Sreeram Kalarical Janardhanan
Luis A. Zugno *Editors*

Emerging Trends in Leather Science and Technology

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Foreword by Dr. Michael Redwood

A long time ago we used to learn that the leather industry was somehow “special”. It battles with “inelasticity” because its raw material supply cannot grow to meet demand. The raw material is complex, impacted not only by species but by climate, husbandry, age and sex. The processing is difficult with different layers and sections often requiring separate treatment and the science is not always fully understood.

As a natural material surface defects can sometimes be difficult to sell and making every part of every piece perfect for its intended purpose is not easy. There is a great deal of skilled craft associated with making a piece of leather that is both beautiful and high performance.

Yet while leather itself is certainly special the factories that make and use it are buffeted by the winds of geopolitics and changing trends as much or more than any other material. Perhaps what has been really special has been leather’s ability to endlessly adapt to serve a changing world over many millennia.

In the beginning, hides and skins were all that was available for covering and containing the multitude of items needed for the daily life of early humans. They were excellent in the raw but with a little treatment, they could be protected from the most aggressive bacteria and made more suited for various purposes. This is tanning. And the thrill for the tanner is the magic and mystery of managing the chemistry and the physical structure, along with mixing art and science.

The arrival of textiles, pottery, glass, paper and metals took end uses away from leather but increasing populations and the growth of society put new, more sophisticated demands on leather. Improved husbandry also means that supply will never catch up with demand.

The discovery and exploitation of plastics changed this balance and now no end uses exist where leather cannot be replaced, but usually elegance and functionality are sacrificed. Now we are learning the environmental damage caused by plastics and we better understand the role leather can play to fight climate change and biodiversity loss. Leather needs the world, and the world needs leather.

Hides and skins are present in nearly every part of the globe and have been traded internationally since the earliest days. As we face the challenges of climate change, poverty and diminishing natural resources using hides and skins well becomes essential. We must add value, make good use of the many jobs leather creates and teach the world the value of producing things that last when looked after and repaired.

I have had a long and happy career working with leather and am very honoured to have worked with many and met most of those involved in the production of this Monograph. It is both timely and prescient.

Michael Redwood.

October 2023

Dr. Michael Redwood
Spokesman for Leather Naturally
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Preface

Leather is a unique commodity that links the product of rural farmers to the fashion world. Leather and its products are among the most widely traded products worldwide, as they are produced from a renewable and readily available resource, a byproduct from the meat industry. A key factor for the development of the leather sector is undoubtedly the strong raw material base. But when talking about sustainability in the leather industry, it does not only mean the sustainable manufacture of leather goods alone. An ideal leather industry network comprises of the following: Livestock (cattle, buffalo, sheep, pig and goat), slaughterhouses, raw hides and skin collection, tanning industry, leather goods manufacturing industries, export market and other allied industries. The other small industries that can co-exist within this network would include glue and manure manufacturing industries, processing of meat into various by-products, etc.

Production and supply have gradually moved from industrialized to developing countries and emerging economies, which are fast becoming the most important suppliers of value-added leather products. It is fascinating to note that more than half of the world's supply of leather raw materials comes from developing countries. As such, leather processing is an important economic activity in several developing countries, and it coincides with the fact that the availability of this raw material is high in developing countries. It is estimated that the international trade of this important material exceeds US$ 80 billion annually and is expected to continue growing alongside the increase in population and urbanization of developing countries. From the above, it is evident that the leather sector occupies a very important place in the economic development of a country on account of its substantial export earnings, the potential for the creation of employment opportunities and favourable conditions for its sustained growth.

However, one of the major challenges of leather processing operations is the potential environmental impact that could have devastating socio-economic consequences. Pollution from the tanneries has a negative long term impact on the growth potential of a country, irrespective of immediate economic benefits. Polluted water, air and soil affect peoples' health and damage the ecological processes that sustain the production of food.

Demand for leather goods is growing, but so is the criticism of its severe environmental impacts, which is driving a keen interest in sustainable alternatives. On this account, the three important aspects of the leather producing industry are environmental sustainability, ethical and social sustainability and economic sustainability. Because of the heterogeneity of this sector and also as sustainability has become unavoidable for any industry nowadays, it becomes essential to analyze several issues and factors that can facilitate the attainment of sustainability in the leather industry.

In addition, the leather goods industry has a history with very distinct shifts in end uses and materials from the use of leather products for specific functional purposes to the current market of luxury goods. Raw materials used in the leather goods industry are as diverse as the products. Leather remains important, but the use of materials such as nylon, polyester, polyurethane fabric and even polypropylene is growing. The leather clothing market is highly volatile because the demand for such products depends largely on consumers' disposable income and, on fashion trends. Historically, leather garments have been less of a luxury and more of a necessity, as other materials were not available for protection against cold. In many regions of the world, leather garments became the primary cold-weather outerwear. However, rising wealth and the emergence of excellent synthetic fabrics for waterproof and insulating garments at affordable cost have steadily weakened the position of leather in the traditional outerwear market in most countries.

Significant changes have also occurred in the industries that supply machinery, components, software and chemicals to the footwear and other leather product industries. The demand for leather footwear has increased over the years. The growing demand for leather footwear, as well as the fact that this demand competes for raw materials with other products, appears to be a significant business opportunity for developing countries including the African continent. The footwear industry is a valuable source of employment for developing countries. It is estimated that 10 million people are employed worldwide in the direct production of footwear and there are significant additional numbers employed in the support industries. Despite the value of the industry in improving the living standards of people in the developing world, there is little coordinated information on the industry as a whole available, particularly in developing countries.

The range of synthetic materials used in the leather goods industry is very wide. Increasingly, materials are being used in combination with leather to achieve a certain look or price range. Synthetic materials can be found in all types of leather goods, in luxury items as well as in economical casual articles. As a rule, the quality of non-leather materials follows the trends of the respective market segments. Today, significant progress has been made to make it possible to manufacture accessories at more competitive prices. In addition, one of the more challenging issues in the leather sector is the design of leather products and accessories. Today digital techniques and artificial intelligence are playing a major role in designing of a wide array of leather products. To sum it up, *"Emerging Trends in Leather Science and Technology"* is a very challenging subject and a comprehensive publication addressing all such major issues is not available in the market for reference by the scientists, technologists, policymakers and other stakeholders from both Global South as well as Global North.

This book has been developed in the above backdrop; thus, its major goal is to channel the concurrent knowledge from the leading scientists and technologists working in the field to the scientific public in developing countries. The contents of the book will also be a very valuable source of information for academics, researchers, industrialists and business communities in developed countries. The monograph will also be a very useful handbook for early career researchers and engineers involved with leather related research and consultancy, irrespective of their location.

The concept of developing such a book emerged during the discussion between Dr. Amitava Bandopadhyay, Director General, NAM S&T Centre, New Delhi and Dr. S. K. Janardhanan, Director, CSIR-Central Leather Research Institute (CLRI), Chennai in early 2021. Since 2018, the NAM S&T Centre has been collaborating with CSIR-CLRI and has so far organized two International Workshops on "Sustainability of Leather Sector" and "Trends in Materials, Design, Innovation and Intelligent Manufacturing of Footwear and Leather Products" for the benefits of scientists, technologists and policymakers from the developing countries.

This book contains 17 chapters that cover various challenges and opportunities of leather manufacturing, product making, environmental management, country status and policies, which the developing world needs to understand, manage and improve in regard to their processing, manufacturing infrastructure and export requirements to achieve sustainability. The chapters in the Monograph have been contributed by scientists and experts from 12 countries, namely Australia, Croatia, Ethiopia, France, Germany, India, Kenya, Switzerland, Türkiye, UK, United States and Vietnam to share their knowledge and expertise in various facets of leather and leather product making and related subjects.

We would like to express our heartfelt gratitude to all the authors who have kindly accepted our invitation to write the chapters, revise the contents based on reviewer's comments and submit the final version well in time in spite of their busy schedule.

We would also like to thank Dr. P. Thanikaivelan, Chief Scientist, CSIR-CLRI for his significant contributions in taking this publication project forward. We are also thankful to Dr. T. Ramasami, Former Director, CSIR-CLRI and former Secretary, Department of Science and Technology, Government of India for his guidance and support during this publication project. Thanks are also due to Dr. Amitava Bandopadhyay and his team at the NAM S&T Centre for all the support rendered towards publication of this Monograph.

We are grateful to Dr. Michael Redwood, Spokesman for Leather Naturally, ILM Opinion Writer and Leather Conservation Trustee for writing the “Foreword” of this book in spite of his extremely busy schedule. We also express our gratitude to Dr. Loyola D’Silva, Executive Editor, Springer Nature, Singapore and his team for making this endeavour a success.

Chennai, India — Sreeram Kalarical Janardhanan
Basel, Switzerland — Luis A. Zugno

Introduction

Leather and its products are one of the most traded goods globally due to their greater durability, good hydrothermal stability, good mechanical properties and resistance to chemical, biological and environmental degradation. The leather industry is a multi-billion dollar global business which has emerged as an important economic activity in several developing countries. The global leather goods market is projected to grow from USD 468.5 billion in 2023 to USD 738.6 billion by 2030, exhibiting a Compound Annual Growth Rate (CAGR) of 6.7% during the forecast period. The process of leather manufacturing involves several stages, including the procurement of raw hides and skins, tanning and processing of the hides and production of finished leather products.

The leather manufacturing industry has faced criticism in the recent years due to concerns over animal welfare, severe environmental impacts and poor working conditions in some countries. Efforts are being made to resolve these issues through improved sustainability. The closedown of manufacturing units, supply chain disruption and economic slowdown during COVID-19 pandemic in 2020, had also severely impacted the global economy of leather industry. However, as the infection rate and spread was reduced, gradually everything returned to track and improved the sustainable consumer spending.

In spite of the implementation of several advanced processing techniques and treatment systems, leather industry is still facing serious challenges from the public and the government authorities. Hence, there is an urgent need to revamp the existing leather processing methods for the sustainability of the leather industry in the future.

Some of the environmental concerns associated with leather production are sourcing of raw materials, use of hazardous chemicals, improper waste management and high water usage as well as air and water pollution. It is crucial for the industry to prioritize these environmental concerns and take necessary actions to address them in order to ensure a more viable future for leather production. Addressing these challenges requires collaboration between industry stakeholders, including manufacturers, suppliers, consumers, R&D institutions and regulatory authorities, to implement measures that promote sustainability, ethical practices and responsible operations throughout the leather supply chain.

In order to address the above mentioned issues, the *Centre for Science and Technology of the Non-aligned and Other Developing Countries (NAM S&T Centre), New Delhi* has brought out this Monograph for dissemination of relevant knowledge and information to the scientists, researchers and managers from the leather sector and other stakeholders interested in the leather industry. The book through its seventeen chapters underscores the various challenges and opportunities of leather manufacturing, product making, environmental management and policies regarding leather processing, which the developing world needs to understand, manage and improve in regard to its processing, manufacturing infrastructure and export requirements to achieve sustainability. The book intends to provide information on smart as well as sustainable leather manufacturing practices to the professionals from the developing countries.

The book brings together scientific communities from Australia, Croatia, Ethiopia, France, Germany, India, Kenya, Switzerland, Türkiye, UK, United States and Vietnam to share their knowledge and expertise to provide a detailed insight into the leather manufacturing and processing, current trends in leather science and technology and policies related to the improvement of leather trade.

I am immensely grateful to Dr. Michael Redwood, Spokesman for Leather Naturally, ILM Opinion Writer and Leather Conservation Trustee, UK for kindly agreeing to write the *Foreword* of this book in spite of his very busy schedule.

I am thankful to Dr. Loyola D'Silva, Executive Editor, Springer Nature, Singapore for his kind support and guidance towards bringing out this Monograph and Ms. Niraja Deshmukh, Production Editor, Springer Nature, India for managing all the technical and administrative tasks for the publication process.

I would like to express my sincere gratitude to the Editors of this book, Dr. S. K. Janardhanan, Director, CSIR-Central Leather Research Institute (CLRI), Chennai, India and Dr. Luis A. Zugno, Secretary and Former President, International Union of Leather Technologists and Chemists Societies (IULTCS), Switzerland, for their initiatives and efforts and sharing their valuable time in reviewing the papers for this book and taking charge of the project. I am especially thankful to Dr. P. Thanikaivelan, Chief Scientist, CSIR-Central Leather Research Institute, Chennai, India for coordinating the entire publication project. The publication of this book would not have been possible without his support throughout the process.

I also acknowledge the valuable support of the entire team at the NAM S&T Centre and am especially thankful to Mr. Madhusudan Bandyopadhyay, Senior Adviser for his support and guidance; and Mr. Pankaj Buttan, Data Processing Manager; Ms. Nidhi Utreja, Former Programme Officer and Ms. Abhirami Ramdas, Research Associate for their contributions in taking this publication project forward and bringing it to a successful conclusion.

I also record my appreciation for the assistance and support rendered by my colleague Mr. Rahul Kumra, Assistant Administrative Officer towards bringing out this Monograph.

I believe that this Monograph would serve as a valuable resource material for scientists and researchers from R&D institutions, professionals from the leather sector, owners of leather industries, technical institutions, government officials, policymakers and students who are actively engaged in the area of leather science and technology.

Amitava Bandopadhyay

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Contents

Science and Technology of Leather Manufacture

Current Trends in Leather and Leather Products

Policies for Promoting Leather Trade

Country Status and Case Studies

Epilogue

Science and Technology of Leather Manufacture

Hides and Skins: Unravelling Nature's Marvel

John A. M. Ramshaw and Balaraman Madhan

1 Introduction

Undoubtedly, the evolution of skin across the animal kingdom is one of nature's marvels. It comes in many formats and is often referred to by other names when it is adapted for human use. These include hide, where the skin is from a large animal and tradable, such as a bovine, or fur for some species when dense hair is retained on the product. In humans, skin is often quoted as being the largest organ of the body, but this is not an opinion held by all (Sontheimer, 2014). Nevertheless, whatever the discussion, skin is a large organ. For a 70 kg person, the skin comprises around 3.9 kg (5.5%) of the body weight, with an area of around 1.7 m^2 (Goldsmith, 1990). And the key component of skin is collagen, especially type I collagen (James et al., 2006; Ramshaw & Glattauer, 2020). Recent advances in genomics have identified 28 genetically distinct collagen types in humans (Ricard-Blum, 2011). Of these, at least 18 are found in human skin (Table 1) (Nystrom, 2016), perhaps more when the roles and locations of the more recently discovered collagens become better defined. The most abundant collagen types that are present (i.e.: types I and III) are involved in the overall structure and organisation of the skin, whereas minor collagens are often associated with the dermal-epidermal junction (e.g.: types IV and VII) (Abreu-Velez & Howard, 2012) or are possibly involved during initial tissue formation (e.g.: types V and VI) (White et al., 2014), subsequently decreasing in their relative amounts or becoming masked by other components (White et al., 2014).

Skin has evolved to fulfil a range of functions, principally as a flexible outer tissue enclosing the body that can provide protection through acting as a barrier against

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Table 1 Collagens involved in the structure of skin

Type	Gene(s)*	Roles	References
I	COL1A1, COL1A2	The most abundant collagen in skin, forming the major fibrillar and fibre bundle structures of the skin	
III	COL3A1	An abundant fibril forming collagen, particularly in young skin and the papillary dermis	Byers et al. (1974)
IV	COL4A1, COL4A2,	The principal collagenous component of basement membranes, found in the dermal-epidermal junction	Yaoita et al. (1978)
V	COL5A1, COL5A2	A low abundance fibril forming collagen found in most tissues, including skin, involved in fibril initiation	Birk et al. (1990)
VI	COL6A1, COL6A2	Also found in most tissues, as a distinct beaded network and possibly involved in the formation of new tissue	Werkmeister et al. (1993)
VII	COL7A1	Present as anchoring fibrils at the dermal-epidermal junction	Rattenholl et al. (2002)
VIII	COL8A1	Part of the collagen formed in association with most blood vessels, including in the skin	Plenz et al. (2003)
XII	COL12A1	A fibril associated collagen that is present with type I containing fibrils, mainly in the papillary dermis	Kronick et al. (1991)
XIII	COL13A1	A transmembrane, epidermal collagen in basal keratinocytes that interacts with basement membranes	Peltonen et al. (1999)
XIV	COL14A1	A fibril associated collagen that is present with type I containing fibrils, mainly in the papillary dermis	Kronick and Landola (1997)
XV	COL15A1	A chondroitin sulfate-proteoglycan, with multiple non-collagenous interruptions, that is found associated with the basement membrane and papillary dermis	Fukushige et al. (2005)
XVI	COL16A1	A fibril associated collagen that is present with type I containing fibrils, mainly in the papillary dermis	Akagi et al. (1999)
XVII	COL17A1	A transmembrane, epidermal collagen in basal keratinocytes that interacts with basement membranes	Zimina et al. (2005)
XVIII	COL18A1	A heparan sulfate-proteoglycan found associated with the basement membrane	Seppinen and Pihlajaniemi (2011)

(continued)

Table 1 (continued)

Type	Gene(s)*	Roles	References
XIX	COL19A1	A fibril associated collagen expressed at the dermal-epidermal junction during development but not in adults	Myers et al. (1997)
XX	COL20A1	A fibril associated collagen expressed weakly in the dermis during development but not in adult skin	Koch et al. (2001)
XXII	COL22A1	A collagen found at tissue junctions, including associated with hair follicles	Koch et al. (2004)
XXIII	COL23A1	A transmembrane, epidermal collagen involved in keratinocyte cell-cell junctions	Koch et al. (2006)
XXVII	COL27A1	A fibril forming collagen that is only expressed in developing pre-natal dermis	Plumb et al. (2007)
XXVIII	COL28A1	Expressed in skin, possibly just in the papillary dermis	Veit et al. (2006)

*Additional genes for some of the collagen types have been described, but these are not found in skin or are only minor compared to the genes noted

mechanical forces and deleterious entities including chemicals and microorganisms, and sensation through a nerve system that detects changes in the environment. And in more complex forms, it is involved in physiological regulation, for example of body temperature via the presence of hair and sweat glands, and in colour.

Skin is seen as a specific tissue of vertebrates, although its form varies between fish, amphibians, reptiles, birds and mammals (Alibardi, 2003). Among the invertebrates, a visible outer coating, an exoskeleton, comprising the polysaccharide chitin or a mineralised shell, has evolved in some lineages. But even in the most primitive extant species there is still tissue that defines and maintains shape and form. The transition from unicellular to pluricellular (colony forming) and thence to multicellular organisms is not understood and a range of theories have been proposed (Niklas, 2014; Tong et al., 2022) to take us through or account for the missing evidence. And it is probable that many different routes led to our different present-day kingdoms, animals, fungi and plants (Parfrey & Lahr, 2013).

The development of multicellularity, especially complex multicellularity, provided advantages or useful trade-offs and diversity for the competition of life, albeit that a significant abundance of lifeforms is still unicellular (Bar-On et al., 2018). For example, multicellularity allows diffusions limits on size to be overcome, it provides for longer lifespans as a single cell can die, (and potentially be replaced), without the entire organism dying, and it provides for complexity as cells with different, distinct functionalities can be formed within a single organism (Michaud & Roze, 2001).

With the evolution of multicellular organisms, systems beyond cell-to-cell adhesion needed to emerge to stabilise the new structures. Collagen has been considered as the system that emerged for the animal lineage. Genomic data indicated that $(\text{Gly-Xaa-Yaa})_n$ sequences, which are characteristic of all collagen types, were present in certain bacteria (Rasmussen et al., 2003), and subsequent studies showed that many form the three chain, triple-helical tertiary structure (Yu et al., 2014) that is also characteristic of all collagens (Brodsky & Ramshaw, 1997). The collagen family is well represented in the genomes of the most primitive of animal species, including *Trichoplax adhaerens,* which is considered as probably the simplest known extant animal. This species is a widely distributed marine invertebrate that possesses only four types of somatic cells and has one of the smallest known animal genomes (Schierwater, 2005). Although it may lack an extracellular matrix (ECM) as seen in higher organisms, its genome, nevertheless, contains some putative collagen genes (Srivastava et al., 2008), while collagen type IV was identified by proteomics (Ringrose et al., 2013). Just a little further up the animal phylogeny, considered as a monophyletic lineage (Müller, 1995), are species with well-defined collagenous ECM structures. These include Porifera (sponges) where putative genes for as many as 13 of the 28 collagen types are represented (*Amphimedon*), of which 8 are found in skin (Srivastava et al., 2010). Similarly, Cnidarians, such as jellyfish and corals, have genomes where putative genes for at least 16 of the 28 collagen types are represented (*Dendronephthya*), of which 9 are found in skin (Jeon et al., 2019). Thus, even at the earliest stages of animal evolution, the genetic potential of the collagen genes that are essential to the later evolution in vertebrates of skin were present. And the evolution of skin has enabled many current industries, notably gelatin and leather production, to emerge during hominid evolution.

Leather is among the oldest materials manufactured by mankind. Other early manufactures, such as bone, antler and stone tools, have since been superseded, yet leather remains a crucial material, retaining applications, for example, in footwear and clothing, and now in furnishings and industrial products. The overall leather products market continues to grow (Anon, 2021a, 2021b, 2022a), and in 2021 is valued around 419 billion US$ and it is estimated to grow at CAGR of above 6% from 2022 to 2030 (Straits Research, 2023).

It is generally accepted that hominids emerged out of Africa. During this evolutionary process, these early people lost body hair and started to migrate to different, more variable and extreme climatic regions. Both these contributed to the need for some form of clothing and protection (Gilligan, 2010). Early hominids lacked the powerful canine teeth that other animals, especially predators, possessed for puncturing and shredding animal hides/skins and the poor ability to digest hair keratin. So, as meat became an increasing feature of diet, so too did the availability of various hides and skins removed from the kill to fill the need for clothing and other lifestyle requirements. Tools, such as stone cutters and scrapers, were available to remove and clean these tissues, not just for butchering.

Early evidence of leather production is limited. Early users of hides and skin would have recognised that the natural material deteriorated, and with the development of cognitive abilities (Epstein, 2002), also noted that accidental treatments, such as by smoke, or immersion in water with plant material, such as bark or leaves, led to an extended lifetime compared to untreated material. The date of this transition from a raw hide to leather-like material is uncertain, as is the transition to a defined tanning process. Early hominids would also have seen that treating dried proto-leather with animal fats could restore the flexibility of the material. Possibly the earliest evidence of processing comes from stone tools found at Hoxne, UK, dated to around 400,000 years ago. When examined for microscopic wear patterns, some indicated their use on hides and skins (Keeley, 1977). Also, later, bone tools from around 120,000–90,000 years ago were found in Morocco and identified as having been used in hide and skin processing (Hallett et al., 2021).

The earliest leather artefacts, however, are relatively recent, dating from the Copper (Chalcolithic) era, with further evidence accumulating during subsequent eras and within specific cultures. The earliest artefact is a shoe, found in a pit in Armenia, dated to between 3627 and 3377 BCE (Pinhasi et al., 2010). Particularly interesting is the wide range of artefacts, from around 2 centuries later, that were found with Ötzi, 'The Iceman', who was found in 1991 in the Tyrolean Alps, adjacent to the present Austria/Italy border (O'Sullivan et al., 2016). The leather was identified as coming from several different species, where a clear selection had been made of optimal materials that could provide for distinct functions (O'Sullivan et al., 2016).

Subsequently, considerable progress has been made with developing and understanding the technology of leather production, as detailed later in this volume. Improvements, documentation, and use of leather making technology appeared in all ancient civilisations. For example, in India around 3000 BCE in the holy scripture of The Rig-Vega, the use of leather in bottles and other goods is first documented, while later, around 2000 BCE leather goods are mentioned in the Sankhya and Likhite law books (Anon, 2022b). In Egypt, artwork from about 5000 BCE indicates use of leather goods, while from around 2300 BCE, artefacts have indicated the wide range of leather goods that were used, including sandals, chariot harnesses and couplings, as well as jewellery. It is also thought that consistent methods for vegetable tanning were developed in Egypt later during the civilisation period (Anon, 2022b). Also, in China, from 1600 BCE or earlier, leather goods included shoes and tunics as armour (Anon, 2022c). The use of leather in Ancient Greece and then Ancient Rome, from about 800 BCE, also included footwear and bags as well as a steadily increasing use in military equipment, such as shields, armour, straps and equestrian fittings, incorporating refinements to the vegetable tanning approach and high-volume production methods. The Romans also developed an alum tawing to produce softer leather that could be dyed, with all forms of leather becoming plentiful, useful materials (Anon, 2022c).

Some significant changes have also happened in more recent times, such as the development of chrome tanning in the mid-nineteenth century. The approach was initially described by Friedrich Knapp (Germany) in 1847, and later, in 1853 by Hylten Cavalin (Sweden) and Rene de Kercado (France) (Nriago & Nieboer, 1988). Subsequently, in 1858, Knapp elaborated on his studies and on batch tanning. Its commercial introduction, however, was much later when Augustus Shultz (USA) patented, in 1884, a two-bath process (Shultz, 1884), followed by Martin Dennis (USA) in 1893 who patented a commercially relevant one-bath process (Dennis, 1893). Subsequently, notable improvements were introduced by Henry Proctor (UK), some of which are retained in current use (Nriago & Nieboer, 1988).

And so, to the present day, where global developments are being focussed on green chemistry and minimising environmental impacts. Fortunately, technical innovation persists and will continue to bring significant benefits to the leather industry.

1.1 Structure and Functions of Hides and Skins

The skins of different mammals are similar, sharing many characteristics. The skin has three main functions, these being protection, temperature regulation and sensation. Beyond this, the skin also is involved in many key physiological functions (Kolarsick et al, 2011). However, many variations also exist, for example within an individual across different parts of the body as well as further changes during aging. For example, in humans skin thickness varies from less than 0.1 mm in the eyelids up to 1.5 mm or more in the palms and in the soles of the feet (Kolarsick et al, 2011), while in other mammals, such as the rhinoceros or hippopotamus, the skin can be up to 50 mm thick. Thus, as well as variations in individuals and between individuals in a species, there are further, and often distinct differences between species. Nevertheless, the key functions including many physiological roles remain constant as do the major structural elements, the epidermis, the dermis, their intervening basement membrane and the subcutaneous zone (Fig. 1). Equally, the various appendages and many distinct specialised cell types are also common themes.

The skin provides protection to the body in its role as the interface with the external environment. This protection is by providing the first defence against external challenges. These can be biological, such as by pathogens, harmful chemicals, or physical through thermal or mechanical injury. In this case the skin repairs through formation of scar tissue, which has composition and characteristics distinct from the skin prior to damage, including for example a greater content of type III collagen (Barnes et al., 1976). Mammalian skin also provides a barrier preventing excessive loss of water, and solutes, while also providing some protection against the adverse effects of UV irradiation (Madison, 2003).

The skin in mammals also plays a key role in body temperature regulation to maintain a constant core temperature. It contains sweat glands allowing evaporation and blood vessels that can dilate to provide some heat loss, while constriction of blood vessels conserves body heat (Fig. 1). Also, all mammals, even including marine mammals such as whales that appear hairless, have hair, which when particularly dense is called fur or wool, providing some (but not humans) with effective insulation when the temperature is cold. Classically, fat is believed to play a role for insulation against cold, although it has been shown that lipolysis is not essential for cold-induced thermogenesis (Shin et al., 2017). Within the skin are arrector pili muscles that link to the hair follicles and can influence the angle of the hair fibres with respect to the skin surface, providing a method for control of the effectiveness of insulation properties

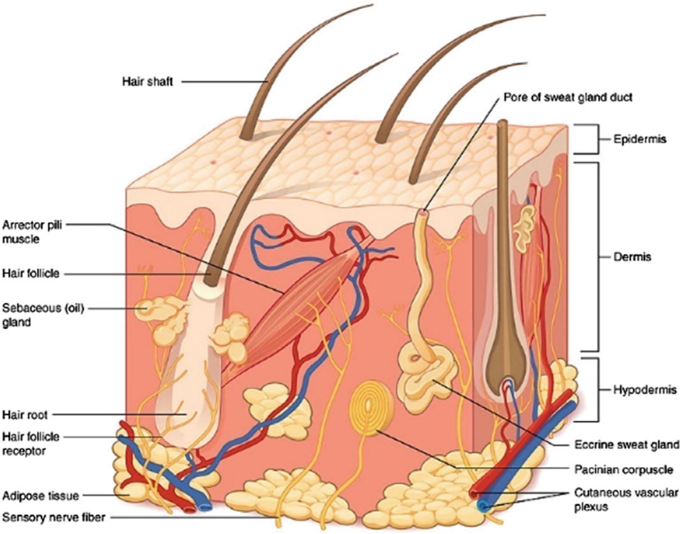

Fig. 1 A schematic representation of mammalian skin (From Betts et al., 2013) (Reproduced under the CREATIVE COMMONS attribution 3.0 unported licence)

(Fig. 1). In some animals, where the hair has evolved into tough, sharp spines, or quills, the arrector pili muscles control these in a host-defence mechanism.

A further primary function for skin is sensation, whereby the state and changes in the external environment can be detected. The skin contains many nerves and receptors that can perceive heat or cold, touch, vibration, pressure and pain from tissue injury or disease. Beyond this, mammalian skin acts as a water-resistant barrier, in part through accumulation of oils, so that internal nutrients and associated compounds are not lost. Other functions of the skin, found in most mammals, include acting as a storage centre for lipids and water. Various gases, including oxygen, may diffuse in small amounts into the mammalian epidermis, and while small compared to overall respiration can be important for the outermost cells.

Depending on the species, some or all of range of secondary functions provided by skin may be present. These include acting to detect infections, via Langerhans cells as part of the immune system (Madison, 2003). The most important biochemical process is the formation of vitamin D by sunlight, essential for the normal absorption of calcium and phosphorous for healthy bones, although for some species, notably dogs and cats, this does not occur (Zafalon et al., 2020). Also, for some species, the hair or fur can be adapted to allow camouflage. Necessarily, as the outermost organ, skin condition is important for social interactions and mate selection as it provides a visible indication of the health and fitness of an individual.

Mammalian skin consists of three principal zones, the epidermis and the dermis, separated by a thin basal lamina or basement membrane, with a hypodermis below, often termed a subcutaneous fatty layer (Fig. 1), with each layer having specific cells and different collagen types present (Table 1). Each of these three zones consists of further subzones, with different structural and functional characteristics and with different cell compositions (Table 2).

The epidermis is the outmost layer of the skin, plays a significant role towards the principal functions of skin, providing the physical and biological barrier, while preventing water loss (Lim, 2021). It is an elastic, stratified layer, with either 4 or 5 sub-layers, depending on the body location. The uppermost of these is the tough, horny layer, the stratum corneum, which consists of layers of flattened dead cells, corneocytes, that are continually abraded or shed. Associated with these cells are various lipids and other cellular components that are converted into an organised barrier which together with the corneocytes provides a barrier against water loss and unwanted chemical or biological penetration (Baroni et al., 2012). The corneocytes are continually being regenerated from keratinocytes in the underlying

Table 2 Structure, composition and function of skin

Skin layer	Sub-layer/ component	Function
Epidermis	Stratum corneum	A barrier that prevents water loss or entry of water, pathogens
	Stratum lucidum	Present in areas where the skin is thickest, i.e., soles and palms. Consist of 3–4 layers of dead keratinocytes, which adds elasticity and serves as an additional barrier
	Stratum granulosum	Acts as transition layer where the keratinocytes skin cells develop and die. These layers protect the underneath skin against physical damage, infection and water loss
	Stratum spinosum	Consist of keratinocytes and desmosomes, which supports for the strength and flexibility of skin
	Stratum basale	By continuous mitosis produces new cells to replace dying cells
	Keratinocytes	Strengthen epidermis, protect against abrasion and prevent water loss
	Langerhans cells	These cells recognise pathogens or foreign materials and determine the appropriate adaptive immune response system
	Melanocytes	Produce melanin to protect skin from UV exposure
	Merkel cells	Specialised neural pressure receptor cell, responding to sensation
Dermis	Collagen	Extracellular matrix protein, the major component of skin that provides physical integrity around which other appendages exist
	Papillary layer	Keeps the body temperature constant through the action of the sweat and fat glands and nourishes the epidermis
	Reticular layer	Strengthens the skin and provides elasticity
	Fibroblast cells	Synthesis of collagen, elastin, fibronectin and collagenase
	Sebaceous glands	Produces sebum, a fatty substance that lubricates skin
	Sweat glands	To regulate the body temperature in a hot environment
	Mast cells	Control and respond to certain bacteria and parasites
	Lymphocytes	Immunosurveillance or recognizing foreign pathogens
	Macrophages	Eliminate foreign substances by engulfing the foreign materials and initiating an immune response
	Hair follicle	Supports growth of hair, that provides warmth
Hypodermis	Subcutaneous fat	Insulation, calorie reservation, cushioning and shock absorption

epidermal tissue and, as they move up lose their nuclei and proliferative ability to become dead flatted cells. The keratinocytes, about 95% of the cells in the epidermis, produce the keratin protein that eventually forms the tough, horny outmost surface. These cells are derived from cell divisions at the base of the epithelium, and move towards the outer surface, undergoing sequential stages of differentiation (Darmon & Blumenberg, 2012), eventually becoming flat and dying as they progress to form the stratum corneum. Lower numbers of other cells are present including melanocytes, Langerhans cells and Merkel cells (White & Yager, 1995). Of these, in mammals, melanocytes produce melanin, a pigment that gives protection against UV damage, while Langerhans cells are part of the immune system as antigen-presenting cells (Dumay et al., 2001), and Merkel cells which are associated with nerves and have a role in sensation. Nutrition and waste removal for all these cells must occur through the underlying dermis or via the environment as the epidermis is entirely avascular. The collagen content of the epidermis is minimal and restricted to membrane-associated collagens, such as XIII, XVII and XXIII that are present at cell junctions, but these are not components of leather as the entire epidermal layer is lost during the processing of hide/skin into leather.

Beneath the epidermis is a thin, yet layered structure, the basement membrane (the dermo-epidermal junction) which links and attaches the dermis to the epidermis. This layer is continuous and has undulations which increase the surface area for exchange of nutrient and waste products between the dermis and the avascular epidermis (Arumugasaamy et al., 2019). Transmission electron microscopy (TEM) suggests the basement membrane consists of two zones, the innermost (dermal) lamina densa which stains well and the outermost (epidermal) lamina lucida which stains lightly (Fig. 2), although the images obtained can be affected by the preparation method (Chan & Inoue, 1994). The main molecular components of the basement membrane are collagen type IV, laminin, nidogen and a heparan sulfate proteoglycan, perlecan (Randles et al., 2017). Type VII collagen is closely associated with this layer and forms a linking network beneath that is critical in attaching the basement membrane to the dermal layer. The structure and distribution of these key components is not completely understood, despite their important medical and commercial roles. Thus, in the leather industry, liming is used and this removes the epidermal layer. Further bating/protease treatment during leather manufacture facilitates the removal of interfibrillary materials. The remaining components of the basement membrane and adjacent proteins then comprise the 'grain surface' of leather, which contributes significantly to its commercial value through the required aesthetic appeal of the finished product. The use of bating and proteases can lead to degradation of this grain surface if not adequately controlled. The use of immunohistology can give an indication of the biochemistry of the grain (Stephens et al., 1993). With liming alone, followed by deliming and pickling, collagen types IV and VII, and laminin were retained (Fig. 2), but if bating, or alkaline protease in particular, was employed, these components were often degraded and partly lost, consistent with observed grain damage in these samples (Stephens et al., 1993). The other minor collagens that are found proximal to the basement membrane are both proteoglycan collagens, types XV and XVIII (Table 1).

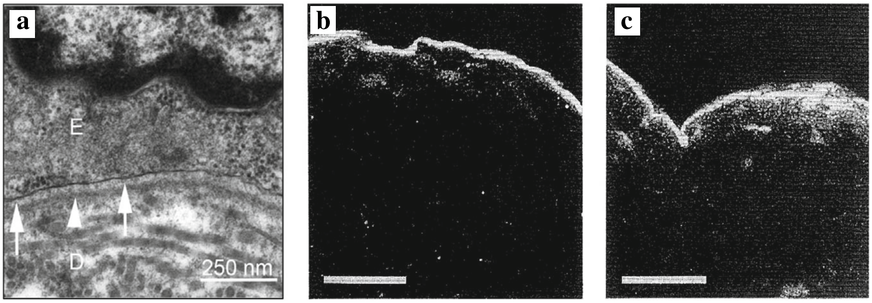

Fig. 2 The basement membrane that forms the dermal-epidermal junction. **a** TEM showing the epidermis, E, the lamina lucida (arrows) and lamina densa (arrowhead) of the basement membrane, and the underlying dermis, D. Bar = 250 nm. (Reprinted from Fig. 4 of Saikia et al., 2018, by permission from Springer Nature). Immunofluorescence, using specific monoclonal antibodies (white is positive) on samples after liming, deliming and pickling, showing **b** type VII collagen, with no bating, **c** laminin, with no bating. Bars = 100 μm (Reproduced from Stephens et al., 1993, by permission of the Society of Leather Technologists and Chemists)

The dermis is the most substantial, inner part of the skin, and supports and provides nutrition to the epidermal layer. It also provides protection to deeper structures in the body through its strength and shock absorbing properties and provides for the initial responses in wound healing (Montagna, 2012). The dermis comprises two zones, the uppermost, thinner papillary dermis, and the deeper reticular dermis which can provide the main bulk of the skin depending on the animal age and species.

The papillary dermis consists of looser connective tissue, containing some elastin and capillaries, and a collagen matrix that is richer in type III collagen compared to elsewhere in the skin (Ramshaw, 1986). There are several collagens associated with the dermal–epidermal junction, but all in small amounts. Nevertheless, despite the low amounts they can have critical roles. Type VII collagen forms the critical anchoring fibril structures that maintain the integrity of the dermal-basement membrane junction, and its absence or mutation leads to blistering diseases (Tamai et al., 2009). Several other fibril-associated collagens are found with the fibrils predominantly in the papillary dermis, including collagen types XII, XIV and XVI, where they may play a role in controlling fibril size (Table 1).

The lower, reticular dermis consists of thicker bundles of collagen, predominantly type I collagen. The type III collagen, which forms mixed fibrils with type I collagen (White et al., 2002), is probably retained but lowers in proportion as type I collagen accumulates. This tissue also contains type V collagen, which plays a key role in the initial fibril and fibre bundle formation (Wenstrup et al., 2004). It is not always evident as it forms the core of the fibrils and becomes masked as tissue accumulates additional type I and type III collagen. The tissue also contains a network of type VI collagen throughout, which may reflect a role in the initial formation of the tissue (White et al., 2014). The underlying reticular dermis contains a variety of cell types, mainly fibroblasts. It also contains elastic fibres, blood vessels that provide for nutrition and waste control, and it supports various appendages.

The appendages are important, integral parts of skin structure (Fig. 1), and comprise the sweat glands with pore exits and the hair follicles, both involved with temperature regulation, and the sebaceous glands that produce oils that are part of the surface film. The sweat and sebaceous glands are both unique to mammals. Fine type III collagen fibrils seem to be in greater concentration near the various appendages, while the minor collagen, type XXII, is associated with hair follicles (Table 1).

Beneath the dermis is the hypodermis or subcutaneous layer (Fig. 1) that consists of connective tissue and fat, which acts as an insulator, along with blood vessels and nerves, and which varies in importance between species, some of which use the skin as a main fat storage depot.

The skins of animals that appeared earlier in evolution than mammals can be used in many cases to make leather, and these skins have distinct characteristics. For example, the marsupials, mainly kangaroo or wallaby, have a skin structure similar to mammals, and produce a leather that is stronger for its thickness than any other leather (Looney et al., 2002). This arises from fine collagen fibres that are arranged more uniformly, parallel to the grain, with a uniform elastin content and a lack of sweat glands and arrector pili muscles. Kangaroo skins frequently have scars, as expected for a wild animal, that prevent its use in large areas in fashion applications. The scars are rich in type III collagen, and generally lead to significant blemishes during processing as the type III collagen in kangaroo is particularly susceptible to loss by proteolytic digestion (Stephens et al., 1988, 1991). In addition, while the main collagenous fibrils in mammals generally have no preferred orientation, in more primitive species the collagen fibrils are often present in layers where the fibres in successive layers are arranged orthogonally to each other (Hawkes, 1974). In other species, significant differences exist with respect to the appendages that are present. For example, there is not hair but rather scales and in birds there are feathers, made of hard keratins. Melanin no longer provides colour, which instead can arise from chromatophores in the dermis, which allow for colour adjustment (Bagnara et al., 1968). Amphibian skin is relatively porous and gases in respiration as well as various chemicals, can be readily absorbed. On the other hand, they frequently have additional glands for host defence, including poison glands in some species (Saporito et al., 2012) and adhesive producing glands in others (Graham et al., 2005). In many species, these variations lead to very distinctive patterning of the surface of a resulting leather, for example with ostriches, with crocodilians, and some fish such as stingrays, which makes these leathers attractive for speciality applications, especially for fashion accessories. These leathers, when properly produced and labelled are often not an issue for those observing some religions where certain mammalian skins can be an issue.

1.2 The Structure and Biosynthesis of Collagen

1.2.1 Structural Considerations

The major protein of skin is collagen. Until 1969, there was thought to be a single collagen protein, now called type I, until a further type, type II was identified from cartilage (Miller & Matukas, 1969). Subsequently, a total of 28 distinct types have been described (Ricard-Blum, 2011). Early studies, necessarily on type I collagen, indicated an amino acid composition for collagen that was rich in Gly, about one-third, as well as Pro and 4-hydroxyproline (Hyp). In 1932, this led Astbury to suggest that a Gly-Pro Hyp repeating unit was a structural element in collagen (Astbury, 1933). It was only some 4 decades later that amino acid sequencing technology had been developed to a stage where data for collagen could be obtained. Combinations of different approaches, including acid and enzymatic hydrolyses, and CNBr cleavage, along with manual and automated Edman sequencing (Edman, 1970) enabled a complete sequence for the α1[I] chain, just over 1000 amino acids long, to be obtained in the mid-1970s, shortly followed by sequences for other fibril forming collagen chains (Fietzek & Kühn, 1975, 1976). These sequences all showed a highly repeating sequence, $(\text{Gly-Xaa-Yaa})_n$, as a characteristic feature, with Pro frequently in the Xaa position while Hyp was generally found in the Yaa position. These sequence data also showed the distribution of the other amino acids, indicating that of the 400 potential Gly-Xaa-Yaa triplets, only a few are frequent, while many, including those with Cys and Trp residues are rare or never found; there were also some strong preferences for certain amino acids in either the Xaa or Yaa positions (Ramshaw et al., 1998). For example, due to steric constraints, amino acids such as Phe, Tyr, or Leu are rarely found in the Yaa position (Ramshaw et al., 1998). While the original amino acid sequencing was slow and tedious, the emergence of DNA sequencing technology and genome analyses has led to a massive increase of the sequence data that are available for study, for all collagen types from numerous species across the full spectrum of the animal kingdom. These data are now readily accessible through, for example, the US National Library of Medicine Databases.

Initial progress in determining the tertiary structure for collagen also went slowly. An initial fibre diffraction was reported in 1921 (Herzog & Jancke, 1921). In 1933, Astbury noted the distinct diffraction pattern obtained from rat tail tendon, (Astbury, 1933). However, it was only at a conference in 1953 that appropriate diffraction pattern photographs emerged, from stretched rat tendon (Cowan et al, 1953). These diffraction studies had clearly indicated that a helical element was present, and a combination of biochemical and biophysical considerations led to the proposal, by Ramachandran, that the tertiary structure for collagen was a triple-helix of three separate chains (Ramachandran & Kartha, 1954) (Fig. 3a). The three-chain model was later supported by additional chemical evidence (Boedtker & Doty, 1956). This broad concept of the triple-helix proved correct, although various refinements were needed before a structure (termed RCII) that accommodated all the experimental

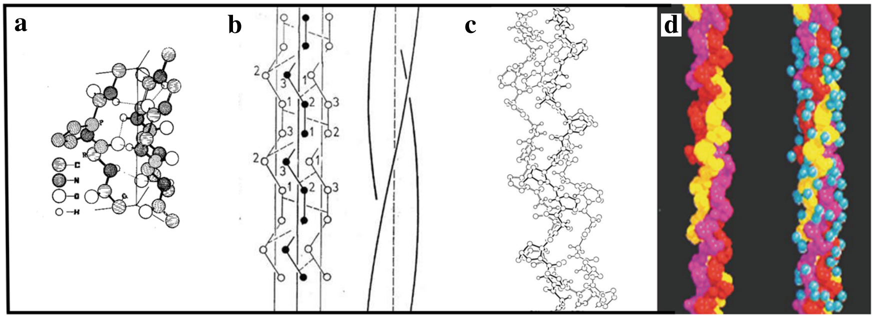

Fig. 3 Key advances in the understanding of the tertiary structure of collagen. **a** The initial proposal of a triple-helical structure (Reproduced from Fig. 1 of Ramachandran & Kartha, 1954, by permission from Springer Nature). **b** A refined structure for collagen consistent with observed properties, (Reproduced from Fig. 2d, e of Rich & Crick, 1961, with permission from Elsevier). **c** A refined molecular model for the collagen-triple helix from X-ray fibre diffraction. (Reproduced from Fig. 3 of Fraser et al., 1979, with permission from Elsevier). **d** A molecular model from an X-ray crystal structure of a collagen-like peptide with well-defined inner hydration. (Reproduced from Fig. 6a, b of Bella et al., 1995, with permission from Elsevier)

evidence, particularly stereo-chemical and hydrogen bonding issues, was achieved (Rich & Crick, 1961) (Fig. 3b).

The structure that emerged, the triple-helix, comprised a three-stranded model in which each chain was in a left-handed helix, and these chains then wound in a right-handed, three-stranded rope-like super-helix, supercoiled about a common axis, with parallel chains staggered by one residue with respect to each other. All three chains in this structure have *trans* peptide bonds and the chain conformation resembles that of the poly-L-proline II structure. This structure allows all the Pro residues, in both the Xaa and Yaa positions, to be included without any distortion. A further feature of this structure was that it placed Gly residues in the centre of the structure, as only Gly, the sole amino acid that lacks a C_β atom, was small enough to fit. This suggested a repetitive amino acid sequence pattern $(\text{Gly-Xaa-Yaa})_n$ that was recognised in early sequence studies and which has become recognised as a characteristic of all collagen molecules (Brodsky & Ramshaw, 1997). Thus, while all Gly residues are buried in the core of the triple-helix, all residues in the Xaa and Yaa positions have considerable exposure to solvent, with the Xaa position being more exposed than the Yaa position. These positions have a high percentage of imino acids and charged residues, although any amino acid could fit these locations. This structure is present in every native collagen, whatever the source, whatever the type and not just those in mammalian tissues.

This model for collagen served well in understanding the structural, biochemical and functional properties of collagen, with the spatial and molecular parameters being defined by Fraser and colleagues in 1979 (Fraser et al., 1979) (Fig. 3c). From quantitative X-ray diffraction data collected from stretched kangaroo tail tendon, the best solution closely resembled the RCII structure. These data gave a value for the unit twist of the native molecular helix of 107.1° ± 0.6°. This value was close to the value expected (108°) for a 10/3 helix (a helix with 10 units in 3 turns) (Fraser et al., 1979), which is now used as the way the native triple-helix is described, although there is no fundamental reason why a naturally occurring helix should have a simple numerical format. (Current crystallographic notation describes a 10/3 helix, with 3.3 units/turn, as a 10_7 helix, while a 7/2 helix, with 3.5 units/turn is described as a 7_5 helix (Bella, 2016)).

Subsequently, a crystal structure for a 30-residue synthetic peptide trimer was determined (Bella et al., 1994) (Fig. 3d). While this followed the expected outline for a triple helical structure, a conundrum emerged in that the helical structure was a 7/2 helix rather than the expected 10/3 helix (Bella et al., 1994). This 7/2 helix was also seen in subsequent peptide-based structures (Bella, 2016). Although the structural difference between 10/3 and 7/2 helices is only small, the difference would lead to major shifts in amino acid positions over the distances of a collagen chain of around 1000 amino acids. However, in all cases, the peptides used for these structures had an unnaturally high imino acid content, much greater than found in any natural sequence of a similar length. But when a peptide structure where a 12-residue naturally occurring segment was sandwiched between $(\text{Gly-Pro-Hyp})_3$ terminal segments was described, the central, natural sequence had a 10/3 conformation, while the imino acid rich terminals had 7/2 structures (Kramer et al., 2001). Thus, it is likely that the overall collagen structure is predominantly close to a 10/3 helix, as indicated by fibre diffraction (Fraser et al., 1979). However, it is likely that some regions that are rich in imino acid content, such as the C-terminal section of the molecule, will tend to transition into a tighter 7/2 helical segment, providing subtle variations along the length of the collagen triple-helical molecule.

The high-resolution crystal structures of the peptide-based triple-helix models for collagen also allowed other features to be examined that could not be established on whole molecules, for example by fibre diffraction. One feature was the hydrogen bonding network, where interchain intermolecular amide (Gly) NH…O=C (Pro) bonds form the innermost and probably most stable H-bonding set, while the presence of regular (Gly) CH…O-C bonds was shown and, in peptides where Pro did not occupy the Xaa position, an additional interchain hydrogen bond, NH (Xaa)…CO (Gly), was observed, formed through one mediating water molecule (Brodsky, 1999) (Fig. 4). While only limited information was obtained on potential side chain interactions that were independent of crystal packing limitations, direct contacts to backbone carbonyl groups the guanidino of Arg side chains in the Yaa-position were seen, potentially accounting for the stability provided by this sequence motif (Yang et al., 1997).

The other important feature to be examined was the hydration network, where ordered water was known to be present that was distinct from bulk water as structural feature that is important in collagen stability (Bella, 2016) (Fig. 3d). The first collagen-like peptide structure that was solved (Bella et al., 1994), had an extensive, complex yet regular hydration network that exists in part as an intrinsic feature of the triple helix (Bella et al., 1995). Thus some 168 water molecules were identified associated with the trimeric peptide structure of 90 residues total, or 10 triplets in length. It was shown that every Hyp OH group along with the C=O of the Gly