Merits and Demerits of Titanium-Based Ingredients in Leather Processing: Benefits and Challenges

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Merits and Demerits of Titanium-Based Ingredients in

Leather Processing: Benefits and Challenges

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Abstract

Nowadays, titanium dioxide (TiO2)or its derivatives are becoming increasingly popular in the field of leather processing. Because of several positive aspects including improved hydrothermal/ thermal stability, self-cleaning properties, UV protection ability, improved dryrub-/ wetrub-/ color-fastness, and antimicrobial property, these materials are increasingly being employed during tanning, post-tanning, and finishing stages. In terms of conferring hydrothermal stability, TiO2 is yet to become at par with conventional chromium tanning agents. In addition, an excessive exposure of TiO2 to the human being is potentially dangerous. Therefore, awareness associated to potential risks linked to TiO2 nanoparticle usage is of high priority. However, keeping the chrome-free leather processing in mind, researches are in progress to develop high-performance titanium based tanning agents comparable to conventional chromium tanning agents. Therefore, the current review work concentrates in beneficial and harmful aspects of TiO2 or derivatives of TiO2 in leather processing.

Keywords: Titanium based tanning agents; nano reinforcing fillers; chrome-free leathers of high hydrothermal stability; structure, property, and applications of TiO2 /collagen composite; shrinkage

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temperature, interactions of Ti4+ with –COOH/ –NH2 / –CONH2–/ –CONH–; UV/ FTIR/ TGA/ XRD of TiO2collagen biocomposite

1. Introduction

Leather manufacturing process involves a series of chemical processes and mechanical operations for converting raw hides and skins (H/S) into finished leather. Leather manufacturing process is generally subdivided into three broad stages, i.e., pretanning, tanning, and posttanning/ finishing operations. Again, each of these stages constitutes of a number of physical operations and chemical processes. Notably, to enhance the properties and performances of the final leather, different types of nano-particulate matters are being regularly employed in multiple stages of leather manufacturing [1]. In fact, superior surface-to-volume ratio, higher surface energy, and enhanced chemically reactivity make these nanopaticles more efficient in achieving the highperformance processed leather.

The present century has witnessed the rapid emergence of nanotechnology as a leading widely popular technology for advancing the material’s design/ performance [2,3]. Extensive research has already been carried out in the area of polymer nanocomposites comprising of discrete nano-scale reinforcing fillers dispersed in the continuous

polymer matrix for the substantial improvement of barrier, physico-chemical, mechanical, and thermal properties [2,4,5]. Among these nanoparticulate matters, titanium dioxide (TiO2) nanoparticles have been drawing wider attention in different applications, owing to their low-cost, chemical inertness, antibacterial ability, high photocatalytic efficiency, and non-toxicity [6–11]. In fact, variable size, shapes, and surface features

can be noticed in different crystalline forms nanoparticulate TiO_2, i.e., anatase, rutile, and brookite [11–14]. However, owing to the small size and high surface area, TiO_2 nanoparticles possess unique physical and chemical properties, and can interact with variable natural, synthetic, and semisynthetic polymers including collagen biomolecules in diverse fashion to enhance the mechanical and physical properties of macromolecules.

Till date, mineral tanning agents are still popular in producing leather of high hydrothermal-, thermal-, and photo-stability. Though salts of chromium are frequently used mineral tanning agents in leather production, current legislations or norms are being increasingly implemented to restrict the usage of chromium based mineral tanning agents. Accordingly, leather processing has been switching toward the production of chrome-free and even metalfree leathers. In doing so, alternative mineral tanning agents based on Al(III), Zr(III), Ti(III/ IV) [15–18], and Fe(II/ III) salts have recently been developed in producing chrome-free leathers of high hydrothermal stability. In this context, the stability of Ti-tanned leathers is governed by various types of interaction including van der Waals force and hydrogen bonding between the collagen macromolecules and Ti species [19]. In addition, abundant functional groups, i.e., –COOH, –NH_2, and –CONH–, on collagen fiber can interact with Ti^{4+}

through chelate formation [20].

In the recent past, the demand of metals/metal oxides in finishing operations is increasing day by day because of the huge potential of these metals/ metals oxides in enhancing various attributes of finished leather including self-cleaning ability, resistance to color fading, protection against micro-organisms, and mechanical resistance. All

of these improved properties enhance the versatility and competitiveness of metal-/ metal oxide-treated leathers. Among different nano-particulate matters used during leather manufacturing, TiO_2 and other Ti-based ingredients offer various important features including antimicrobial characteristics [21], self-cleaning capability [22,23], and significantly enhanced thermal resistance in finished leather [24]. In particular, because of some inherent properties, i.e., antifungal activity, superhydrophilicity, water vapor permeability, and resistance against shearing force, TiO_2 nanoparticles can be employed in leather finishing to produce high-quality finished leather [25,26]. Importantly, the anatase form of TiO_2 nanoparticles can impart self-cleaning properties in the finished leather surfaces. In fact, TiO_2 is often used as a pigment and filler during white leather finishing [27].

Therefore, titanium-based ingredients are becoming increasingly popular in different fields of leather manufacturing. The current review has focussed on the structure, property, and applications of titaniumbased ingredients in developing high-performance leather materials.

2. Results and Discussion

2.1. Titanium based ingredients during tanning operations

In the recent past, hydrothermal stability of wet-white leather prepared using titanium-based tanning agents was compared with that of conventional leather tanned with chromium tanning agent [18]. In fact, the as-determined layer-wise shrinkage temperatures of the wet-white leather were noted to fall within 73.9–77 °C. Though the shrinkage temperature was significantly less than that of conventional chromium tanned leather, these findings should be important from the point of view of chromefree leather processing. In comparison to raw collagen, the enhanced hydrothermal stability of TiO_2-tanned leather was ascribed to the formation of hydrogen bonding among >C=O groups of collagens, bound water molecules, and TiO_2 nanoparticles [5].

Figure 1. (a) Chemical structure of collagen (Type I) molecule, (b) protein secondary structure of collagen (Type

I), (c) hydrogen bonds between proline of collagen (Type I) molecule (yellow) and TiO_2 nanoparticles (red and grey), (d) electrostatic potential mapping of collagen (Type I) surface, and (e) hydrophobic force map of collagen

(Type I) surface. The figures were originally published by Yang et al. [19] and approved for reuse by Elsevier.

In this regard, the secondary structure of collagen was almost preserved in TiO_2-tanned leather, indicating a minor conformational change of collagen in presence of TiO_2 nanoparticles [5]. Recently, molecular dynamics simulation was conducted to identify the main driving force behind adsorptive interaction of collagen with TiO_2 nanotubes [19]. These simulation results indicated the major contributions of physical adsorption including van der Waals force and hydrogen bonds between proline residue of collagen and TiO_2 nanotubes (Figure 1). In this context, the interaction was noted to be highly dependent on the size of the nanotubes (Figure 2). In fact, TiO_2 nanotubes with diameters around 100 nm displayed a higher adsorption amount and faster adsorption speed than that of 30 nm TiO_2 nanotubes. The calculated interaction energies indicated that the TiO_2 nanotubes with bigger dimensions had higher interaction energies, thereby leading to the higher collagen adsorption [19]. More importantly, abundant functional groups, such as –COOH, –NH_2, –$CONH_2$ and –CONH–, of collagen fiber can interact with Ti^{4+} of TiO_2 by means of chelation at the time of titanium tanning [20]. In the past, the

interactions between TiO2 nanoparticles and collagen were investigated by FTIR, XRD, and thermal analyses (Figure 3) [28]. In the absence of TiO2 nanoparticles, FTIR spectrum of collagen hydrolysate film exhibited broad peaks at 3420 and 2663 cm”1 ascribed to O–H str. and C–H str., respectively. Once

the TiO2 nanoparticles were added to the collagen hydrolysate film, the nature of these two broad peaks altered depending on the extent of TiO2 nanoparticles in the collagen hydrolysate., In addition, collagen specific peak at 2663 cm-1 shifted to 2661 cm-1 after addition of TiO2 nanoparticles, ascribed to the intermolecular interactions between O–H, C–H, and N–H groups of collagen with TiO2 nanoparticles (Figure 3). Likewise, a substantial increase in O–H str. intensity at 3420 cm-1 was noted as the proportion of TiO2 nanoparticles was increased. Furthermore, intermolecular interactions between collagen with TiO2 nanoparticles were substantiated from the emergence of distinct anatase specific peaks in TiO2-collagen hydrolysate film. Notably, the intensity of anatase-specific diffraction peaks increases with further addition of TiO2 nanoparticles. Additionally, interaction of collagen with TiO2 nanoparticles was substantiated from the attainment of continuously increasing residue with gradual addition of TiO2 nanoparticles in the collagen hydrolysate during TGA analyses (Table 1). Consequently, the degr dation onsets (TOS1, TOS2, and TOS3) in all the stages (S1, S2, and S3) were shifted to the higher temperature, suggesting enhanced thermal stability in TiO2-collagen hydrolysate film in comparison to merely collagen hydrolysate [28].

Figure 2. Trajectory of MD simulation in equilibrium: (a) collagen (Type I) and 1.23 nm armchair TiO2 nanoparticles and (b) collagen (Type I) and 2.72 nm armchair TiO2 nanoparticles, and trajectory of an MD simulation in equilibrium: (c) collagen (Type I) and 1.22 nm zigzag TiO2 nanoparticles and (d) collagen (Type I) and 3.16 nm zigzag TiO2 nanoparticles. The figures were originally published by Yang et al. [19] and approved for reuse by Elsevier.

Figure 3. (a) XRD of TiO2 nanoparticles and collagen hydrolysate film and (b) FTIR spectra of collagen hydrolysate film and TiO2 nanoparticles incorporated collagen hydrolysate film. The figures were originally published by Erciyes et al. [28] and approved for reuse by Wiley.

Table 1. Thermal degradation characteristics of TiO2-collagen hydrolysate films with varying TiO2 content

TiO2

S1 S2 S3 Residue

nanoparticles

(%) TOS1

ΔWS1

TOS2

(%)

(oC)#

(%)$

(oC)

0 50.84 4.22 173.30 32.84 314.34 38.33 14.45

0.5 52.43 4.98 235.94 33.24 314.72 42.20 17.51

1.0 62.09 5.64 244.14 34.11 323.77 42.74 19.58

2.0 64.74 6.59 256.93 35.58 324.48 43.38 24.61

TOS1, TOS2, and TOS3 were degradation onsets in S1, S2, and S3 stages, respectively.

$ ΔWS1, ΔWS2, and ΔWS2 were the weight losses in S1, S2, and S3 stages, respectively.

2.2. Titanium based ingredients during post-tanning and finishing stages

The leather finishing step, i.e., the final stage of leather production, primarily involves a series of operations to attain various objectives including elimination of imperfections, improvement in the tactile feel, dye levelling, removal of surface irregularities, and enhancement of shine/ brilliance of the leather surface. Earlier, adhesion characteristics of leather were improved upon applying nano-TiO2 in leather coating. Enhanced adhesion characteristics were ascribed to the nano-TiO2 driven

ΔWS2

TOS3

ΔWS2

(oC)

(%)

(%)

increased intermolecular linkages between the finished film and leather surface. In fact, because of the smaller size, nano-TiO2 particles were able to penetrate easily through the diverse pores in leather substrate. In addition, the larger surface area of nano-TiO2 particles facilitated intermolecular interactions between the finished film and leather surface [26]. Furthermore, nano-TiO2 was noted to confer the self-cleaning properties in finished leather. Notably, TiO2 nanoparticle-embedded composites materials comprising acrylic binder, nitrocellulose lacquer, and pigmented paste were used for leather surface finishing, where self-cleaning properties offered by the

doped TiO2 nanoparticle were confirmed by spectrophotometrical measurements and CIELab color coordinates recording [23]. Upon exposure to both UVA (= 365 nm) and visible light, the finished leather film containing doped TiO2, nanoparticles effectively degraded and removed methylene blue stains from the leather surface [23]. In this context, leather surface treated with Fe–N co-doped TiO2 nanoparticles presented substantial activity for MB spot degradation under visible light irradiation. Furthermore, nano-TiO2 was noted to confer UV protection ability in finished leather (Figure 4).

λ

In this way, nano-TiO2 particles can impart shielding effect against UV light and thereby prevent yellowing of finished film [27]. Later on, utilizing the UV protection ability of nano-TiO2, nano-scale TiO2-SiO2 composite was employed to improve various characteristics including dryrub-/ wetrub-/ color-fastness of finished leather [27]. The thermal stability of leather treated with silica doped TiO2 nanoparticles increased tremendously, as understood from differential scanning calorimetry measurements and associated activation energies of 2.083 × 104, 2.36 × 104, and 6.576 × 103 J mol–1 for leather treated with 10% silica doped TiO2, leather treated with 20% silica doped TiO2, and untreated leather, respectively [22].

More recently, tribological behavior of goat leather surface treated with sputter-deposited Ti-Ag-O films was examined [29]. Initially, the untreated crust leather was sputter deposited with Ti-Ag-O films containing 5 atomic% of Ag. Thereafter, tribological characteristics and hence durability of a set of Ti-Ag-O film-deposited leathers were examined using ball-on-disk test followed by characterization of the worn leather surfaces to determine the coefficient of friction and associated abrasive or adhesive wear mechanisms.

Notably, a reasonably high level of wear resistance was recorded when polytetrafluoroethylene was utilized as the counter body during the ball-on-disk test performed on Ti-Ag-O film-deposited leather surface. In fact, the coefficient of friction is an important parameter

determining the level of friction generated during surface rubbing of some important leather articles including garment and upholstery [24]. In those articles, coefficient of friction can particularly adjudge the long-term durability of leather finishes. Very recently, another group of workers attempted to develop a smart leather surface using titania in the finishing formulation [24]. In comparison to untreated rutile TiO2, ascorbic acid modified rutile TiO2 showed the enhanced ability to impart color-fastness in the finished film [24]. In fact, the time-dependent color variation became minimized when ascorbic acid modified rutile TiO2 was employed during leather finishing.

In this context, the anti-oxidant property of ascorbic acid might be indirectly responsible behind the enhanced stability of the color. In addition, all the treated or untreated TiO2 nanoparticles significantly enhanced abrasion resistance of the finished film. Additionally, the finished film acquired substantial antimicrobial properties when polyethylene glycol-functionalized titania nanoparticles were added to the finishing formulation.

Similarly, enhanced antimicrobial property recorded in assynthesized Ag–TiO2 nanoparticles was employed in leather finishing [21]. In this case, Ag was identified as the main antimicrobial agent. In this context, merely TiO2 nanoparticle decorated finished film showed the minimum antimicrobial activity in comparison to the leather finished with films having Ag–TiO2 nanoparticles.

Though these works reported the minimum activity of TiO2 nanoparticle against bacterial growth, another group of workers synthesized TiO2-nanoparticles by an eco-friendly approach using a probiotic bacterial strain L. plantarum [25]. In fact, treatment with as-synthesized TiO2nanoparticles inhibited the growth of P. expansum on

leather surface. In this context, the mechanical properties remained almost unaltered even after 21 days of fungal inoculation of TiO2- nanoparticle-treated leather. By contrast, massive drop in tensile parameters were noticed after 21 days when the same fungal inoculation was administered on the leather without TiO2-nanoparticles.

Figure 4. (a) UV-vis diffuse reflectance spectra forTiO2 nanoparticles, (b) absorbance spectra for a 20 ppm MB solution in the presence of 0.1% doped and undoped TiO2 nanoparticles after 1 h visible light irradiation, (c) absorbance spectra for a 20 ppm MB solution in the presence of 0.1% doped and undoped TiO2 nanoparticles after 1 h UV irradiation. The figures were originally published by Petica et al. [23] and approved for reuse by Springer.

3.3. Health perspectives

In particular, during leather finishing operations, exposure to TiO, nanoparticles may occur while mixing spray formulations and when working in close proximity to spray booths [1]. In fact, inhalation has been established as the primary route of occupational exposure to TiO2 nanoparticles. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated a threshold limit value of 10 mg m–3 as a time-weighted average (TWA) for a standard 8 h workday and a 40 h workweek. The Occupational Safety and Health Administration (OSHA) has prescribed permissible exposure limits-timeweighted average (PEL-TWA) of 15 mg m–3 for TiO2 dust. Earlier, the National Institute for Occupational Safety and Health (NIOSH) proposed a Recommended Exposure Limit (REL) for TiO2 nanoparticles at 0.3 mg m–3, a 10fold lower magnitude than the REL for TiO2 dust. As compiled by the New Energy and Industrial Technology Development Organization (NEDO) in Japan, the Risk Assessment of Manufactured Nanomaterials TiO2 Executive Summary has estimated an acceptable exposure concentration of 1.2 mg m–3 as TWA for an 8 h workday and a 40 h workweek. However, a contemporary study has demonstrated exposure during TiO2 handling well below the presently established limits.

4. Conclusions

Therefore, TiO2 and TiO2-derived nano-particulate matters have been emerged as a promising ingredients during tanning, post-tanning, and finishing operations in leather processing industries. In processed leathers, TiO2 and TiO2-derived nano-particulate matters confer hydrothermal and thermal stability, self-cleaning properties, UV protection ability, improved dryrub-/ wetrub-/ colorfastness, and antimicrobial properties. At the same time, over-exposure of TiO2 to the human being can be potentially dangerous. Hence, by raising the awareness of both positive aspects and potential risks linked to TiO2 nanoparticle usage, this review aims to serve as a guide to industry professionals and researchers, helping them to make decisions during leather processing with special consideration in the health perspectives of workers of the leather production sector, especially at the time of leather finishing.

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