases, some disadvantages of the original polymer coating can be efficiently overcome as a consequence. For example, as a material widely applied in garment, personal adornment and upholstery, leather, for safety considerations, must have specific flame retardancy. However, conventional polyurethane coating is generally combustible, which leads to an increase in flame risks of finished leather.^{73,74} In order to improve the flame retardancy of leather coating, various flame retardants, such as halogen and phosphorus, are usually added into polyurethane resin. Unfortunately, these conventional flame retardants emit irritants during incineration, which are harmful to human health.⁷⁵ Therefore, a growing demand to avoid these disadvantages has resulted in the development of novel flame retardants that are environmentally-friendly and high-efficient. Recently, a waterborne polyurethane/MMT nanocomposite dispersion was successfully developed for flame retardant leather finishing.⁷⁶ Due to the accumulation of MMT layers on the combusting surface of the condensed phase serving as a barrier to O₂ supply and the pyrolysis gases, the nanocomposite coating exhibited increased oxygen index, decreased afterflame time, afterglow time, char length and weight loss in flame test, which indicated improved flame retardancy (see TABLE I). Meanwhile, the thermal stability and mechanical properties of the nanocomposite coating were also greatly enhanced.

A second example of functional leather coating derived from polymer nanocomposites is breathable polyurethane with *in-situ* generated nanoparticles. As has been widely recognized, shoes and garments must be water vapor permeable, or breathable, to be comfortable. This breathability allows sweat to evaporate promptly when activity level increases; thus the heat generated by metabolism can be continuously dissipated and regulated, guarding against a damp and overheated feeling. However, conventional polyurethane coating generally exhibits high resistance to water vapor permeation, which significantly compromises the wear comfort of the finished leather.^{77,78} Previous reports indicated that the water vapor permeability (WVP) of

TABLE I
Flame retardancy of leathers finished with waterborne polyurethane/O-MMT nanocomposites⁷⁶

O-MMT content (wt%)	Thickness (mm)	Afterflame time (s)	Afterglow time (s)	Char length (cm)	Weight loss (%)	Oxygen index (%)
0	1.4±0.1	32.6	3.4	9.27	5.31	26.3
1	1.4±0.1	29.7	3.1	8.63	4.83	27.4
2	1.4±0.1	26.1	2.6	7.76	4.26	28.2
3	1.4±0.1	21.9	2.2	6.51	3.57	29.1
4	1.4±0.1	19.0	1.8	5.62	2.94	29.9
5	1.4±0.1	18.2	1.6	5.43	2.78	30.1

polyurethane finished leather decreased by 30-50% compared with the crust. Especially as far as split leather for shoes was concerned, the WVP would decrease from 1152g/m²·24h to 816g/m²·24h. after traditional finishing, or to 600g/m²·24h after lamination coating.⁷⁹ As a consequence, the perspiration accumulated inside the leather shoes or garments, uncomfortable to the wearers with further risk of bacterial contamination. In general, the presence of impermeable filler particles in polymer will lead to a systematic reduction in mass transport. Physically, such barrier phenomenon can be attributed to more tortuous diffusion path that penetrants are forced to experience when they traverse the composite.^{80,81} However, the establishments of the principle above are ideally based on conventional composite theory, which postulates that the properties of each phase in the composite are the same as if the other phase were not there. It absolutely excludes the possibility that under specific circumstances, the properties of interface layer between two phases may have been altered relative to either the bulk polymer or filler regions. Such phenomenon can have a significant influence on the overall permeability of the composite if only the polymer/filler interfaces are large enough. Y. Chen et al.^{82,83} developed an organic-inorganic nano hybridization technique to modify polyurethane leather coating with *in-situ* generated nanoparticles. This technique was convenient since it was incorporated into the established wet phase inversion coating-forming process. Once chemically triggered during wet coagulation, sequential hydrolysis and condensation of nano precursor that was pre-dissolved in the polyurethane resin occurred, *in-situ* generated nano-sized inorganic particles within the organic polymer matrix. In opposition to conventional principle of increased tortuosity, the hybrid coating showed significantly enhanced water vapor/gas permeability while maintaining comparable hydrostatic pressure to control. In order to rationalize such counter-intuitive phenomenon, incompatibility between organic polyurethane and inorganic nanoparticles was proposed,

which resulted in mesopores (pore size larger than water vapor/gas molecules while far smaller than water droplets) formed at the interface that allowed fast penetrant diffusion (see Figure 5). Due to the tremendous surface area possessed by nanoparticles, the interfacial mesopores were so many that their influence became amplified, which dominated over conventional composite theory that predicted decreased permeability.

Another noteworthy disadvantage of conventional polyurethane leather coating lies in its susceptibility to microbial contamination. First, the polyether or polyester segments of polyurethane macromolecules can serve as carbon sources for microbial growth.⁸⁴ Second, extra components in the coating, such as plasticizers, lignocelluloses, stabilizers and colorants, are also partially responsible for microbial attack.⁸⁴ Once contaminated, the coating will be degraded, discolored and odorous, which shorten the lifespan of the products. In addition, microbial contamination results in increased infection danger and baneful influence of toxins, which severely threaten human health. Currently, various antimicrobial agents are employed industrially to manufacture polyurethane leather coating with antimicrobial function. These agents generally include phenols, chloro-phenols, organic-mercury salts, organic-tin salts and so on. However, most of them are extremely irritating and toxic, not friendly to wearers and environment.⁸⁵ For example, there had been many reports in Europe about dimethyl fumarate (DMF) causing skin contact dermatitis to consumers by the end of 2008. DMF is a commonly used antifungal agent in leather products, which can provoke allergic reactions causing skin itching, irritation, redness, burns and rheumatic pain.⁸⁵ Thus how to develop antimicrobial polyurethane leather coating with skin-friendly property seems important, especially in this era when a hygienic, safe and eco-friendly life style is pursued. In 1985, T. Matsunaga et al. reported for the first time the antimicrobial function of titanium dioxide (TiO₂)

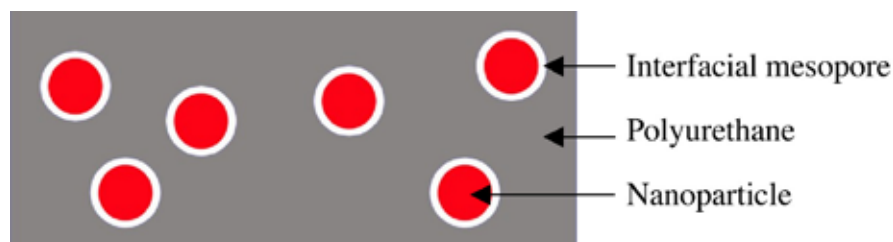
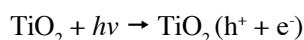
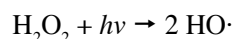
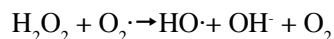
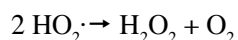
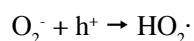
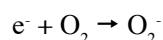
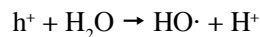
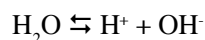


Figure 5: Schematic illustration of possible morphology of polyurethane leather coating with *in-situ* generated nanoparticles.

photocatalytic reaction.⁸⁶ Since then, blending nano-TiO₂ powders to traditional materials such as fabrics, paints, paper pulps and ceramics, for antimicrobial function has attracted great scientific attention considering the high photo-reactivity, cheapness, chemical stability and non-toxicity of nano-TiO₂.⁸⁷⁻⁸⁹ X. Zhang et al.⁹⁰ prepared hydrophilic polyurethane nanocomposite coating with physically-blended nano-TiO₂ particles (Trade name: P25; composition: 80% anatase and 20% rutile; specific surface area: 50m²/g; primary particle size: 25-30nm; source: Degussa, Germany). The nanocomposite coating exhibited strong antimicrobial activities against *Escherichia coli* (*E. coli*) and *Candida albicans* (*C. albicans*) under visible light irradiation. Especially when 0.25% nano-TiO₂ particles were incorporated into the coating, over 95% sterilization of *E. coli* and 90% sterilization of *C. albicans* could be achieved within 4h, and both antimicrobial ratios reached 100% as the testing time elapsed to 24h. The origin of such antimicrobial activity was ascribed to the well-known photocatalytic activity of TiO₂. Briefly, when exposed to photons, TiO₂ will be activated to generate electron-hole pairs:



The electrons reduce oxygen to produce superoxide anions, and the holes oxidize water to produce hydroxyl radicals:



These reactive species are capable of decomposing and mineralizing a wide spectrum of organisms such as bacteria and fungi by redox reaction.^{89,91,92}

Technically, the main difficulty in preparing polymer nanocomposite leather coating lies in how to prevent agglomeration of nanoparticles in the polymer. This is extremely important not only for the stability of the nanocomposite, but also for the final performances of the resultant coating. Generally speaking, agglomeration of nanoparticles leads to phase separation between components,⁴⁶ poor optical properties⁶⁶ and compromised mechanical strength⁹³ of the nanocomposite coating. In order to obtain a homogenous structure, ultrasonic treatment with strong shock wave and tiny shooting flow, which greatly weakens the interaction between nanoparticles, is considered a useful way for physical blending.^{69,90} However, high temperature should be avoided during this process because with increasing heat energy, the frequency of particle collision increases, and thus agglomeration still occurs.⁶⁹ Additionally, in order to make inorganic nanoparticles compatible to organic polymers, dispersants or coupling agents can be used to treat nanoparticles for reduced surface tension, increased steric resistance or altered surface charges.^{49,52,69} Another method to achieve even distribution of nanoparticles in polymer matrix is melt compounding. This technique employs an extruder, injection molder or other processing machine to press polymer and nanoparticles together, in which shearing forces facilitate exfoliation or dispersion. However, oxidation and β -scission lead to degradation of polymer during melting, adding extra parameters apart from the dispersion degree of nanoparticles.^{94,95} *In-situ* hybridization is a fourth method to produce nano-scale inorganic particles in organic polymer with even distribution. This method involves the hydrolysis and subsequent condensation reaction of metal alkoxides, all within the polymer, to produce metal oxides. In order to allow versatile access to chemically designed organic-inorganic nanocomposites, complicated hybrid parameters such as temperature, solvent, water-to-alkoxide ratio, type and concentration of catalyst in the system need to be manipulated.⁹⁴ Except dispersion degree of nanoparticles, unexpected degradation of polymer in the presence of nanoparticles should also be avoided. According to previous reports, anatase TiO₂ nanoparticles were found to be a catalyst

that accelerated photodegradation of polyurethane, while rutile counterparts acted as an effective stabilizer retarding the degradation of polyurethane.⁹⁶ Therefore, modification with nanomaterials should be prudent; otherwise durability of the leather coating can probably be deteriorated.

Effluent Treatment by Nanotechnology

The processes of leather manufacturing are successively composed of (1) cleaning of hides or skins from unwanted materials in beamhouse; (2) permanent preservation of the leather by means of tanning; (3) addition of aesthetic properties through a series of post-tanning operations. During these processes, a variety of chemicals, such as lime, sodium and ammonium salts, fatliquors, bactericides and fungicides, tanning agents and dyes, at significant quantities are employed. However, not all the chemicals utilized can be retained in the resultant leather, and the unabsorbed chemicals end up in the effluents, contributing to a considerable amount of pollution load. Due to their complicated constituents, the polluted effluents from tannery can impose serious environmental consequences and health hazard to human beings. Therefore, the effluents must be treated before discharge. Conventional method for the treatment of tannery effluents consists of physico-chemical processes followed by biological treatment.^{97,98} This treatment system can remove pollutants such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, chromium, etc. Unfortunately, the tannery effluents contain a high amount of total dissolved solids (TDS), which cannot be removed by conventional treatment. The constituents that contribute towards TDS are sodium, chloride, sulphate, calcium, magnesium, residual organic impurities, etc. The discharge of these salts bearing effluents will greatly deteriorate the texture of soil and reduce crop yield.⁹⁹ Therefore, TDS must be removed from the tannery effluents in order to alleviate environmental stresses.

Nanofiltration technology provides an efficient solution to the problem above. This technology is a relatively recent membrane separation process, which takes place on an organic semipermeable membrane usually constructed from polyether-sulphone, polyamides or cellulose derivatives. The driving force for the separation is the pressure difference between the feed and the permeate side. The pore size of the nanofiltration semipermeable membrane is typically between 0.5 and several nanometers that correspond to a molecular weight cut-off of 200-1000g/mol. Because of its size selectivity, several components in a dissolved mixture, which are smaller than the membrane, pore size pass through the membrane while everything else is retained on the feed side as retentate or waste. Because nanofiltration membranes also have selectivity for the charge of the dissolved components, monovalent ions will pass through the membrane while divalent and multivalent ions will be rejected (see Figure 6).¹⁰⁰⁻¹⁰² The advantages of nanofiltration technology include:¹⁰⁰⁻¹⁰²

- Selective separation of hardness constituents;
- Separation of bacteria and viruses;
- Reduced energy consumption;
- Reduced expenses in consequent treatment;
- No chemical additives;
- Reduced corrosion problems.

R. Suthantharajan et al.¹⁰³ investigated the suitability of applying nanofiltration in combination with reverse osmosis for TDS removal from tannery effluents. The nanofilters used in this study were spiral-wound polyamide membranes with pore size of 100 (individual nanofiltration) and 2 nanometers

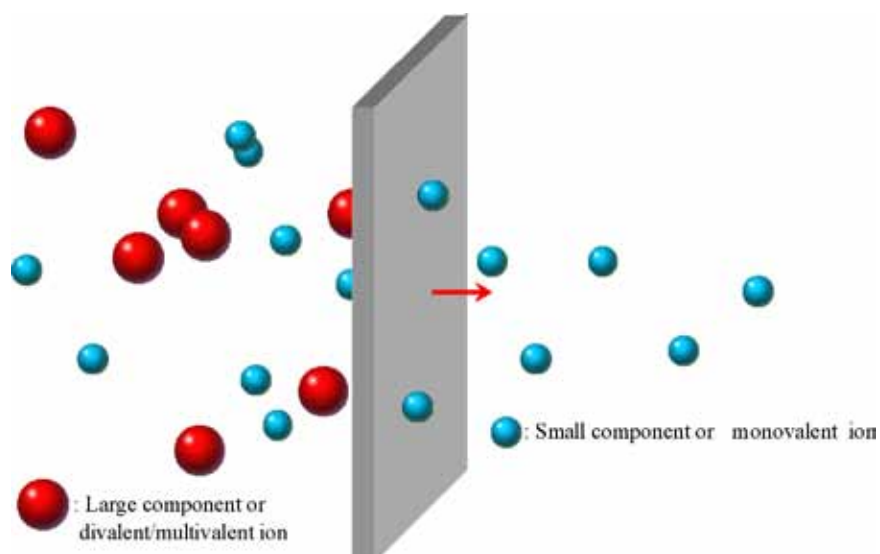


Figure 6: Schematic illustration of separation process through nanofiltration membrane.

(in combination with reverse osmosis) respectively. Experimental results indicated that approximately 65% of Mg^{2+} and 55% of Ca^{2+} could be removed by such combination system while the sulphate removal efficiency was as high as 98%. In addition, approximately 94-98% of Na^+ and Cl^- could also be effectively removed from the tannery effluents. As calculated as a whole, the TDS removal efficiency of this nanofiltration system reached 98%. However, except high investment and operating costs, nanofiltration still exhibits several technical disadvantages, including inability of accommodating variable flow rates and potential of membrane fouling.^{103,104}

Dyestuffs in the tannery effluents are another serious threat to the environment. It is estimated that 10-20% of dyes are lost in tannery effluents as a result of inefficiency during the dyeing process.¹⁰⁵ Some of these dyes are hazardous when they enter the environment. For example, the photocytotoxicity of triphenylmethane dyes based on the reactive oxygen species production has been investigated intensively using photodynamic therapy.¹⁰⁶⁻¹⁰⁸ Meanwhile, a great deal of concern has arisen regarding the thyroid peroxidase-catalyzed oxidation of triphenylmethane dyes due to the generation of *N*-de-alkylated primary and secondary aromatic amines, which have structures similar to hazardous aromatic amine carcinogens.¹⁰⁹ In addition, effluents containing azo dyes may also lead to the formation of carcinogenic aromatic amines when they degrade under anaerobic conditions.¹¹⁰ In order to de-pollute the tannery effluents with dyestuffs, a number of methods, including chemical oxidation and reduction, chemical precipitation and flocculation, photolysis, adsorption, ion pair extraction, electrochemical treatment and advanced oxidation, have been investigated.^{111,112} Advanced oxidation using nanomaterials is one of promising technologies for the removal of dyestuffs from contaminated tannery effluents due to its high efficiency, nontoxicity and low cost. C.C. Chen et al.¹¹³ employed photocatalytic TiO_2 nanoparticles (P25, 80% anatase, 20% rutile and primary particle size ~20-30nm) to treat crystal violet dye (CV, *N,N,N',N',N'',N''*-hexamethylpararosaniline) in aqueous solution under visible light irradiation. Via visible light illumination, the CV was excited to produce singlet and triplet states (CV^*). Subsequently, CV^* injected an electron into the conduction band of the semiconductor TiO_2 nanoparticles, with CV being converted to the radical cation $CV^{+\bullet}$. In turn, the injected electron on the TiO_2 nanoparticles, $TiO_2(e^-)$, reacted with adsorbed oxidants, usually O_2 , to produce reactive oxygen radicals. The radical cation, $CV^{+\bullet}$, ultimately reacted with reactive oxygen radicals and/or molecular oxygen to yield a series of *N*-de-methylated intermediates, which leads to a final 92% photodegradation of CV at the end of 112 h irradiation time.

Despite the favorable properties of TiO_2 nanoparticles in the decomposition of dyes, they are not thermally stable when

applied independently in a powdered form. This is further exacerbated by the fact that the powdered TiO_2 nanoparticles tends to dissolve and lose their surface area readily in the solution, making recovery of the TiO_2 catalyst difficult.¹¹⁴ J.W. Lee et al.¹¹⁴ attempted to deposit nano- TiO_2 with shell thickness less than 37nm onto the surface of SiO_2 cores to solve the disadvantages above. Upon excitation by ultraviolet, the nano- TiO_2 shell absorbed the ultraviolet to generate electron-hole pairs, the latter of which interacted with water to produce OH radicals. The highly labile radicals presumably decomposed methyl orange (azo dyes) by attacking the N=N bond persistently, eventually breaking open its linear chains from the rings. In the presence of dissolved oxygen, the hydroxyl produced new bridging with the detached N=N in the ring opening to form NOOH or intermediate *N*-phenyl *N*-methyl carbamic acid, in some cases. On the other hand, the electrons generated from the shell were immediately pulled towards the internal SiO_2 core, thereby effectively preventing the recombination of the electron-hole pairs and facilitating the production of the radicals (see Figure 7). The SiO_2 cores also assisted in maintaining the TiO_2 shell from degradation due to the insulating character of the SiO_2 cores and their high stability under extreme conditions. In this way, complete decomposition of methyl orange dyes could be obtained in less than 370min under ultraviolet irradiation.

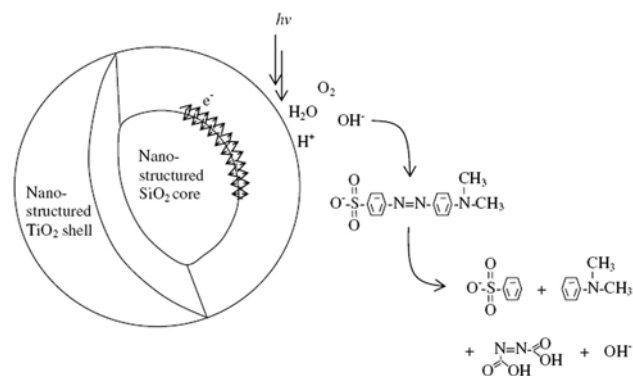


Figure 7: Schematic illustration of nano-core shell structure model and the simplified reactions for the decomposition of methyl orange dyes.¹¹⁴

Potential Risks of Nanotechnology

According to the discussion above, nanotechnology has the potential to improve traditional processes for leather manufacturing, and contribute to competitiveness of the final products. With the merits of nanotechnology currently being put forward in leather industry, there have already been many commercial leather products that are nano-labeled, and there will be more that can be modified utilizing nanotechnology. However, taking a novel technology from the laboratory to an industrial scale is not without challenge. Expect for economic concern, the current development approach for nanomaterials without prior notification of their potential health and environment properties is not acceptable. Nowadays, there

have been approximately thirty organizations from different countries investigating the potential risks of nanomaterials, with the aim of developing appropriate test methods to assess their possible side effects on human health and environment.¹¹⁵ The experimental results obtained thus far indicate that our understanding regarding the potential risks of materials in nano scale still remains rudimentary. One safety aspect which may easily be overlooked is that of dust explosions during manufacture, for the small size of some nanoparticles greatly affects their ease of ignition and the subsequent explosion severity.¹¹⁶ Other researches (largely on small animals) on the potential ill effects of nanoparticles have concentrated on exposure by inhalation, with subsequent effect not only on the lungs but possibly by transfer via the blood stream to other organs.^{117,118} For example, recent evidences indicate that single-walled carbon nanotubes may behave like asbestos fibers, which can produce adverse respiratory effects including an elevated incidence of lung cancer.^{119,120} TiO₂ nanoparticles, even with inherently low toxicity, have also been demonstrated to cause pulmonary inflammation and tissue damage at sufficiently high doses.¹²¹ Besides, the pro-inflammatory effect of nano-silver and the possibility of allergic effects of TiO₂ nanoparticles have been warned.^{122,123} As for environmental risks, the effects of free nanoparticles on the air or water are not as yet known.

Fortunately, competent authorities have gradually recognized these potential risks of nanomaterial's. In June 2008, the European Commission published a Communication on regulatory aspects of nanomaterials, based on a regulatory review of legislation in relation to health, safety and environment aspects of nanomaterials.¹²⁴ The review concluded that the current European Union (EU) legislative framework covered in principle the potential health, safety and environmental risks in relation to nanomaterials but that current legislation might have to be modified in the light of new information becoming available, for example as regards thresholds used in some legislation. Ahead of a regulatory review in 2011, the Belgian EU Presidency is proposing to create a specific register for nanomaterials under the bloc's REACH chemicals regulation and wants to make it mandatory to label their presence in consumer products.¹²⁵ Issues to be addressed include simplified registration for nanomaterials produced in quantities of less than one ton per year and notification of all nanomaterials placed on the market on their own, in preparation or in articles. All aspects related to existing environmental legislation on water, waste and air, as well as worker safety, will also be addressed. The Belgian Presidency expects the forthcoming European Commission Action Plan on Environment and Health from 2011 onwards to include the challenge of nanotechnology and nanomaterials as one of its priorities. In the long term, these actions aim at urging cautious approach to the utilization of nanomaterials in industries, considering there is still scientific uncertainty about the safety of nanomaterials in many aspects. As for

daily necessities such as leather that contain nanomaterials, such prudence appears much more important since frequent contact during manufacturing or utilization increases the risks of inhalation, swallowing and skin penetration of incorporated nanomaterials. Therefore, the only realistic way to make nano-labeled leather products acceptable to the wider public in the future is to reduce uncertainty about their effects by more extensive investigation. Otherwise, the market risks being disrupted by individual or collective citizens' initiatives of rejecting nanomaterials in leather products, as happened with genetically modified organisms and radiation sterilization.

REMARKS AND OUTLOOKS

Because of its undeniable capability to improve traditional leather manufacturing processes and performances of the final products, nanotechnology has created a new promising field that deserves continuous investigations in leather industry. With in-depth researches in the future, this cutting-edge technology may possibly penetrate into almost all processes of leather manufacturing beyond those illustrated in this review. Considering the multiple pressures that the leather industry is struggling against in the new millennium, the combination of leather processing and nanotechnology will offer the manufacturer opportunities to innovate, restore competitiveness and ultimately lead the industry towards a high-efficient, low-cost and environmentally-sound perspective. However, any revolutionary technology usually raises fears of hypothetical and ill-defined adverse side effects in the minds of the general public. In order to prevent biasing consumer information by only advocating the merits of nanotechnology, any combination of leather and nanotechnology should be accompanied by careful investigation of uncertain risks to human health and environment. Meanwhile, although there has been an effort to make nanotechnology compatible with conventional leather manufacturing equipment, it is inevitable that investments will have to be made because new equipment for making nano-labeled leather will be required. This will further add economic complexity to the future role of nanotechnology in the leather industry. Therefore, with recent technological advances, science will not be the major obstacle to bring nanotechnology to fruition in leather manufacturing — risk and money will.

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