

# A review of the green chemistry approaches to leather tanning in imparting sustainable leather manufacturing

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## **Abstract**

Leather is made of collagen protein polymer, which is used in the manufacture of a variety of products including footwear, automotive upholstery, garments, and sports equipment. Animal skins/hides are converted into leather using a series of chemical processes. Of them, the tanning process is the most important chemical process that converts animal skins into leather

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by stabilising collagen fibre so that they do not putrefy. However, it is a hazardous process because of the use of various toxic chemicals in tanning, re-tanning and fatliquoring treatments producing toxic effluent. Over the years many tanning treatments based on chromium sulphate, and vegetable and synthetic tannins in combination with heavy metals, have been developed but tanning with chromium sulphate (known as Cr-tanning) is still the most effective, cheap, and widely used tanning process in the leather industry. Although the development of various improved Cr-tanning methods highly reduced the chemical and water consumption in leather tanning, it is still under scrutiny because of the production of effluent containing a harmful level of Cr and there is strong evidence that when the treated leather is disposed into the environment, part of the released trivalent chromium is converted into carcinogenic hexavalent chromium. Many sustainable alternatives to Cr-tanning based on chemical and enzymatic crosslinking, various bio-derived polymers, enzymes, modified zeolites, and nanostructured materials have been developed over the years with limited success. The alternative methods are either not as effective as Cr-tanning, affect the dyeability and other functional and organoleptic properties of leather, and or are cost-prohibitive. In this comprehensive review article, various tanning methods used in industry or studied in the laboratory are critically reviewed, and their advantages and disadvantages are outlined. The consumption of tanning agents, total chemicals including various auxiliaries and fatliquoring agents, and water in tanning, and the tanning performance and mechanical properties of the processed leather are compiled and compared. The reaction mechanisms of novel tanning agents with leather collagens and the future directions to make leather tanning more sustainable are outlined. This review article will be a guide for academicians/researchers/manufacturers involved in leather processing to develop more sustainable leather materials.

Keywords: Leather; tanning chemistry; tanning mechanisms; shrinkage temperature; mechanical properties; organoleptic properties

## **1. Introduction**

The UK leather industry encompasses specialist high-end manufacturers of automotive upholstery, furniture, shoe uppers and soles, chamois and wet blue leather, and exports more than 80% of its leather production. The current decline of the leather industry in the UK is due to the high cost of leather processing, high labour cost, environmental issues related to the effluent produced, loss of the local customer base, and intense competitive pressures from substitute products. According to the Statista, a Hamburg-based online platform specialised in market and consumer data, the revenue in the luxury leather goods segment in the UK in 2022 was £2.19 billion expected to grow annually with a compound annual growth rate of 4.69% (Statista, 2022) [1]. According to the British Leather Federation, The British leather industry employs approximately 8,500 workers in 23 tanneries and numerous leather goods manufacturing companies, with an annual turnover of £305.8 million [2].

From prehistoric times, animal hides/skins have had wide ranging uses as garments for covering the body as well as providing protection from environmental conditions, and water carriers to keep the drinking water cool. Leather is made from animal hides/skins, which are a by-product of the meat industry. Leather is used in the manufacturing of a variety of products including clothing, footwear, handbags, furniture, and tools because of its reasonably high strength, flexibility, and thermal properties. Raw animal hides/skins undergo various processes, including tanning and dyeing, to make them suitable for manufacturing shoes, handbags, garments, and other products. Leather is a material made from animal skins/hides

with their original fibrous structure retained and tanned to prevent spoiling. Hair or fur may have been removed. Leather may be split into layers before or after tanning. Any surface coating applied is not thicker than 0.15 mm [3]. Hides/Skins are often split to create leather with different properties. The top surface split of leather is called grain leather and the remaining split can be used to make suede leather. Cowhide is mostly used in manufacturing leather goods. Buffalo, goat and sheep hides are also used but their use is relatively low.

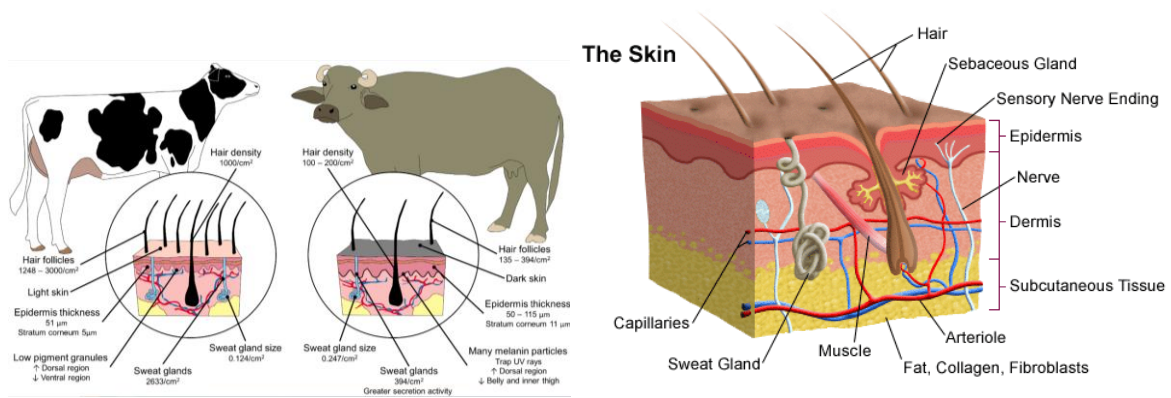
The primitive preservation process involved drying the raw hides/skins in the sun and vegetable extracts were used to convert the raw hides/skins to leather. At present, Cr tanning is the most efficient, best performing, and cost-effective tanning process used in the leather industry. To improve the environmental credentials of leather, hexavalent chromium or Cr(VI) was replaced with trivalent chromium or Cr(III) for leather tanning, as Cr(III) is not a carcinogen like Cr(VI), although it is still highly toxic. However, the chrome-tanning process produces effluent containing elevated levels of Cr(III), some of which convert to Cr(VI). Therefore Cr-tanning is restricted in the developed world [4,5]. Leather goods manufacturers around the world, including the UK, are now looking for sustainable but cost-effective alternative tanning processes to make leather goods that are free from toxic Cr and sustainably produced.

A number of reviews on sustainable processing of leather have been published over the years [6,7]. However, most of them refer to only a few tanning methods and has not considered the chemistry approaches studied to make the tanning process sustainable, and also the effect of tanning treatments on the physicochemical and mechanical properties and biodegradability of leather. In this review article, all types of tanning methods developed to the present day are critically reviewed, and their merits and demerits are outlined. The tanning performance, mechanical properties and organoleptic properties of the processed leather tanned by using various processes are compiled and compared on the basis of the

treatment conditions. The chemistry and mechanisms of tanning are also discussed and future directions to make leather tanning sustainable are outlined.

## **2. Biology of animal skin**

Animal skin has three layers: the top epidermis layer, the hypodermis layer inside the body, and, in between, the dermis layer. There is a slight variation in the dermal layer, animal to animal and between breeds in terms of epithelium thickness of sweat glands; otherwise, all animal skin has three dermal layers. The outermost layer, the epidermis, consists mainly of keratinocytes, melanocytes, Langerhans cells, Merkel cells, and sensory nerves protecting the skin from damage caused by the surrounding environment. The epidermis layer consists of five sub-layers that work together to continually rebuild the surface of the skin. The dermis layer, located just under the epidermis layer, has blood vessels, lymph vessels, hair follicles, sweat glands, sebaceous glands, and nerve endings. The dermis is held together by fibrous collagen protein fibres. The dermis layer is much thicker than the other two layers and works as a thermoregulator. The dermis layer consists of two sub-layers: the papillary layer, which is composed of thin collagen fibres, and the reticular layer, consisting of thick collagen fibre. The innermost hypodermis or subcutaneous layer consists of a network of fat and collagen cells. Its function includes protecting the inner organs, storing fat as an energy reserve, and working as a heat insulator. The difference in morphological characteristics of cow and buffalo's skin is depicted in a schematic diagram in Fig. 1.



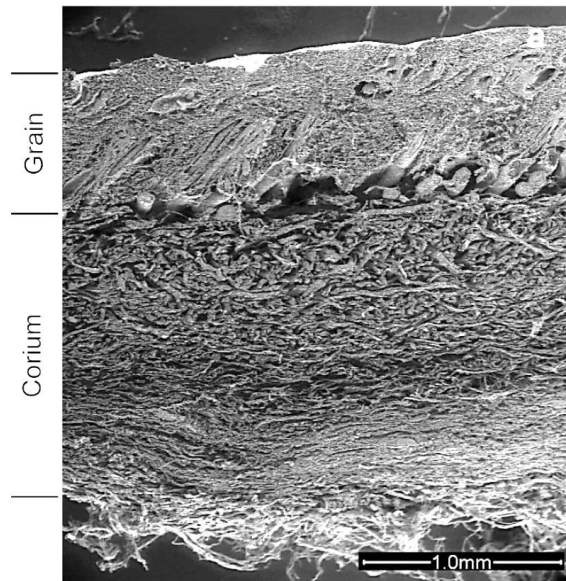
**Fig. 1.** The difference in skin characteristics between cattle and buffaloes [8].

### 3. Conversion of animal hide/skin to leather

Raw animal skin is composed of 60–65% water, 30–33% protein (mostly collagen), 2–6% fat and 0.5–1.0% minerals [3]. All leathers show a considerable decrease in water content (as low as 10%–15%) after the tanning process [9]. Leather is a skin-derived fibrillar type I collagen material. In the conversion of skin/hide to leather by tanning, fats are removed, and the collagen fibres are compacted and bonded together by the tanning agent, making the leather strong and durable. The flexibility and tensile stiffness of leather depends on the inherent properties (e.g., Young's modulus) of the skins or hide [10], which can be affected by treatment processes (e.g., fat-liquoring) and the moisture content [11,12]. Leather has a two-layered structure with an outer grain layer and an inner corium where the size and packing of collagen molecules are different, as shown in Fig. 2. The corium and the grain are composed of a larger diameter fibre (100 μm) and a smaller diameter fibre (1 μm) [13] respectively, allowing interweaving of the smaller fibre in the grain layer to create a smooth surface, while the larger fibre in the corium is constructed more loosely, allowing fibre

movement for stretching as well as resisting tear propagation [14]. Not only the fibre size, but also the arrangement of collagen fibril bundles in the collagen fibre affects the mechanical properties of the leather, which vary from one animal species to another [15]. The fibril arrangement, as well as the mechanical properties of leather, can be affected by mechanical or chemical treatments [16]. The study of the structural basis of flexibility in leather using small-angle X-ray scattering shows that higher moisture content offers greater flexibility to the material, as water absorption inside collagen fibrils produces a larger lateral spacing between collagen molecules [16]. This possibly provides a lubricating effect in collagen fibrils enabling greater flexibility [17]. However, in tanned leather, the collagen molecules align in the strain direction and pack closer together, reducing the ability of the molecules to move relative to each other, resulting in increased stiffness.

The conversion of raw hide/skin to leather has many processing stages. Globally, approximately 30% of hides/skins are processed without preserving the hide. The remaining 70% are preserved by salt curing, where the hides are soaked in salt water for 24 hours to saturate them with brine which prevents rotting. The salted hide/skin has three layers: a woolly top layer, and a bottom fat layer, in between, a matrix skin layer. Brine curing is the most cost-effective way to preserve the hides/skins for further processing and can preserve the salted hides/skins for up to a year. The hides/skins then undergo unhairing, fleshing, delimiting, pickling and tanning. During the leather processing, the tanning process is the most hazardous, as it produces foul-smelling and toxic effluent. 90% of hides/skins are chrome tanned, the rest are vegetable tanned.



**Fig. 2.** Two-layered structure of the leather. Reproduced from [17].

#### **4. Importance of tanning**

Untanned, dried skins or hides have extremely poor strength and dimensional stability, low shrinkage temperature (the temperature at which under moist heat the leather starts shrinking), poor dyeability and degrade easily as they have no protection against bacteria. The tanning process is a chemical process that converts animal hides or skins to leather. Without tanning, the leather has high flexibility and poor strength as collagen fibres are loosely arranged in the dried hide/skin. The purpose of tanning is to preserve the hide/skin, enhance its strength and make it durable by limiting degradation, especially when the leather is wet by compacting collagen fibres in the leather, making it imputrescible. Tanning agents include heavy metals, crosslinking agents, and plant polyphenols to bind the collagen fibres together, providing dimensional stability and reducing swelling that occurs when the leather becomes wet. The tanning treatment also considerably enhances thermal stability by



increasing the thermal shrinkage temperature.

## **5. Assessment of tanning performance**

Leathers are a popular industrial product because they are natural and comfortable, and because of their good breathability, heat insulation, malleability, longevity, water resistance, aesthetics, surface pattern (grain structure), easy maintenance and repairability, and recyclability. However, for their application as a material, properties such as shrinkage temperature, tensile strength, tearing strength, thickness rate and organoleptic properties are important to the leather industry. The shrinkage temperature of leather is especially important for footwear manufacturing processes. During the manufacturing of footwear, moist heat is applied to leather, and any shrinkage creates issues, including a reduction in the size and shape of the produced footwear, resulting in poor aesthetic properties. Raw hides or skins shrink very easily at temperatures of about 55 °C (depending on the type of animal), while chrome-tanned leather exhibits shrinkage temperatures higher than 100 °C. The shrinkage temperature is measured by various test methods, but the most popular is the ISO 3380 (ISO 3380: 2015: *Leather — Physical and mechanical tests — Determination of shrinkage temperature up to 100 °C*). Originally developed by the International Union of Leather Technologists and Chemists Societies (IULTCS), a leather sample of predetermined size is hung from a hook, and then soaked in a vessel of distilled/deionised water. The leather specimen in water is then heated at  $2\pm 0.2$  °C/min until sudden shrinkage occurs. The temperature at which the shrinkage occurs is considered the shrinkage temperature. Another test method is the SATRA TM 17:1997 developed by UK-based SATRA Technology. Both methods are based on the same principle, but the ISO 3380 method only allows the

measurement of shrinkage temperature up to 100 °C. The SATRA method uses glycerol-mixed water, which increases the boiling point and therefore allows the measurement of shrinkage temperature up to 130 °C. Cohen et al. developed a dynamic mechanical thermal analysis-based shrinkage temperature measurement method [1] which is not used by the leather industry. Ning et al. proposed a new method based on non-contact electrical measurement by a single-chip microcomputer, which allows simultaneous measurement of shrinkage temperature of multiple samples [19].

The *ISO 3377-2: A method for determining the tear strength of leather using a double-edged tear*, which is sometimes described as the Baumann tear test, is a popular standard test method for measuring the tearing strength of leather. A rectangular leather sample of predetermined size is held between the lower and upper jaws of a tensile tester, and the upper jaw is pulled apart at 100 mm/minute until the sample breaks. The tear strength is measured in newtons. The *ASTM D2209-00(2021): Standard Test Method for Tensile Strength of Leather* or *ISO 3376: A method for determining the tensile strength, elongation at a specified load and/or break of leather* are used for the measurement of tensile strength of leather. The leather specimen is cut into a ‘dog bone’ shape so that it is narrower in the part between the grips and will therefore break in this region. The leather specimen is held between two jaws of a tensile tester at 50 mm apart and the upper jaw is pulled apart at 100 mm/minute until the sample breaks. The tensile strength and elongation are calculated in megapascals (MPa) and %. The thickness rate is measured by measuring the thickness of leather before and after the tanning treatment. The increase or decrease in thickness is measured in terms of percentage.

Organoleptic or sensory properties, such as softness, fullness, grain flatness, grain smoothness, grain tightness (break), dye uniformity and general appearance are mostly subjectively measured. The softness of leathers can be measured by standard test methods such as *ISO 17235:2015: Leather — Physical and mechanical tests — Determination of*

*softness developed by IULTCS using a leather softness tester. The fullness of crust leather (leather that has been dried after tanning but not yet dyed) is evaluated by compression-resilience performance using the method described by Peng et al. [20]. The grain surface of crust leather is observed with a stereo microscope and the grain width is measured. The apparent density of leather is measured according to the ISO 2420: 2017: *Leather — Physical and mechanical tests — Determination of apparent density and mass per unit area.**

## **6. Tanning process**

The tanning process is carried out in a tannery. Before the tanning process, the beam-house process is carried out; where hides/skins are soaked, dehaired, neutralised, fleshed, scudded, and washed, after which the skins are ready for tanning. After tanning, the leather is re-tanned and dyed to make it ready for use.

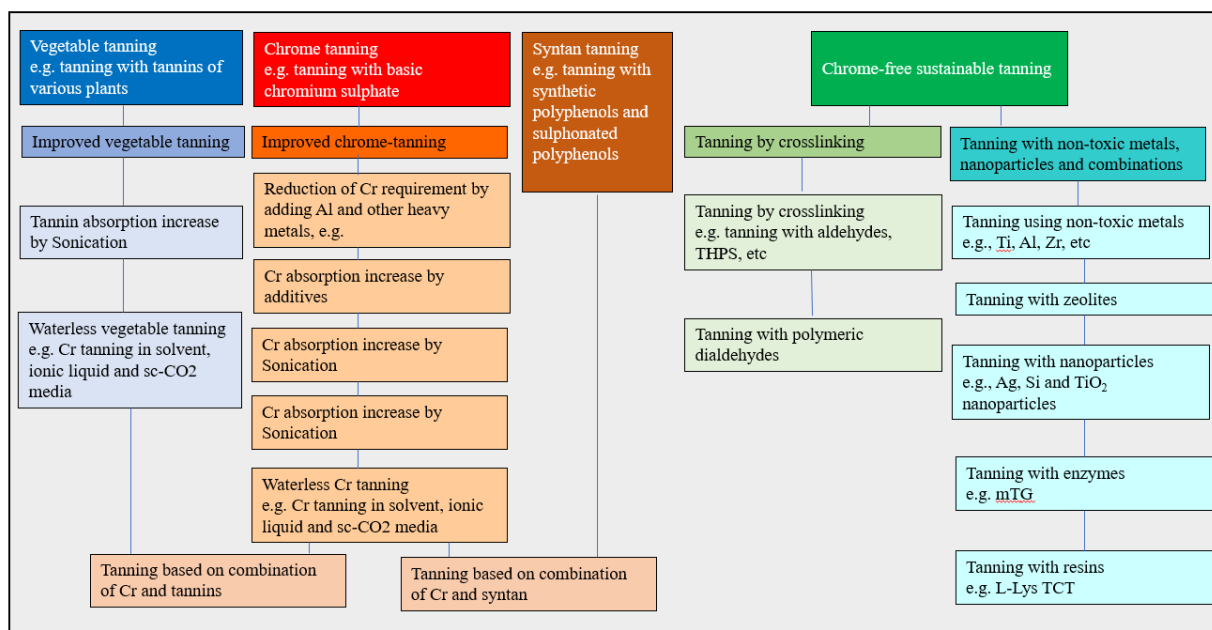
### **6.1. Dehairing of skin**

Dehairing is the major and most heavily polluting process in the tanning operation, during which the hair, epidermis layer of skin, globular proteins, fats, and other cementing materials are removed from the skin. In the traditional dehairing method, the flesh side of the hide/skin is covered with a paste of lime and sodium sulphide. The hair root, made of cysteine-rich keratin, is hydrolysed by the action of the sodium sulphide and lime, allowing easy removal of hair from the grain side of the skin. The application of sodium sulphide makes the dehairing process highly polluting, as it is a hazardous chemical which decomposes to produce toxic hydrogen sulphide gas [21], and its toxicity is evident as it caused tracheal injury and cell death in broiler chickens [22]. The treatment damages the skin due to overexposure to sodium sulphide and produces toxic effluent. Residual sodium sulphide

needs treatment before it can be discharged into watercourses [23]. Various sustainable alternatives have been studied, including enzymatic depilation that causes no damage to the grain [24]. The enzymes studied were protease enzymes from various organisms, such as *C. brefeldianus* [24], and *Pseudomonas aeruginosa* strain MCM B-327 [25]. Keratinase enzyme also has been studied for the depilation of hair, which is quite resistant to the commonly known proteolytic enzymes such as trypsin, pepsin and papain [26,27]. The complex mechanism of dehairing by keratolysis involves the cooperative action of sulphitolytic and proteolytic actions [28]. A novel serine alkaline protease (AprA) gene from alkaliphilic *Idiomarina sp.* C9-1 was cloned and expressed in *Escherichia coli* [29]. The purified AprA and its pre-peptidase C-terminal (PPC) domain-truncated enzyme (AprA-PPC) showed maximum activity at pH 10.5 and 60 °C and was active and stable in a wide range of pH levels and temperatures. Ca<sup>2+</sup> significantly improved thermostability and increased the optimal temperature to 70 °C. AprA-PPC was effective in dehairing cattle hide and skins of goat, pig and rabbit in 8–12 h without causing significant damage to hairs and grain surface.

## **6.2. Tanning methods**

Traditionally, leathers are processed by the three types of tanning methods including vegetable tanning, chrome tanning and syntan tanning but recently the tanning processes are quite improved with the development of various sustainable tanning methods. Fig. 3 shows various tanning methods that are studied until the present.



**Fig. 3.** Various tanning methods.

### 6.2.1. Vegetable tanning

Vegetable tanning is the oldest tanning method, developed to produce leather from hides/skins. In the vegetable tanning process, tannin extracted from barks, nuts, leaves, fruits, and wood is used. Tannin is a polyphenolic agent known to bind to protein. The tannin is extracted from acorn [30], chestnut (*Castania sativa*) wood [31], Tara (*Caesalpinia spinosa*) pods [32], mimosa (*Acacia mearnsii*) barks [33], Black wattle (*Acacia mearnsii*) [34], quebracho wood (*Schinopsis lorentzii*) [35], myrobalan (*Terminalia chebula*) [36], pine bark [37,38], Pala indigo (*Wrightia tinctoria*) plant [39], *Xylocarpus granatum* bark tannin [40] and medicinal herbs [41]. Tannin, also known as tannic acid, is a natural polyphenolic compound, which has acidity due to the presence of many phenolic groups. In this method, the delimed and dehaired hides are soaked in a tannin solution for several weeks to months, which makes the leather water-insoluble and resistant to microbial attack. However, vegetable tannins alone are ineffective as a tanning agent and therefore they are usually used

with metal mordants and syntans to improve their durability and performance. Therefore, in vegetable tanning, the hides/pelts are pre-tanned mostly with syntan and then tanned with vegetable tannin, followed by re-tanning with another tannin or syntan.

The effluent produced by vegetable tanning is less toxic than that produced by the popular chrome tanning process. Vegetable-tanned leather is eco-friendly, has a natural smell, and has a low environmental impact as only natural tannins are used in the tanning process. The leather has a natural look with a rich and beautiful patina, which improves with time.

However, the quality and performance of vegetable-tanned leather is nowhere near that of chrome-tanned leather. The vegetable tannins are usually used in combination with other tanning agents, e.g., tannin + metals salts, syntan + metal salts, or tannin + syntan. The production of vegetable-tanned leather takes a long time, and the strength, stability, and durability of the leather is inferior to that of chrome-tanned leather. Bacardit et al. showed that tannin extracted from Tara (*Caesalpinia spinosa*) fruits at a 9% level in combination with a maximum of 2% of naphthalene sulphonic can be used as a green tanning agent without using syntan [42].

### 6.2.2. Chrome tanning

The chrome-tanning method is the most popular tanning method and produces durable, high-performance leather. In the chrome tanning method, the delimed and dehaired hide/skin is soaked in a Cr(III) salt solution, preferably basic chromium sulphate (BCS) with a chemical formula of  $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$ , which is less toxic than the highly toxic hexavalent form of chromium. Carboxylic acids are used as a masking agent, which is used to suppress the formation of polychromium(III) chains, allowing slow penetration and binding to the collagen of the animal hides. The Cr (in terms of  $\text{Cr}_2\text{O}_3$ ) is applied at the level of 1.5% to 8%

on the weight of animal skin (ows) [43,44]. After the tanning process, sodium carbonate is added to the tanning bath to raise the pH to 3.8 to 4.0, the pH increase is accompanied by an increase in heating up to 40 °C, forming a strong bond with the collagen. The processed leather is called wet blue leather, and has 4% to 5% Cr. The key advantages of this method include quick and cheap tanning, as the tanning can be carried out within a day, and the developed colour is stable for the lifespan of products made with this type of leather. The chrome tanning process produces a softer and thinner leather than vegetable tanning. However, the chrome tanning process generates a considerable level of Cr pollution in the resulting effluent. Moreover, the produced leather does not look natural, and has a chemical smell. Cr tanned leather has become an important source of Cr allergy, which affects around 1% of the general population [45]. It is reported that in the case of tanning with chromium sulphate, conversion of Cr(III) to Cr(VI) takes place and the quantity of the Cr(VI) in effluent is increased with an increase in the chromium sulphate dosage [46-48], which is a known carcinogen [49,50]. Cr(III) is the dominant form released from chrome tanned leather. The amount released is sufficient to stimulate allergic reactions in some Cr allergic individuals when they are exposed repeatedly and can cause occupational allergic contact dermatitis [51]. It is reported that not only Cr(III) but also Cr(VI) showed similar allergic effects [52].

### *6.2.3. Synthetic tanning*

The synthetic tanning process is a chemical tanning process, which is faster than chrome tanning. In synthetic tanning, the hides/skins are treated with various synthetic polyphenols known as 'syntan', and the tanning process is known as wet white tanning. Syntans are sulphonated condensation products of aromatic and phenolic compounds with formaldehyde or other aldehydes that can react with amine groups of collagens. They are mainly used for

the re-tanning of leather. The first developed syntan was a condensation product of phenol sulphonic acid and formaldehyde. The development of syntans completely changed the leather tanning process. The degree of sulphonation affects the re-tanning performance of aromatic syntan. Molecular dynamic simulation studies of various aromatic phenolic syntans show that the degree of sulphonation of syntan was a major contributor to electrostatic interaction and hydrogen bonding in the syntan–water system, and greatly affected the aggregation and dispersion of syntans in aqueous solution [53]. The next development of the condensation product of urea phenol sulphonic acid formaldehyde resin (which forms covalent bonding cross-linking in skins) considerably improves the thermal stability and strength of leather with greater lightfastness, softness, and fullness without causing any yellowing [54]. However, these condensates contain unreacted phenolic compounds and formaldehyde, risking the liberation of toxic formaldehyde from the treated leather during its use. According to EN 15987, leather that has less than 1,000 ppm of metals been considered metal-free. The key aim of leather tanning is to increase the thermal stability of the skin to enable shaving. The leather tanned with syntans needs a heavy re-tanning treatment for the manufacturing of various products. Yu et al studied the tanning of leather with a syntan having active chlorine groups (SACG) synthesised by the condensation of cyanuric chloride with a phenol sulfonic acid condensation product, which showed good thermal stability [55].

#### *6.2.4. Tanning performance*

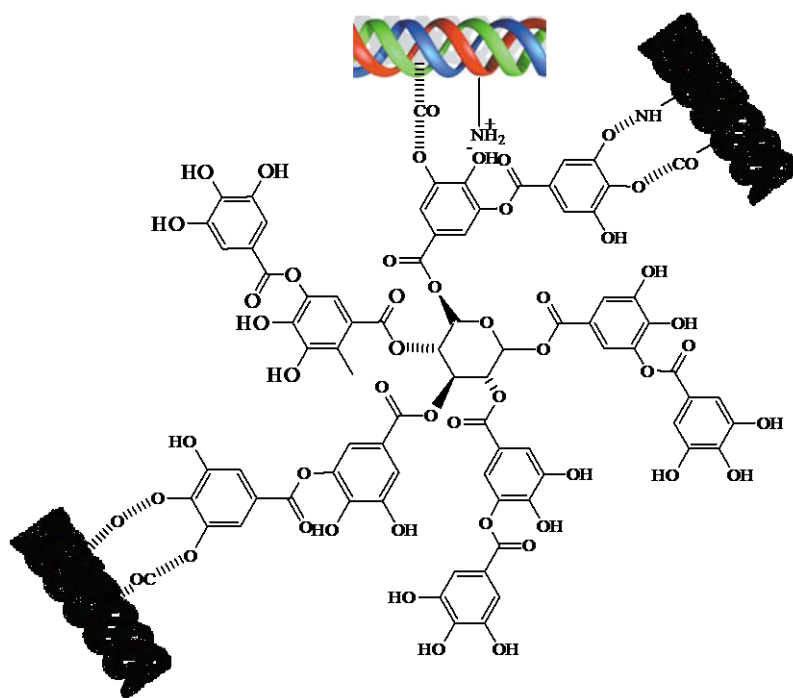
Table 1 shows the tanning performance of leather tanned by traditional processes. Before tanning, animal skin has very poor thermal stability and mechanical properties. Bovine skin shows higher thermal shrinkage temperature (54.8 °C) when compared to goatskin (40.1 °C) and sheepskin [56,57]. The tanning process greatly increases the shrinkage temperature of the



produced leather. Cowhides tanned with 8% Cr at pH 3.6 for 240 minutes increased the shrinkage temperature to  $110 \pm 1$  °C [43]. Goatskin tanned with 6% Cr at pH 3 for 420 minutes showed a shrinkage temperature of 92.4 °C [57] and for increased treatment time, Zhu et al found the shrinkage temperature was increased to 103.4 °C [48]. However, Suresh et al. found that the goatskin treated with 1.5% Cr at pH 2 increased thermal stability to  $120 \pm 2$  °C [44], when more than 80 °C is good enough for various applications, such as manufacturing of footwear and fashion accessories.

Tanning with vegetable and sytan tanning agents alone does not provide an acceptable level of thermal stability and mechanical properties. Goatskin leather tanned with pala indigo plant tannin at 8% Cr increased the shrinkage temperature to only 70 °C [39]. The sheepskin leather treated with 3% Cr *Xylocarpus granatum* bark tannin +3% Cr mimosa tannin exhibited considerably higher shrinkage temperature [40]. Like tannins, syntans alone are unable to provide an acceptable level of thermal stability and mechanical properties. A goatskin treated with a condensation product of phenol sulphonic acid/formaldehyde had a shrinkage temperature of 71 °C [54], but when treated with the sulphone sytan in combination with Al (aluminium), the thermal shrinkage temperature increased to 81 °C [58]. The basic aluminium sulphate (BAS) is the mostly used aluminium salt, which is prepared by masking aluminium sulphate  $[Al_2(SO_4)_3, 18H_2O]$  with sodium citrate and then basifying with sodium carbonate. The acorn tannin alone as a tanning agent only increase the shrinkage temperature to a certain level but in combination with a sytan increased it to 75 °C [30]. Cr based tanning is superior in terms of improvement in thermal stability, mechanical and organoleptic properties and protection against degradation. It is sometimes difficult to get plant-based tannins with consistent quality and expensive compared to the BCS. Similarly, syntans are expensive and many syntans have some level of toxicity, though they are not as toxic as Cr and are not carcinogenic. However, alone they have limited tanning ability and

are usually applied in the tannery as a re-tanning agent. Many commercially available formaldehyde condensate-based syntans release free formaldehyde ranging from 1,500 to 15,000 ppm [59].



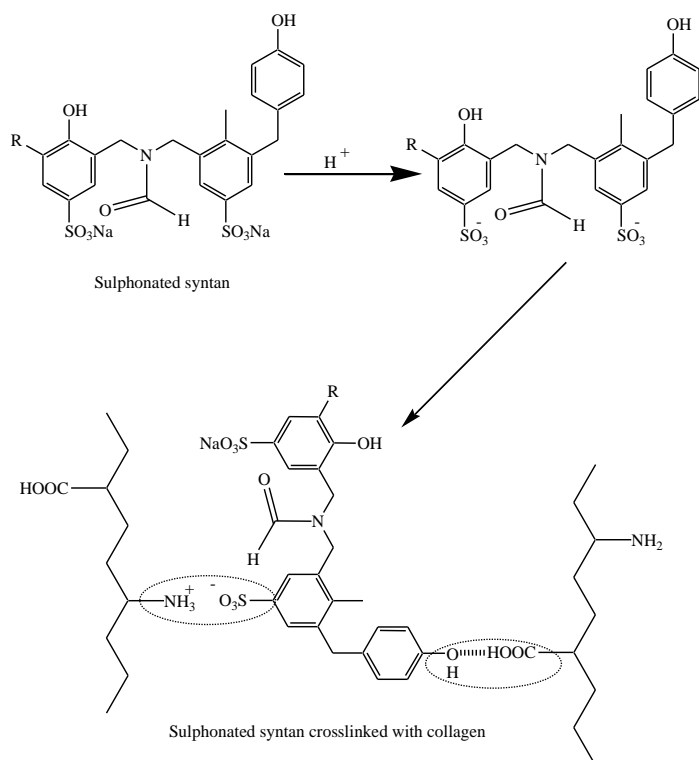
**Fig. 4.** Mechanisms of tanning of leather with natural tannins (polyphenols).

#### 6.2.5. Tanning mechanisms

The mechanism of tanning varies from tanning agent to tanning agent. Most of the tanning agents form crosslinked networks in the skins either by ionic or by covalent bond forming crosslinking. Tanning agents based on heavy metals including Cr, polyphenols, and syntans fall into the former category. The mechanisms of tanning with various heavy metals, such as Cr and Al, are shown in Fig. 4. The isoelectric point of collagen is 4.7 to 4.8 [60], below which the surface of the leather is cationic and above which the surface is anionic. Cr tanning is carried out at a quite low pH (2 to 3) to minimise the size of the polychromium complex

and also to minimise chromium substantivity towards collagen, resulting in uniform Cr adsorption into leather, as Cr has low substantivity under those conditions. The metallic ions ionically bind to the opposite ionic moieties of collagen. For example, cationic Cr binds to carboxylic groups of amino acids of collagen, and the nitrogen of amino groups of collagen forms ligands with Cr, combinedly forming a metal complex with amino acids of collagen. Metallic ions are very small, allowing them good penetration into collagen fibres which provides high tanning performance and excellent durability to washing.

Another popular tanning agent is vegetable tannin (natural polyphenols). The mechanism of tanning with natural polyphenols is shown in Fig. 4. Natural polyphenols (e.g., tara and mimosa tannins) have plenty of phenolic groups that make them weakly anionic, and tanning is carried out at pH 3 to 4 as they are attracted to the cationic amino groups of collagens. The weakly anionic phenolic groups form ionic bonding with the amino groups and hydrogen bonding with the carboxyl groups of collagens. The molecular weight of tannin is a few hundred to a few thousand, allowing absorption into collagen fibres.



**Fig. 5.** Mechanism of tanning of leather with sulphonated syntans.

The molecular weight of syntans is much smaller than the molecular weight of polyphenols, and therefore they can be more readily absorbed and diffused into collagen fibres than tannins. Earlier syntans had only phenolic groups and their tanning mechanism was like tanning with vegetable tannins. Newer sulphonated syntans also have sulphonate groups that are strongly anionic, enabling the formation of strong ionic bonding with the amino groups of collagens. The mechanism of tanning with syntans is shown in Fig. 5.

## 7. Improved traditional tanning processes to tackle environmental issues

Chrome tanning produces effluent containing toxic Cr(III). Vegetable and syntan tanning also produce effluent containing toxic heavy metals that are used for improving the durability of tanning to washing. To decrease environmental impacts and enhance the sustainability of traditional tanning processes, various novel methods have been developed recently. The methods are described briefly below:

### *7.1. Improved chrome-tanning methods*

#### *7.1.1. Reduction of Cr requirement*

As more than 90% of the leather is processed using the Cr-tanning method, initial emphasis was given to the reduction of the Cr requirement for tanning by partially replacing it with metal ions, such as iron (Fe), aluminium (Al), and zirconium (Zr) [61]. Zeolite was added to the Cr tanning bath to increase the Cr uptake, reduce the Cr requirement to achieve satisfactory tanning performance, and to reduce chrome loading in the effluent [62].

It was found that in the case of a 100% aqueous tanning system, intraparticle diffusion is the rate-limiting step and additives are used to overcome that issue. A range of additives, such as leather trimming protein hydrolysate [63], dispersion of poly butyl acrylate nanoparticles [43], amphoteric vinyl polymer/ZnO nanocomposites [64], amphoteric vinyl polymer/montmorillonite nanocomposites [65], carboxyl-terminated hyperbranched polyester oligomer [66], amino-terminated hyper-branched polyamide [67], epoxy-terminated hyperbranched poly-(amine-ester) materials or EHBP [68, 69], and hydroxyl-terminated dendrimer [70] have been studied to increase the adsorption of Cr. Some of these additives considerably increased the leather's Cr uptake. Instead of direct Cr salt, Cr(III) loaded nanoparticles formed by self-assembly of poly [poly (ethylene glycol) methyl ether acrylate-

co-acrylic acid-co-glycidyl methacrylate (PEGMA-co-AA-co-GMA)] terpolymers were also studied as a tanning agent [48]. A protein-based polymeric syntan derived from leather waste was applied as a tanning bath additive, which increased chrome exhaustion, belly-filling, fullness, softness, and dye exhaustion in the post-tanning process [71].

### *7.1.2. Improvement of Cr adsorption by ultrasound and microwave irradiation*

Other than tanning bath additives to increase Cr exhaustion in leather, Cr treatment under sonication has also been studied [72]. Chrome tanning under sonication increased the chrome uptake and the shrinkage temperature of the processed leather and decreased elongation, with little effect on tearing strength compared to the control. Mäntysalo et al. also achieved similar results for cowhides treated with Cr under sonication [73]. Sonication accelerates the transport of Cr ions from the bath to the leather. The application of ultrasound to increase the adsorption and Cr uptake considerably increased the Cr adsorption and also improved the shrinkage temperature of the processed leather compared to the Cr tanning without sonication. Few European leather industries have adopted sonicated Cr-tanning technology.

Microwave treatment was also studied to increase the Cr uptake by leather [74]. However, the installation of ultrasonic transducers and microwave energy sources in the existing tanning drum is cumbersome, needs additional energy input, and modifications of existing machinery and the benefits that can be achieved are marginal compared to the overall cost, which limits industrial implementation.

### *7.1.3. Waterless solvent-based chrome tanning*

All of the above-mentioned chrome-tanning processes produce effluent containing toxic Cr compound, which still needs treatment to discharge into watercourses. The uptake of Cr in the traditional chrome-tanning process is about 60–70%. The remaining 30–40% of unfixed Cr remains in the effluent [62]. Moreover, leather manufacturing by chrome tanning is water-intensive, as 35–40 m<sup>3</sup> of water is consumed for the processing of 1 ton of raw hides/skins [75]. To overcome the production of effluent, the aqueous medium was replaced with solvents including eutectic solvents and subcritical carbon dioxide. It was reported that the addition of propylene carbonate to the chrome tanning bath considerably enhanced the chrome uptake [76]. Chrome tanning using an organic solvent provided complete exhaustion of the tanning baths, along with much higher Cr binding compared to the traditional aqueous chrome-tanning method [77,78]. Chrome tanning in ethanol provided almost 87% and 95% chrome uptake for the pickled and non-pickled skin, considerably higher than aqueous tanning [79]. It was reported that the chrome uptake reached almost 100% when the water was fully replaced with propylene carbonate. The process also eliminated the need for a preservative, as the solvent itself has antimicrobial properties [80,81]. The Cr adsorption in 100% propylene carbonate followed the pseudo-second-order kinetic. It was found that for 100% replacement of water with propylene carbonate, surface sorption was a rate-limiting step.

As some of the solvents studied for chrome tanning are harmful or highly flammable, eco-friendly alternatives have been sought. In this regard, supercritical carbon dioxide (SCCO<sub>2</sub>) was found as a viable alternative. It was found that the chrome-tanning in subcritical carbon dioxide halved the requirement of Cr compared to the conventional tanning process due to enhanced chrome uptake [82,83]. Abbott et al. showed that chrome-tanning carried out in deep eutectic solvents comprised of a 1:2 molar ratio of choline chloride and ethylene glycol accelerated chrome uptake with enhanced flexibility and the processed leather showed better

ductility compared to the leather chrome-tanned in an aqueous medium [84]. The use of the eutectic solvent also allowed the transportation of a hydrophobic lysochromic dye throughout the cross-section of the leather and prevented leaching the dye into the aqueous wash solution. The Cr and sulphate concentrations in the generated effluent were highly reduced resulting in improved sustainability. The SCCO<sub>2</sub>-based chrome-tanned when washed or further processed, some of the surface-bound Cr are leached and contaminate the effluent.

However, Cr-tanned leather shows extremely poor biodegradability compared to vegetable-tanned leather. Moreover, the Cr-treated leather produced by the improved process still has Cr which could potentially release when they are disposed of in the environment. Therefore, Cr-free tanning could be the best eco-friendly sustainable process.

#### *7.1.4. Chrome tanning with resins*

The reduction of Cr consumption was also studied by using Cr tanning in combination with tannin [40], syntan [44], crosslinking agents (e.g., oxazolidone) [85], and various resins including carboxyl-functionalised epoxy resins [86], acrylic resin with montmorillonite [87] and Si nanoparticles modified with PMMA [88]. The hydrothermal stability and tensile strength of leather tanned by carboxyl-functionalised epoxy resin with 3% chrome were similar to or better than those of the leather produced by conventional chrome tanning with 8% chrome, suggesting that the requirement of Cr to achieve an acceptable level of tanning performance can be achieved by using other resins. Recently, synthesis of a novel Cr complex was reported for the pickle and basification-free single pot chromium tanning of leather. The authors claimed that by using the new Cr-complex, they managed to increase the Cr adsorption by leather to 99% [89].



### *7.1.6. Tanning performance*

Table 2 shows the tanning performance of leather tanned with various improved chrome-tanning methods. 5.7% Cr in combination with 3% zeolite increased the shrinkage temperature of sheepskin leather to 105 °C along with a substantial increase in tensile and tearing strength and a decrease in elongation [59]. Cowhides treated with 1.5% Cr in combination with 0.66% Fe increased the shrinkage temperature to 107 °C and even with 1.1% Cr, 0.77% Al, and 0.33% Fe showed a shrinkage temperature of 101 °C [90]. The results show that the required dosage of Cr can be substantially reduced by adding other metal ions and zeolites.

Muñoz et al. hydrolysed chrome tanned scrap leather at 95 °C under highly acidic conditions until all leather scraps were dissolved, which was used for the sustainable tanning of leather [91]. The addition of a raw trimming leather waste-derived product (TLWP) at the level of 6% to the tanning bath showed Cr exhaustion at the level of 93% and the processed leather showed a high shrinkage temperature, which was more than 100 °C [63]. Suresh et al. prepared Cr and polymeric syntan complex, which was used for the tanning of goat leather, and improved chrome uptake to 90% [44]. Ma et al. studied the polycarboxylate/montmorillonite nanocomposite as a Cr-tanning bath additive that increased the Cr uptake and reduced the Cr loading in the effluent from 2302 mg/l to 131 mg/l [92]. The treatment also elevated the shrinkage temperature to above 100 °C along with increased tensile strength, tearing strength, elongation at breaking point and organoleptic properties. Of the additives studied to increase the Cr uptake and reduce the requirement of Cr to achieve an acceptable level of tanning performance, dispersion of poly butyl acrylate nanoparticle and amphoteric vinyl-polymer/ZnO nanocomposite showed the best results, as the shrinkage temperature of the processed leather increased to 126±1.2 °C [42]. Amino-terminated hyperbranched polyamide was added to the chrome-tanning bath, which increased the chrome

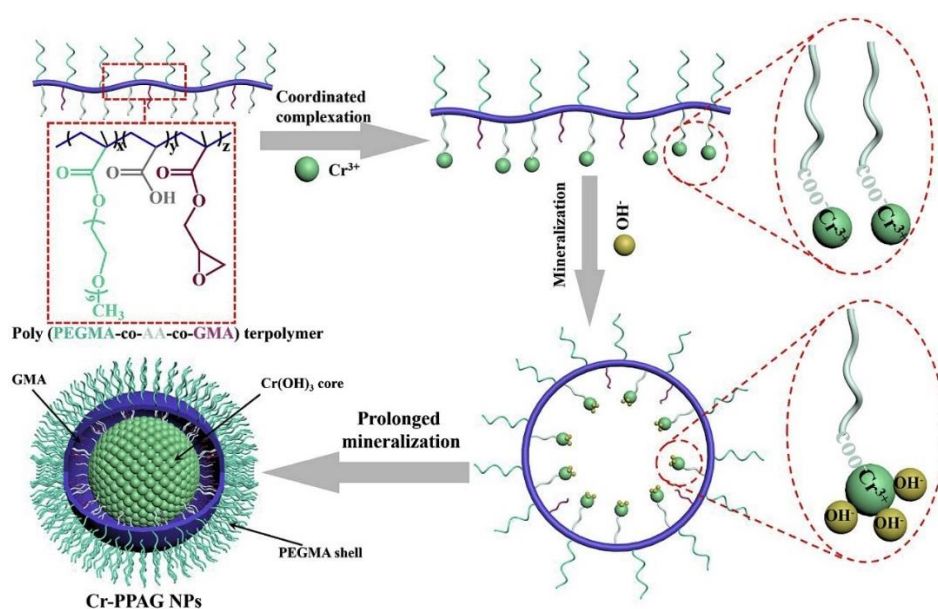
uptake to 83.3% with improved hydrothermal stability [65]. Cr-loaded poly [poly(ethylene glycol) methyl ether acrylate-co-acrylic acid] or poly(PEG-co-AA) copolymer nanoparticles also were used as a tanning agent, resulting in Cr adsorption efficiency in leather higher than 90% and less Cr discharge in wastewater [93]. Leather tanned with acrylic resin/montmorillonite (AR/MMT) nanocomposite in combination with 2% Cr provided wet-heat resistance and tensile, slit and burst strength similar to that of the leather tanned with 8% Cr by the traditional process [85].

Zhang et al. carried out tanning of leather in 20% Cr sulphate solution for 6 minutes followed by a 5 min microwave treatment at 40 °C, which increased the shrinkage temperature of the processed leather to 103.8 °C and slightly increased the tensile strength compared to the traditional chrome tanning, probably due to the better Cr diffusion into leather [72]. Cr tanning in solvents (e.g., propylene carbonate) including deep eutectic solvents and supercritical carbon dioxide medium has also been studied. However, the tanned leather showed lower thermal stability compared to Cr tanning carried out in an aqueous medium. Cowhide Cr tanned with urea/ $\text{KCr}(\text{SO}_4)_2 \cdot 10\text{H}_2\text{O}$  deep eutectic solvent, showed a shrinkage temperature of 80 °C – quite poor compared to Cr tanning carried out in the presence of various additives mentioned earlier [83].

A goatskin tanned with 2% Cr followed by crosslinked with 7% oxazolidine had a shrinkage temperature of 106.7 °C with increased tensile and tearing strength [83]. However, goatskin tanned with 1.5% Cr and 1.5% syntan had a very high shrinkage temperature ( $118 \pm 2$  °C) [44]. The results show that the Cr requirement can be substantially lowered by the inclusion of Cr bath additives and also by post Cr tanning crosslinking with syntans and other crosslinking agents.

### 7.1.7. Tanning mechanism

The tanning mechanism of improved Cr tanning is similar to tanning with Cr, but with modified Cr nanoparticles, the tanning mechanism is different from ordinary Cr tanning. Fig. 6 shows the mechanism of tanning of leather with core-shell Cr/poly (PEGMA-co-AA-co-GMA) nanoparticles. Due to the core-shell structure, the terpolymer shell protects  $\text{Cr}^{3+}$  from reacting with skin collagen during the penetration process, leading to increased and uniform delivery of  $\text{Cr}^{3+}$  to the raw hide's interior. When  $\text{Cr}^{3+}$  ions are released from Cr-nanoparticles, they can bind to the carboxyl groups of skin collagen and poly (PEGMA-co-AA-co-GMA).



**Fig. 6.** Schematic illustration of leather tanning process with Cr-nanoparticles modified with poly (PEGMA-co-AA-co-GMA) terpolymer [48].

## 7.2. Improved vegetable-tanning methods

### 7.2.1. Vegetable tannin in combination with non-toxic metals and polymers

As vegetable-tanned leather has low durability compared to chrome-tanned leather, vegetable tannin in combination with various metals has been studied to improve durability and other performances. The studied vegetable tannin combinations may include BAS + vegetable tannin [94,95], phenolic syntan + Wattle tannin + myrobalan tannin + Al-syntan + protein syntan [92], BAS + zinc sulphate (ZS) + sodium citrate (SC) [96], BAS + synthetic clay nanoplatelets (Laponite) and active aluminium salts [97], BAS + zinc sulphate (ZS) + sodium citrate (SC) + syntan and BAS/ZnS + SC + sodium tartrate (ST) + phthalic acid (PA) + syntan [93], BAS + henna tannin [98] and BAS + Tara tannin [36].

### *7.2.2. Sonicated tanning*

Vegetable tannins are quite large molecules which reduces their absorption by leather and diffusion into the leather, leaving a large quantity of tannin in the spent dyebath. Due to the strong substantivity of tannin towards protein, they agglomerate on the leather surface resulting in decreased diffusion of tannin into leather. Ultrasound was found effective in the disintegration of organic dye compound aggregations, enhancing their transfer and diffusion into fibres [99]. The ultrasound was also studied to enhance the tannin diffusion into the leather by disintegrating the tannin agglomerates formed on the surface of leather, enhancing tannin uptake and grain quality, and reducing the requirement of tannin dosage [100].

### *7.2.3. Zero-effluent tanning with tannin*

A zero-effluent tanning treatment is always preferable to overcome the issue of effluent disposal. SCCO<sub>2</sub> is the only zero-effluent vegetable tanning process that has been studied, as tannin has low solubility in many solvents. The SCCO<sub>2</sub>-based tanning with tannin not only improved tannin uptake but also improved the thermal stability of the tanned collagen

because of the better diffusion of tannin into the leather, as the tanning in this process is carried out under high pressure [101]. Onem et al. reported SCCO<sub>2</sub>-based vegetable tanning of leather with acorn tannin with an 8 h treatment showed 83.8% uptake [102], which is considerably higher than that of aqueous tanning. Recently, Pradeep et al. developed a chrome-free waterless tanning process with vegetable tannins and aluminium, which conferred high dimensional stability and improved dyeability to goatskin leather [103]. The solvent-based extraction of tannin and tanning in ethanol improved the thermal stability of the tanned collagen at the microscopic rat tail tendon and macroscopic leather level [104].

#### 7.2.4. Tanning performance

Table 3 shows the tanning performance of various types of leather tanned by a range of improved vegetable tanning methods. Tannin and syntan in combination with multivalent heavy metal ions and/or a second tannin, provided tanning performance comparable to Cr-tanned leather. Syntan in combination with Al/Zn and sodium citrate (SC) showed good tanning ability as the tanned goatskin had a shrinkage temperature of  $91 \pm 2$  °C [96]. The goatskin tanned with wattle tannin in combination with myrobalan tannin and Al had a shrinkage temperature of 94 °C along with increased tensile and tearing strength [94,95]. Syntan in combination with Al/Zn, SC, sodium tartrate (ST) and phthalic acid (PA) also provided a similar shrinkage temperature to goatskin, but tensile strength was inferior to that of goatskin treated with BAS + ZS + SC + syntan [96]. Goatskin treated with henna (*Lawsonia inermis*) leaves tannin at 20% ows in combination with BAS exhibited the shrinkage temperature of  $97 \pm 1$  °C along with increased tensile and tearing strength [98].

Ultrasound-assisted vegetable tanning of buffalo pelt with wattle tannin alone also showed an acceptable tanning performance as the shrinkage temperature of the tanned leather was 85

°C [105], but the effect of such tanning on the mechanical properties of the leather was not studied. Vegetable tanning in SCCO<sub>2</sub> was also studied as a zero-effluent tanning treatment without any additives or with Al. The pickled sheepskin treated with 15% ows valonea tannin for 120 min at pH 4.5 and 32 °C under 100 bar pressure showed poor thermal stability as the shrinkage temperature only increased to 69.5 °C [102]. However, the increase in CO<sub>2</sub> pressure and time increased the tannin absorption and also increased the shrinkage temperature to 74.5 °C. Pradeep et al. treated goatskin in 20% wattle tannin and 1.5% Al dissolved in SCCO<sub>2</sub> for 120 minutes at pH 3.8 and 25 °C, which increased the shrinkage temperature of the treated leather to 84 °C and tensile strength to 29 MPa [103]. Although tanning in SCCO<sub>2</sub> is effluent-free, installing the necessary high-pressure machinery requires major capital investment, and performance is inferior to other Cr-free tanning methods.

## **8. Sustainable and eco-friendly chrome-free tanning processes**

Various sustainable Cr-free tanning agents including crosslinking agents, reactive polymers and non-toxic metals in combination with tannins and syntans, metallic and silica nanoparticles and various chemical compounds have been investigated recently to overcome the performance and environmental issues of traditional tanning methods. They are as follows:

### *8.1. Tanning by crosslinking*

Various types of reactive crosslinking agents, such as aldehydes, oxazolidine, tetrakis hydroxymethyl phosphonium sulphate (THPS), and dialdehyde polymers (e.g., starch aldehydes) that form covalent bonds between macromolecular chains of collagen and between collagen fibres have been studied for tanning of leathers.

### *8.1.1. Tanning by crosslinking with reactive crosslinking agents*

Aldehydes, oxazolidines, and THPS are the primary crosslinking agents studied as a tanning agent for replacing the toxic chrome tanning agent [106-108]. The mostly used dialdehydes are glutaraldehyde [109], and glyoxal [110] but they are not used alone and are usually used with another tanning agent. The dialdehydes are crosslinking agents that are known to readily react with amino groups of collagen, and thereby improve the functional properties of leather, such as improving thermal stability and strength, along with reducing water absorption.

Oxazolidines are popular tanning agents studied for the tannage of leather [111]. In acidic conditions, oxazolidine undergoes a ring-opening reaction caused by hydrolysis and produces an intermediate with two N-(hydroxymethyl) groups. The subsequent nucleophilic attack of the amino groups of collagen by this intermediate product causing formation of covalent bonds. Oxazolidine derivatives, such as (3,5-dimethyl-1*H*,3*H*,5*H*-oxazolo[3,4-*c*]oxazol-7*a*(7*H*)-yl) methanol, in combination with polyallylamine, have been studied as an alternative to toxic tanning agents [112]. The tanned leather had good fullness, softness, smoothness, colour and general appearance compared to leather tanned with glutaraldehyde alone. A novel combination of tanning using dihydroxynaphthalenes (DHNs) and oxazolidine was studied for imparting high stability to leather [113]. The hydrodynamic shrinkage temperature changed very little, but a covalent bonding formed between DHNs and collagen through oxazolidine.

Other than oxazolidine, its dialdehyde version was also studied for leather tanning [114], which is obtained by reacting amino-hydroxy compounds with formaldehyde. As aldehydes do not have any ionic groups, they cannot be adsorbed into collagen readily by electrostatic attraction, resulting in very poor adsorption into collagen and producing inferior

performance. Moreover, aldehyde tanning agents are not only biotoxic, but also poorly soluble in water, have colour, they are costly [115] and formaldehyde, which is classed as a Class 3 carcinogen, is released from the treated leather [116]. It was also reported that formaldehyde is released not only from aldehyde-tanned leather, but also from tetrakis (hydroxymethyl) phosphonium-tanned leather [117]. Other than aldehydes, pre-condensates of urea-formaldehyde and melamine-formaldehyde also have been studied as chrome-free tanning agents [118]. To improve the adsorption of aldehyde by leather, sulphonated urea-formaldehyde was developed and applied in combination with vegetable tannins of chestnut or mimosa that improved the shrinkage temperature of the treated leather to that of chrome-tanned leather, along with achieving good colour stability [119]. It was reported that the re-tanning of aldehyde-treated leather with polyacrylic acid and non-ionic Gemini polyurethane surfactant considerably reduced formaldehyde release from the treated leather [120]. The ligands studied in combination with metallic ions were N-hydroxysuccinimide [121] and biomass-derived hydroxycarboxylic acid (BHCA) + ZrS [122]. In the case of BHCA, the leather was re-tanned with 2% neutralisation syntan, 3% acrylic resin, 1% melamine resin, 2% dicyandiamide (DCD) resin, and 5% mimosa tannin. The resins studied in combination with metallic ions may include biomass-derived aldehyde (BAT) with an acrylic resin [123] and an epoxy-terminated hyperbranched poly(amine-ester) or E-t-HPAE prepared by reacting with epichlorohydrin [124]. THPS in combination with a sulphonic syntan (Tanicor KW) followed by re-tanning with a biopolymer resin or BPR (Tergotan EF, THPS and BAS [125], and amine-functionalised octa(aminopropylsilsesquioxane) or POSS-NH<sub>2</sub> in combination with THPS [126] were also studied as tanning agents.

### *8.1.2. Tanning with polymers having multi aldehyde groups*



The studied aldehyde polymers may include soybean polysaccharide dialdehyde [127], carboxymethyl cellulose dialdehyde (CMC-D) [128], waste paper cellulose dialdehyde (WPCD) [129], biomass-derived polyaldehyde (BPA), alone and with low molecular weight chitosan (LMC)[130], Tara gum dialdehyde [49], starch dialdehyde [49], Al-masked corn cob hemicellulose aldehyde (Al-m-CCA) [131], Al-masked microcrystalline cellulose aldehyde (Al-m-MCA) [132], Zr-masked hemicellulose dialdehyde Zr-m-HCD[133], sugarcane bagasse cellulose dialdehyde (SBCD) [134], ethylene glycol glycidyl ether grafted corn starch dialdehyde (CSD-g-EGDE) [135], epichlorohydrin modified hydroxyl-terminated hyperbranched poly-(amine-ester) or EH-PAE-OH [136], copolymer of polyhedral oligomeric silsesquioxane and methacrylic acid/aluminium sulphate or P(POSS)-MAA)-AS [57], polyethylene glycol triazine (TA-d-PEG) [137] and corn starch dialdehyde [138,139]. In most of the cases, these aldehyde-containing reactive polymers were studied along with other tanning agents to provide better tanning performance, as alone their tanning ability is just average, and poor compared to the chemical crosslinking agents. For example, leather tanned by Zr/oxidised starch complexes as ligands presented considerably better physical and organoleptic properties than those of traditional Zr-tanned leather [140]. Aldehyde groups are introduced in various biobased polymers mainly by periodate or peroxide-based oxidation treatments to use as a tanning agent. Jiang et al. produced Al-m-CCA [131] and Al-m-MCA [132] containing aldehyde and carboxyl groups from corn cob hemicellulose and microcrystalline cellulose respectively by microwave irradiation-based hydrothermal reaction in the presence of AlCl<sub>3</sub> catalyst followed by peroxide oxidation. Tanning of leather with this Al-m-CHA in combination with zirconium sulphate (ZrS) considerably improved tanning performance and other physicomechanical properties. Dialdehyde groups were introduced in carboxymethyl cellulose by oxidation to apply as a tanning agent to improve the shrinkage temperature, fullness, and organoleptic properties of hides/skins, but the production of toxic

formaldehyde was detected. Starch dialdehyde with aldehyde contents was prepared from native corn starch by sodium periodate oxidation and was used as a tanning agent [140], which provided excellent tanning ability. Lactic acid-based agents (LAAs) were studied as tanning agents, but the tanning ability was not comparable to the chrome-tanned leather reaction [141].

### *8.1.3. Tanning performance*

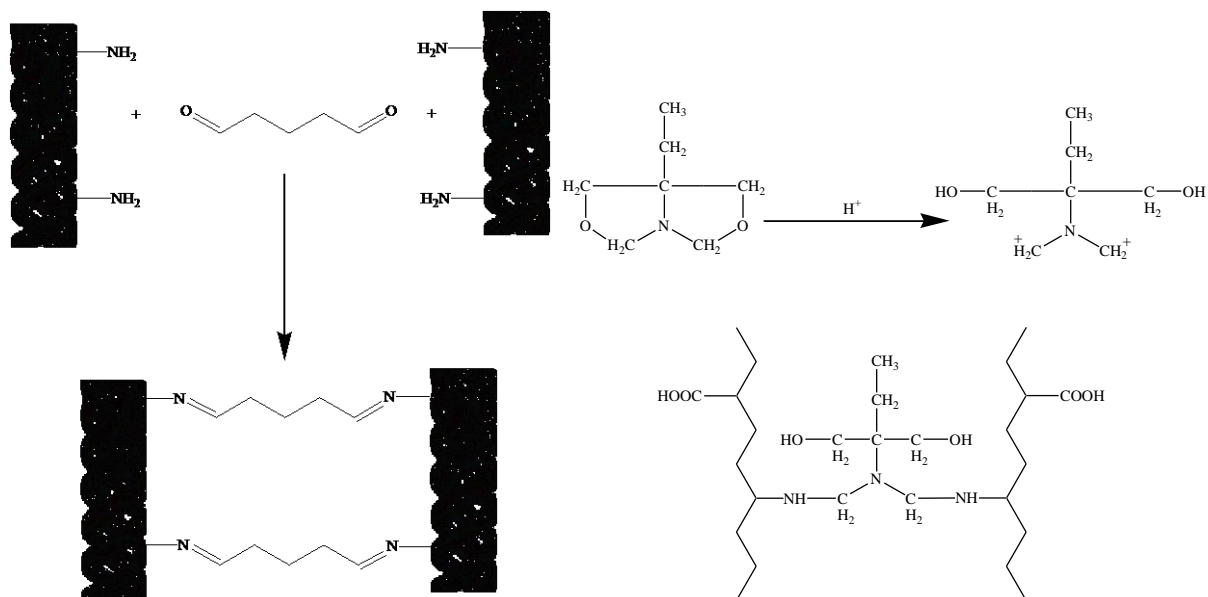
The tanning performance of leather tanned with crosslinking agents and dialdehyde-containing polymers is presented in Table 4. Tanning with 6% glyoxal at pH 5.0 increased the shrinkage temperature of the processed leather to 82 °C, along with a 40% increase in thickness [110]. The two-stage treatment of goatskin crosslinked with 2.5% ows glutaraldehyde, followed by treatment with 2% ows syntan increased the shrinkage temperature of the tanned leather to 85 °C and enhanced the fullness but showed poor grain characteristics [106]. Goatskin crosslinked with 2.0% ows glutaraldehyde followed by treatment with 12% ows tara tannin increased the shrinkage temperature of the tanned leather to 92±1 °C [32]. Similarly, cowhides treated with tara tannin, aluminium, and syntan, and then crosslinked with glutaraldehyde showed excellent thermal stability with shrink resistance of 103 °C [142]. The tanning ability of oxazolidine is like glutaraldehyde tanning. Leather tanned with glutaraldehyde, mimosa tannin and oxazolidine showed similar shrinkage temperature improvement. The tanning treatment of leather with phenolic compounds derived from the oxidation of kraft-lignin (kraft-lig phenol) increased the shrinkage temperature of the treated leather to 80 °C [143]. Of the crosslinking tanning agents investigated, glutaraldehyde and D-Lysine in combination with syntan provided the best tanning performance. The de-pickled goatskin treated with 1% ows D-Lysine and 2%

ows glutaraldehyde followed by treatment with 4% ows syntan (Basyntan FB 6) had thermal stability similar to 8% ows Cr-tanned leather, and the shrinkage temperature increased from  $93 \pm 3$  °C to  $120 \pm 8$  °C along with increased tensile strength and decreased elongation [108], which is similar to the best Cr-tanned leather. It was reported that leather tanned with Tara tannin in combination with aluminium and glutaraldehyde showed improved shrinkage temperature, which was around 90 °C [32]. Leather tanned with 6% cage-like octa (aminosilsesquioxane) combined with 2.5% THPS had a shrinkage temperature of above 83 °C and a thickness rate of 44.6% [126]. 15% Tara tannin in combination with 5% aluminium sulphate and 20% syntan followed by crosslinking with 1% glutaraldehyde elevated the shrinkage temperature to more than 100 °C, offering excellent thermal stability [142]. Pickle-free semi-metal tanning employing aluminium, vegetable tannins and silica, followed by post-tanning using environmentally benign chemicals enhanced the shrinkage temperature of leather to 100 °C, along with decreased chemical oxygen demand (COD) and biological oxygen demand (BOD) of the produced effluent [144]. Chestnut or mimosa tannin combined with sulphonated melamine-urea-formaldehyde (SMUF) resin tannage in 50/50 and 75/25 weight ratios exhibited the best performance in improving shrinkage temperature and other physical properties of leather [119]. It was reported that 20% henna (*Lawsonia inermis*) tannin in combination with 1.5% THPS provided a shrinkage temperature of 96 °C [145]. The tanned leathers showed an opened-up, split compact fibre structure, suggesting no major change or destruction of the fibre structure of the leathers occurred, and also offered a considerable reduction in the discharge of total dissolved solids in the wastewater. Al and Zn in combination with sodium citrate, increased the shrinkage temperature of the processed leather to 91 °C, but Al/Zn with sodium citrate, sodium tartrate and phthalic acid provided the best tanning performance with a shrinkage temperature of 95 °C. A biomass-derived aldehyde (BAT) treated leather re-tanned with a cocktail of acrylic resin (AcR), amino resin

(AmR) and mimosa tannin then crosslinked with Al, exhibited good hydrothermal stability (shrinkage temperature of 88 °C), mechanical strengths, uniform colour, and comparable smooth grain surface [123]. Long-Fang et al. found that leather tanned with 2% THPS and 7% AlCl<sub>3</sub> followed by re-tanning with 6% Tergotan EF (a formaldehyde-modified biopolymer resin) exhibited shrinkage temperature of above 88 °C but degraded more easily compared to chrome-tanned leather [125]. However, the level of formaldehyde released from the treated leather was 57.5 mg/kg. Gao et al. also studied amine-functionalised octa (aminopropylsilsesquioxane) or POSS-NH<sub>2</sub> in combination with THPS [126]. The goatskin treated with 6% POSS-NH<sub>2</sub> and 2.5% THPS showed a shrinkage temperature of 83 °C, much better than the P(POSS-MAA)-AS treated goatskin [57]. Leather tanned with 8% EHBP followed by treatment with 6% aluminium tanning agent improved the hydrothermal stability of the resultant crust with enhanced dyeability and yellowing resistance [69]. Sheepskin collagen in combination with pomegranate polyphenols (PPP) was used as a tanning agent, which improved the thermal stability [146]. Fe(III)/N-hydroxysuccinimide ligand (Fe-NHS) was also studied as a tanning agent, and showed considerable improvement in shrinkage temperature and organoleptic properties [121]. Biomass-derived hydroxycarboxylic acid compound in combination with zirconium as a tanning agent provided remarkably better tanning performance than that of conventional lactic acid–zirconium complexes [123].

Polymeric crosslinking agents provided lower thermal stability and needed a higher quantity compared to the chemical crosslinking tanning agents. Ethylene glycol glycidyl ether (EGDE) was grafted onto dialdehyde corn starch (SD-g-EGDE) and was applied to leather as a tanning agent, which increased the shrinkage temperature (85.2 °C), mechanical properties, and whiteness of the leather [135]. Liu et al. prepared epichlorohydrin modified hydroxyl-terminated hyperbranched poly-(amine-ester) or EH-PAE-OH and applied it as a tanning agent, which increased the porosity of the leather, but the thermal shrinkage only increased to

75 °C [136]. Water-soluble soybean polysaccharide dialdehyde (SPDA) prepared by oxidation of soybean polysaccharides as a tanning agent applied to leather resulted in improved mechanical properties and hydrothermal shrinkage temperature of 79 °C [147]. The leather produced by tanning with 4% ows Al-m-CCA in combination with 4% ows ZrS (in terms of ZrO<sub>2</sub>) and 4% ows Al-m-MCA in combination with 2% ows ZrS (in terms of ZrO<sub>2</sub>) increased the shrinkage temperature to 83.5 °C [131] and 85.5 °C [132] respectively. A novel tanning agent consisting of Al- oligosaccharides complexes produced via efficient AlCl<sub>3</sub>-catalysed cellulose depolymerisation [148]. The interaction between AlCl<sub>3</sub> and depolymerised cellulose prevented the overloading of Al species onto the leather surface, allowing their penetration into the leather matrix. When the active Al species were released from the Al-oligosaccharides complex, they strongly coordinated with the amino (-NH<sub>2</sub>) groups of the collagen fibres and thus contributed to achieving a satisfactory tanning performance. Triazine derivatives of polyethylene glycol (TA-d-PEG) were studied as a chrome-free tanning agent for wet-white leather manufacturing, which increased the hydrodynamic shrinkage temperature to above 80 °C with no pickling treatment needed [137].



**Fig. 7.** Mechanism of leather tanning with glutaraldehyde (left) and oxazolidine (right) through cross-linking.

#### 8.1.4. Tanning mechanisms

The mechanism of leather tanning with all aldehydes is very similar. The reaction mechanism of glutaraldehyde is shown in Fig. 7 as an example of leather tanning with aldehydes. The aldehydes react only with the amino groups of collagens, blocking some of the dyeing sites for leather, affecting its dyeability with acid and natural dyes. As these aldehydes are not ionic, they cannot be readily absorbed into collagen. Therefore, they are mostly used in combination with natural polyphenols to achieve high tanning performance.

#### 8.2. Tanning with nontoxic metals, zeolites, nanoparticles, and chemical compounds

### *8.2.1. Tanning with non-toxic metals*

Other than Cr, non-toxic metal ions such as aluminium [149], iron [150,151], and titanium [152] salts were studied as tanning agents for leather. After Cr, aluminium salts are the most studied metal salts as a tanning agent for leather, but they are ineffective on their own. Al salts are thus usually used with other metal salts, including Cr, zirconium, titanium, and also with vegetable tannin, in which case Al salts are used as a binder (mordanting agent) between collagen and tannin. Like aluminium, iron salts are not used alone, but with Cr to reduce the demand for Cr for effective tanning [153,154]. Titanyl sulphate masked with citrate was investigated as a tanning agent to produce high-quality bovine upper leather on a pilot scale, which showed comparable physical-mechanical properties to those of traditionally Cr-tanned leathers [155]. Aluminium (III)/titanium (IV) mixed complex with a salt of a polyhydroxymono-carboxylic acid as a masking compound was also studied as a tanning agent [156]. Peng et al. studied ultrasound-assisted tanning of leather with titanium to increase its exhaustion into pig skin, which provided hydrothermal stability similar to Cr-tanned leather [157].

### *8.2.2. Tanning with zeolites*

Zeolite is a porous hydrated aluminosilicate mineral that has alkali and alkaline-earth metals containing various cations ( $\text{Al}^{+++}$ ,  $\text{Ca}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and other anions), which makes them cationic. The particle size of zeolites varies from 20 nm to a few microns [158]; for better penetration into leather, they need to be as small as possible. Karaman and Gülümser also studied the tanning of leather with aluminosilicate, a type of zeolite, alone and in combination with aluminium triformate, which increased the shrinkage temperature, tensile strength, and decreased elongation to 75 °C and 82 °C, 15.5-20.5 MPA and 17-21.8 MPA, and 68-72% and 75-78%, respectively [159]. Recently, Netherland-based Smit & Zoon marketed a zeolite-

based leather tanning process (commercially known as the Nera tanning process) as chrome- and aldehyde-free leather tanning process [160]. Huang et al carried out self-driven directional dehydration of cattle skin using ethanol and zeolite, followed by treatment with 0.8% silica nanoparticles dispersed in ethanol and then treated with 10% polydimethylsiloxane, which increased the mechanical properties of the processed leather [161].

Non-toxic metals alone cannot offer the desired level of tanning performance and therefore they are used with other metallic and plant-based tannins as they change the inherent colour of the leather. Zeolite tanning produces white-coloured leather with improved strength and thermal stability, like chrome-tanned leather but with better biodegradability. In the case of tanning with zeolites, as they remain on the surface of collagen fibres in the treated leather, dyeing needs to be carried out before the treatment, otherwise, in the case of acid dyes, the dyes will remain on the surface of fibre, binding to the zeolite and causing ring dyeing, and may produce poor colourfastness when the leather is washed.

### 8.2.2. Tanning with various nanoparticles

In the development of a Cr-free tanning method for leather, various metallic and silica nanoparticles in combination with tannin or crosslinking agents have been explored as novel sustainable tanning agents [39]. The nanoparticles studied are *Wrightia tinctoria* tannin-induced silver (Ag) nanoparticles (Ag)[39], silica [162] and polyhedral oligomeric silsesquioxane (POSS) [57]. However, nanoparticles (NP) are not studied alone as a single tanning agent but are usually used in combination with other tanning agents. The NPs studied most frequently are Si NP and the combinations studied are BAS + wattle tannin + Si NP [144], Si NP + vegetable tannin [162], Si NP + octadecylsilane + vegetable tannin [162],



BAS+ silica NP (sodium metasilicate or SMS) + tannic acid (TA) followed by re-tanning with syntan [163], and BAS + SMS + THPS followed by re-tanning with syntan [164]. Silica nanoparticles prepared from tetraethyl silicate modified with poly(methacrylic acid) (PMA-m-Si NPs) were applied as a tanning agent [165].

### 8.2.3. *Enzymatic tanning*

Several enzymes including transglutaminase can work as protein crosslinkers and are capable of covalently crosslinking collagen molecules together. However, transglutaminase tanning does not improve the shrinkage temperature of native bovine hides, either when used in isolation or together with other proteins and bifunctional diamines as crosslinking facilitators [166]. However, Cheng and Chen found that pickled bovine hide tanned with 0.6% microbial transglutaminase (mTG) at pH 6.0 for 2 hours exhibited a shrinkage temperature above 80 °C compared to 54.8 °C exhibited by the control leather [56]. The pre-tanning treatment with 0.6% mTG, then post-tanned with 4% Cr sulphate at pH 1.5, increased the shrinkage temperature to 105 °C. Collighan et al. may have used the wrong pH conditions, which caused either the denaturation of the enzyme or affected the absorption of the enzyme into hides, resulting in no improvement in tanning ability as transglutaminase is a proven protein crosslinker [167].

### 8.2.4. *Tanning with various synthetic and bioderived resins/chemicals*

In the development of a Cr-free tanning method for leather, silicic acid alone or in combination with tannin has been explored as a novel sustainable tanning agent [168]. Interestingly, goatskin leather tanned with silicic acid exhibited better tanning performance and strength compared to leather tanned with silicic acid in combination with valonia tannin.

Various triazine compounds, such as N, N'-di-(4,6-dichloro-[1,3,5]-triazinyl)-2,6-diaminohexanoic acid, (L-Lys TCT)/2-(4,6-dichloro-[1,3,5]-triazinyl-2-amino)-3-[4-(4,6-dichloro-[1,3,5]-triazinyl-2-oxy)-phenyl]-propionic acid, and (L-Tyr TCT)/N, N'-di-(4,6-dichloro-[1,3,5]-triazinyl)-2-amino-5-guanidyl pentanoic acid, were used as tanning agents; the treated leather satisfied basic demands, and mechanical properties met the standard requirements for shoe uppers [169]. Other chrome-free tanning agents may include Al-masked hyperbranched PEG400 (polyethylene glycol of molecular weight 400)-melamine polymer (Al-m-HPEGM400) complexed with BAS [170], urea-formaldehyde (UFD), phenol-formaldehyde (PFD), and sulphonated phenol-formaldehyde (s-PFD) resins in combination with aluminium or titanium [171]. Fish oil was replaced with jatropha oil as a tanning agent to produce chamois leather that offered thermal shrinkage similar to the fish-oil treated leather [172].

Recently chrome-tanned leather waste was also studied as a possible tanning agent [173]. In this method, collagen polypeptide was extracted from chrome-tanned leather waste by enzymatic treatment with industrial trypsin and then it was modified with ethylene glycol diglycidyl ether. The modified collagen peptide (CP-EDGE) was studied for the tanning of pickling-free and salt-free tanning processes. The treated leather showed better thermal shrinkage temperature (84.9 °C), fullness, mechanical properties, softness, yellowing resistance and also amniotic fat liquor and dye absorption than most of the chrome-free tanning studied. Ding et al reported the preparation of cochineal carmine tanning agent by periodate oxidation, which was used as a tanning agent and a dye [174]. The brown-coloured leather showed meagre improvement in thermal shrinkage temperature (70 °C), which further increased to 80 °C after fat-liquoring treatment with an aluminium compound. Gao et al produced Al-oligosaccharide by microwave-assisted AlCl<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation, which produced aldehyde and carboxyl groups in the oligosaccharide. The tanning of leather with this

oligosaccharide with Al/Zr species enhanced the thermal shrinkage of leather from 70.4 to 91.6 °C and tearing strength up to 77.7 N/mm [175]. Wang et al reported that the tanning of leather with triglycidyl isocyanurate modified starch increased the thermal shrinkage temperature of leather to 84.2 °C [176]

#### *8.2.6. Tanning performance*

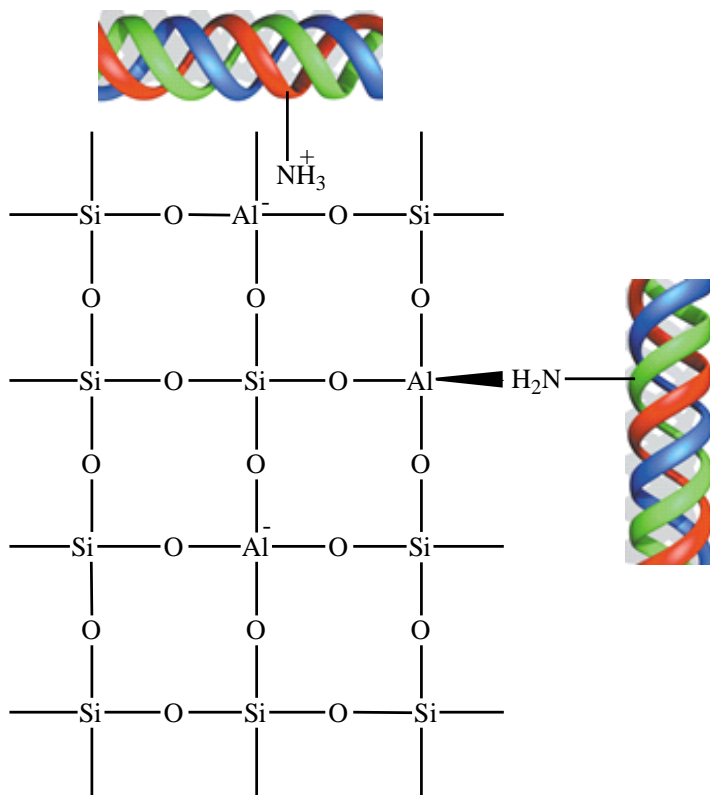
Table 5 shows the tanning performance of various types of leather treated with various non-toxic metals, zeolites, metallic and silica nanoparticles, enzymes and chemical compounds. Peng et al. reported that tanning goatskin leather with 7.5 ows (eqv. to TiO<sub>2</sub>) lactate-masked titanium sulphate (L-m-TS-1) increased the shrinkage temperature and tensile strength to 93 °C and 30.7 MPa, but the increase in titanium concentration to 10% ows increased the shrinkage temperature to 102 °C [152]. Bi et al. found that goatskin treated with 7% ows lactate-masked titanium sulphate (L-m-TS-2) increased the shrinkage temperature to 97 °C, with excellent improvement in softness [153]. The treated leather had better strength and fullness than the Cr-tanned leather and was superior to Al- and Zr-tanned leather. Not only metal salts but also titanium metal wastes were applied to bovine hides as a tanning agent, which increased the shrinkage temperature from 75.3 °C to 77.0 °C [154], which is only a small increase. To increase the exhaustion of titanium, ultrasound was studied for the titanium tanning of pig skin, and a shrinkage temperature of 105.6 °C was achieved [157].

Leather tanned with 7% ows zeolite in the presence of formic and oxalic acids and sodium hydrogen sulphate increased the hydrothermal stability to only 74.9 °C, which is poor compared to other Cr-free tanning studied [160]. Huang et al carried out self-driven directional dehydration of cattle skin using ethanol and zeolite, followed by treatment with 0.8% silica nanoparticles dispersed in ethanol and then treated with 10%

polydimethylsiloxane [161]. The shrinkage temperature increased to 86 °C and the organoleptic qualities and the strength of the leather tanned by this method were similar to those of chrome-tanned leather. The treatment uniformly dispersed the collagen fibres in the leather and increased the tensile strength to 24.56 MPa along with a decrease in the moisture content to 5.2%.

Raji et al used tannin-induced Ag nanoparticles as a tanning agent, which offered satisfactory tanning ability [39]. The silica nanoparticles modified with poly (methacrylic acid) provided the best results; the highest shrinkage temperature of the wet-white sheepskin reached 76 °C and the thickness increase reached 105%. Leathers tanned with nanosilica (2.3% ows) and vegetable tannin (45% ows) exhibited a shrinkage temperature and tensile strength of 76 °C and 27.2 MPa respectively; with the addition of octadecylsilane, these increased to 80 °C and 36.6 MPa respectively. The tannin level required to achieve an acceptable level of hydrothermal stability is very high, which would change the colour of the treated skin. Goatskin tanned with Si NP formed in the presence of wattle tannin and BAS increased the hydrothermal stability to 100 °C and the tensile strength to 27.2 MPa [144]. Goatskin tanned with 1.5% Al, 10% Si nanoparticles and 1% ows THPS exhibited a shrinkage temperature of 86 °C and tensile strength also increased to 26.8 MPa [164]. Leather tanned with PMMA-modified Si NP only showed a shrinkage temperature of 76 °C. Pickled cowskin treated with 0.6% ows mTG increased the thermal shrinkage temperature to an acceptable level (80 °C). Goatskin tanned with 10% ows silicic acid and 5% ows valonia tannin exhibited a shrinkage temperature and tensile strength of 83.0±0.8 °C and 16.2 MPa, whereas the same skin treated with 15% silicic acid alone exhibited a shrinkage temperature and tensile strength of 91.2±1.3 °C and 17.0 MPa [168]. Of the triazine compounds studied, L-Lys TCT provided the best results, as sheepskin tanned with it at 20% ows increased shrinkage temperature to 82.5 °C. Goatskin tanned and re-tanned with Al-m-HPEG400 at

18% ows increased the shrinkage temperature to 86.2 °C [170]. Of the non-toxic metals, zeolites, metallic and silica nanoparticles, enzymes, and various chemical compounds studied as tanning agents, L-m-TS, silicic acid, BAS + wattle tannin + Si NP, and s-PFD + Ti showed the best overall results in terms of improving tanning performance and mechanical properties of leather. L-m-TS and silicic acid could be the most cost-effective treatments but may not be the most durable.



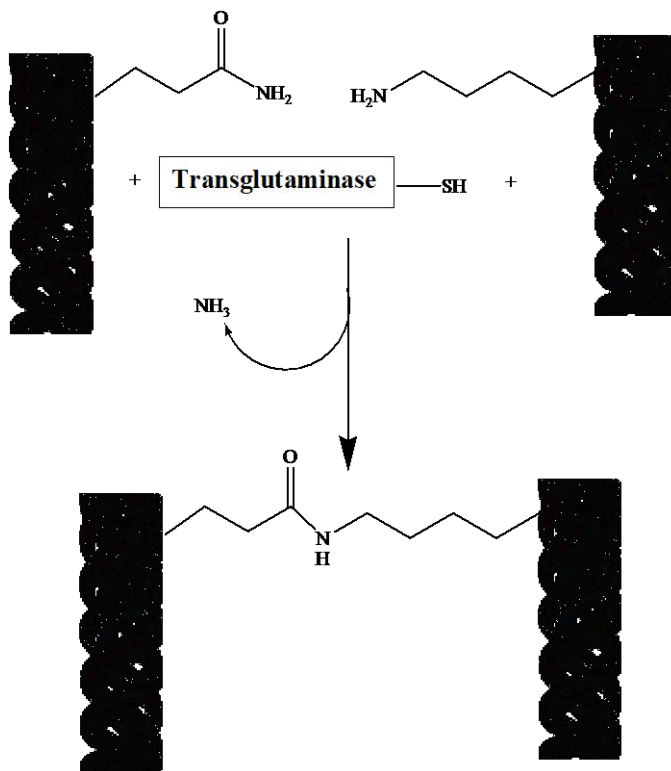
**Fig. 8.** Mechanisms of tanning of leather with zeolite.

### 8.2.7. Tanning mechanism

The mechanism of tanning leather with other non-toxic metals is the same as the Cr-tanning mechanism. However, the tanning mechanism of zeolites with leather is different,

and is shown in Fig. 8. Zeolites are anionic because of the introduction of aluminium salts in the silicone cage, which ionically binds to the cationic amino groups of leather collagen. The aluminium also can be conjugated with amino groups of leather collagen, providing high durability of the treatment to washing.

The mechanism of tanning of leather by transglutaminase crosslinking is shown in Fig. 9. Transglutaminases ( $\gamma$ -glutamyl-peptide, amine- $\gamma$ -glutamyl transferase) are calcium-dependent enzymes that catalyse acyl-transfer reactions between a  $\gamma$ -carboxyamine group of a collagen peptide and a primary amino group of another collagen peptide, including the  $\epsilon$ -amino group of lysine or lysyl residues in proteins.



**Fig. 9.** Mechanism of leather tanning by enzymatic crosslinking with transglutaminase.

## 9. Effect of tanning on the properties of leather

### *9.1. Effect on structural and other properties*

Different varieties of tanning agents are used in leather tanning depending on the desired properties and performance for specific applications. The tanning treatment permanently changes the protein structure of the animal skin. Sizeland et al. studied the effect of different tanning agents applied to leather on their various properties [177]. The studied tanning agents were Cr, zirconium, mimosa, oxazolidine or tetrakis hydroxymethyl phosphonium sulphate (THPS), or their combinations. The highest percentage of biodegradability was found for the metal-free leather sample (84%) compared to 45% and 80% of the chrome leather and wet-white leather samples [178].

The penetration and reaction of tanning agents in leather greatly influence tanning performance and leather quality [169]. Aldehyde tanning agents are widely used in leather manufacture, but their penetration and reaction in leather cannot be detected easily. Because aldehyde can form a fluorescent Schiff base with amino groups of collagens, the distribution and reactivity of typical aldehyde tanning agents in leather during the tanning process can be visualised using a fluorescence microscope. The results showed that glutaraldehyde in leather was easily observed under the fluorescein isothiocyanate (FITC) filter system. The fluorescence intensity of pelt/leather gradually increased with the penetrating of glutaraldehyde, basification, and heating, which was consistent with the formation of Schiff base and the increase in Ts of pelt/leather. Oxidised sodium alginate and dialdehyde sodium carboxymethyl cellulose in leathers were also detected using a fluorescence microscope, because the aldehyde group of the two tanning agents formed a fluorescent Schiff base with amino groups of collagens. The oxazolidine-tanned leather and the tetrakis hydroxymethyl phosphonium-tanned leather emitted little fluorescence as they crosslinked collagen with the hydroxymethyl group.

Kang et al. studied the effect of sweat on untanned and Cr, glutaraldehyde, and formaldehyde-tanned leathers by soaking them in artificial perspiration, which resulted in gradual decrease in shrinkage temperature of the leathers with time [179]. After 15 days' of soaking in artificial perspiration, the Cr and formaldehyde-tanned leather showed dry heat shrinkage ratio decreased from 46% to 35% and 43% to 35% respectively. The Cr and formaldehyde tanned cattlehide collagen fibres exhibited the best ability of sweat resistance in all the four samples studied.

### *9.2. Effect on biodegradability*

It is known that chrome-tanned leather takes years to degrade in the environment. European Directive 94/62 revealed that vegetable-tanned leather completely degrades in aerobic aquatic media in 100 days, but chrome-tanned leather only degrades to 30.2% during that time indicating the inhibition of biodegradation of leather by Cr [180]. Leather tanned with Ti-Al showed a higher rate of biodegradation than leather tanned with Ti-Zr and chrome-tanned leather [181].

## **10. Conclusion and future directions**

Alternatives to chrome tanning have been developed over the years, but none provide the tanning ability, dyeability, protection, mechanical and organoleptic properties at a reasonable cost that Cr tanning offers. Alternative metal and zeolite tanning produces wet white leather rather than the wet blue leather produced by chrome tanning. The increase in chrome exhaustion caused by adding various additives to the chrome tanning bath reduced chrome



content in the effluent, but does not eliminate Cr, and the effluent still requires further treatment for discharging them to local water streams. When Cr-tanned leathers are dumped into the environment they release Cr, contaminating the soil and aquatic environment. All heavy metals have some levels of toxicity; therefore, it would be wise to completely eliminate the use of any heavy metals in the tanning process. Leather tanned with vegetable tannin in combination with nano clay and aluminium sulphate or syntan and lactate-masked-titanium sulphate exhibited tanning performance similar to the chrome-tanned leather but may not provide similar durability. Enzymes and ionic biopolymers as tanning agents and zero-effluent energy-efficient tanning may have a future for the sustainable tanning of leather.

Most of the sustainable alternative chrome-free tanning treatments do not simultaneously offer high tanning performance with minimal effects on the dyeability and colourfastness properties of the leather at a price similar to Cr tanning. Further research is needed to develop a novel tanning process that is effective, sustainable, economically feasible, and does not affect the leather's dyeability and colourfastness properties. The future leather industry will need to be circular and sustainable for its future growth and to compete with future leather alternatives.

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**Table 1.**

Tanning performance of various types of leather tanned with traditional tanning agents.

Tanning agents	Type of leather	Dosage (% ows)/pH/Temperature (°C)/Time (min)	Hydrodynamic shrinkage temperature (°C)	Tensile strength (MPa)/Elongation (%)/Tearing strength (N/mm)	Thickness rate (%)	Reference
Control leather	Pickled bovine hide	-	54.8	-	-	56
Control leather	Pickled goatskin	-	40.1	15.5/27.3/39.0	41.2	57
<u>Chrome-tanning</u>						
Cr tanning with BCS	Wet salted cowhides	8/3.6-4.0/-/240	110±1	25.6±0.5/76±3/-	-	63
Cr tanning with BCS	Goatskin	1.5/2.0-3.0/-/150	120±2	29.4±1.2/57±6/65.7±2.9		44
Cr tanning with BCS	Pickled goatskin	6/3.0-4.0/25/420	92.4	21/32.2/49.9	65.8	57
Cr Tanning with BCS	Pickled sheep skin	6/3.0-4.0/-/660	103.4	12.9/100.8/30.6		48
Cr tanning with BCS	Sheepskin	6/2.5-3.0/25/240	102.2	13.3/15.0/49.6	47.0	55
<u>Vegetable tanning</u>						
Pala indigo plant tannin	Raw goatskin	8/-/-	70	45/19/48	-	39
<i>Xylocarpus granatum</i> bark tannin + mimosa tannin*	Pickled goatskin	3+3/3.8-4.0/25/450	86.3±1.5	29.2±1.4/42.5±2.1/38.2±4.5		40
<u>Tanning with syntans</u>						
Condensation product of phenol sulfonic acid/formaldehyde	-	8/4.0/-	71	-/-	-	54
Sulphon syntan/Al	Pickled goatskin	10+3/4.0-4.5/-/1440	80.9±0.4	17.2±1.3/16.9±2.4/40.0±1.6	-	58
Acorn tannin/syontan	-	8+2/3.5-3.6/30/510	75.5	-		30

Table 2. Tanning performance of leather treated by improved traditional Cr tanning process.

Tanning agents	Type of leather	Dosage (% ows)/pH/Temperature (°C)/Time (min)	Shrinkage temperature (°C)	Tensile strength (MPa)/Elongation (%)/Tearing strength (N/mm)	Thickness rate (%)	Reference
<u>Chrome-tanning with other metals and zeolites</u>						
BCS + sodium zeolites	Pickled sheepskin	5.7+3/3.2/-/360	105	24.4/46.0/94.0	n/a	62
BCS (as Cr <sub>2</sub> O <sub>3</sub> ) + FS (Fe <sub>2</sub> O <sub>3</sub> )	Cowhides	1.54+0.66/2.6/-/600	110	26.4/74/75.6	n/a	90
BCS (Cr <sub>2</sub> O <sub>3</sub> ) + AS (Al <sub>2</sub> O <sub>3</sub> ) + FS (Fe <sub>2</sub> O <sub>3</sub> )	Cowhides	1.1+0.77+0.33/2.6/-/600	109	24.7/53/81	n/a	
BCS + BAS + ZS	Cowhides	1.1+0.77+0.33/2.6/-/600	119	43/84/79.1	n/a	
<u>Cr tanning with Cr adsorption increasing additives</u>						
Cr sulphate + TLWP	Pickled cow pelt	6+6/3.8-4.0/-/260	106±0.5	27.0±0.3/58±1/57±1	n/a	63
Cr sulphate + dispersion of polybutyl acrylate nanoparticles	Wet salted cowhide	8+4/3.6-4.0/-/240	126±1.2	27.9±0.6/84±4/-	n/a	43
Cr + amino-terminated hyper-branched polyamide	Pickled pigskin	8+4/3.0-4.0/-/480	107.5	-/-/-	n/a	67
EHBP + BCS	Pickled goatskin	8+6/3.8-4.2/25/380	108.6±1.1	15.0±3.7/93.8±6.3/30.6±6.3	74.2	34
Cr (III)-loaded nanoparticles of PEGMA-co-AA-co-GMA	Pickled sheep skin	50 (eqv. to 2% Cr)/3.0-4.0/- /660	101.5	12.4/98.8/30.5	n/a	45
<u>Cr adsorption increase by sonication</u>						
Sonicated Cr treatment using BCS	Cow hides	6*/2.5/-/10	104.5	13.8/40.1/56.2	n/a	54
Sonicated (150 Watt/40KHz) Cr treatment using BCS	Picked cow hide	50*/2.8/	116±1	-/33.2±1.3/70.0±4.0	n/a	65
Sonicated (300 Watt/28 KHz) Cr treatment using BCS	Pickled goatskin	20*/2.5/25/15	105.2	13.8/40.1/56.2	n/a	54
Sonicated Cr treatment using BCS + microwave	Pickled goatskin	20*/3.0-4.5/25/3+5	103.8	15.4/-/34.2	n/a	55
<u>Waterless tanning</u>						
Waterless tanning with Cr in propylene carbonate	Cattle skin	9%/5 MPa/150 min	100	n/a	n/a	56
Tanning in 2:1 urea/KCr(SO <sub>4</sub> ) <sub>2</sub> ·10H <sub>2</sub> O deep eutectic solvent	Cow hides	62/4/25/1080	83	30.3/42.5/-	n/a	84



Table 3. Tanning performance of leather treated by improved tanning process with tannin.

Tanning agents	Type of leather	Dosage (%owl)/pH/Temperature (°C)/Time (min)	Shrinkage temperature (°C)	Tensile strength (MPa)/Elongation (%) /Tearing strength (N/mm)	Thickness rate (%)	Reference
<u>Tannin in a combination with heavy metal ions and another tannin/synton</u>						
Tara tannin + BAS	Pickled sheepskin	12+4/4.52/-/300	93±2	-/-/-	-	32
Henna tannin + BAS	pickled goat skins	20+2+2/2.8-4.7/375	97±1	22.6±0.2/57±0.7/42.2±0.7	-	98
Phenolic synton + wattle tannin + myrobalan tannin + Al-synton + protein synton	Pickled goatskin	2+14+2+4+4/4-4.7/-/575	94	25.1±0.9/59±3/44.1±3.1	-	94,95
BAS + ZS + SC + synton	Pickled goatskin	2+0.2+2/3.8-4.0/-/315	91±2	38.6±0.3/50±1/52±1	-	96
BAS + ZnS + SC + ST + PA + synton	Pickled goatskin	2+0.06+0.06+0.06+2/3.8-4.0/-/315	95±1	25.9±0.3/51±2/51±1 <sup>a</sup>	-	96
<u>Sonicated tanning</u>						
Wattle tannin under ultrasound (210 Watt/20 KHz)	Pickled buffalo pelt	20 <sup>7</sup> -/35/300	85	-/-/-	-	34
<u>Waterless Cr-free tanning</u>						
Valonea tannin in SCCO <sub>2</sub> at 100 bar	Pickled sheepskin	15/4.5/32/120	69.5±0.3	-	-	102
Valonea tannin in SCCO <sub>2</sub> at 100 bar	Pickled sheepskin	15/4.5/32/360	74.5±0.3	-	-	102
Wattle tannin/Al in SCCO <sub>2</sub>	Salted goat skin	20+1.5 <sup>7</sup> /3.8/25/120	84.0	29±2/34±2/61±7	-	103

<sup>a</sup>soaked in % tannin or tannin+Al solution

Table 4. Tanning performance of chrome-free leather tanned by crosslinking.

Tanning agents	Type of leather	Dosage (% ows)/pH/Temperature (°C)/Time (min)	Shrinkage temperature (°C)	Tensile strength (MPa)/Elongation (%)/Tearing strength (N/mm)	Thickness rate (%)	Reference
<u>Tanning by chemical crosslinking</u>						
Glyoxal	Pickled goatskin	6/5/-/-	82	-/-/-	40	110
Glutaraldehyde + Basyntan FB 6	Salted goatskin	2+11/2.8-/265	90±4	15±2/72±6/-	n/a	109
Glutaraldehyde + syntan	Salted goatskin	2.5+2/-/-/-	85	15.6-/44.1/-	n/a	106
Glutaraldehyde + Tara tannin	Pickled sheepskin	2+12/4.0-4.2-/300	92±1	23.0±1.8/-/51±7.8	n/a	32
Tara tannin + BAS + syntan + glutaraldehyde	Cow upper skin	15+5+20+1/3.3-/2400	103	-/-/-	n/a	142
d-Lysine + glutaraldehyde + Basytan FB 6	Salted goatskin	1+2+4/3.5-4.5-/265	120±8	18±3/56±6/-	n/a	109
Syntan (Tanigan RFS) + Mimosa tannin + oxazolidine		15+4+20/4/25 & 50/1235	98	16.6/-/44	n/a	33
Glutaraldehyde + Mimosa tannin + oxazolidine		1+4+20/3 & 3.2/25 & 50/1255	104	21/-/50.9	n/a	33
THPS + BAC + syntan (Tergotan EF)	Salted goatskin	6+7+6/3.5+3.8+3.8/35+45- /1275	91	-/28.5/28.4	n/a	125
BAT + AcR + AmR + mimosa + BAS	Pickled sheepskin	2+3+2+4+1 (Al2O3)/8.0+4+4.6/ 20+35+60/960	88	17.5/85/15	42	123
Cage-like octa(aminosilsesquioxane) + THPS	Salted goatskin	6+2.5/5.5 & 3.2-/420	83	17.1/102.2/74.5	44.6	126

Table 5. Tanning performance of leather chrome-free tannage with sustainable tanning processes.

Tanning agents	Type of leather	Dosage (% ows)/pH/Temperature (°C)/Time (min)	Shrinkage temperature (°C)	Tensile strength (MPa)/Elongation (%)/Tearing strength (N/mm)	Thickness rate (%)	Reference
<u>Tanning with non-toxic metals and zeolites</u>						
L-m-TS	De-pickled goatskin	7.5 (eqv. TiO <sub>2</sub> )/2.0-3.5/-/480	93	30.7/31.8/79.7	58	152
L-m-TS	De-pickled goatskin	10.0 (eqv. TiO <sub>2</sub> )/2.0-3.5/-/480	102	n/a	58	152
L-m-TS	De-pickled goatskin	7.0 (eqv. TiO <sub>2</sub> )/2.0-3.5/-/480	97	n/a	n/a	153
Titanium metal waste (74.7%Ti + 24.9% Al)	Cow pelt	8/2.2-2.3/25/450	77	n/a	n/a	154
Zeolite+formic acid+oxalic acid+sodium hydrogen sulphate	Bull hides	7/3.64/-/725	74.9	n/a	n/a	160
<u>Tanning with nanoparticles and silicic acid</u>						
<i>Wrightia tinctoria</i> tannin-induced Ag nanoparticles	Raw goatskin	n.a./-/-	73	57/17/52	n/a	39
Nanosilica + vegetable tannin	-	2.3+45/-/35/1260	76	27.2/58.5	25	162
Nanosilica /octadecylsilane + vegetable tannin	-	2.8+45/-/35/1260	80	36.6/54.5	22	162
BAS + wattle tannin + sodium metasilicate (Si NP)	Pickled goatskin	2.5+20+5/4/25/300	100	26.3±0.6/58±4/3138.1	n/a	144
BAS+ metasilicate (Si NP) + TA + syntan	Delimed goatskins	5+5+10+6/3.8-4.0/-/300	95±1	17.8±0.5/62±2/53±3.9	n/a	163
BAS + metasilicate (Si NP) + THPS	Salted goatskin	1.5+10+1/3.8-4/-/210	86	26.8±0.2/75±2/80.4±2.0	n/a	164
PMA-m-Si nanoparticles	n/a	3/4/-/540	76	17.8/241.6/-	105	165
P(POSS-MAA) + BAS	Pickled goatskin	6+10/6.5+3.0/25+40/780	73.5	18.1/56.9/67.9	71.6	57
<u>Tanning with enzymes</u>						
mTG	Pickled cowskin	0.6/6.0/25/120	80	-	-	56
Tanning with various chemicals						
Silicic acid	Pickled goatskin	15/2.0-2.5/40/630	91.2±1.3	17/34.5/-	140	168
Silicic acid + Valonea tannin	Pickled goatskin	10+5/2.0-2.5/40/630	83.0±0.8	16.2/44.5	125	168
s-PFD + Ti	n/a	n/a	>100	n/a	n/a	171
L-Tyr TCT	Limed sheep hides	20/6-7/35/540	81.2	16.2/27.6/37.6	n/a	169
L-Lys TCT	Limed sheep hides	20/6-7/35/540	82.5	17.2/26.4/34.5		169

BAS tanning + HPEGM400 re-tanning	Salted	8+10/2.2/-/940	74 ± 0.2	18.12 ± 0.19/ 34 ± 0.10/	40.7 ± 1.3	170
	goatskin			41.16 ± 0.06		
Two tanning and re-tanning with Al-m-HPEGM400	Salted	8+10/2.2/-/940	86 ± 0.3	24.08 ± 0.11 / 38 ± 0.12/	59.9 ± 2.1	170
	goatskin			52.18 ± 0.11		

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