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A Review on Collagen as Biopolymer to Produce biodegradable Textiles

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Abstract

The most prevalent protein in the animal kingdom, collagen plays a crucial role in the extracellular matrix (ECM). Resources both natural and manmade are used to extract collagen. The finest materials are those found in nature, such as (fish wastes, animal skin, and Waste Bovine). Due to its availability, affordability, and intriguing physical and chemical properties—particularly its biocompatibility and biodegradability—collagen has garnered significant interest across a number of industries. Nevertheless, collagen has poor chemical and physical properties (enzyme resistance, thermostability, and mechanical strength). Collagen must be altered throughout the processing procedure. Collagen is an environmentally beneficial substance that may be utilized in the dyeing of textiles (wool, cotton), finishing (water repellent, antibacterial, antistatic, and UV protection), printing (3D printing), and the production of biodegradable products.

Keywords: Collagen beneficial substance, biodegradable products, dyeing agent, finishing, 3D printing.

Introduction

The need for comfortable, and health-conscious textile items has grown dramatically during the past ten years. However, there has been a rise in public awareness of environmental preservation and sustainability. Numerous strategies have been used to create safe and useful textiles utilizing greener ingredients and techniques in order to meet consumer and environmental standards. Technologies using supercritical fluids, plasma treatment, and nanotechnology replace traditional textile processing procedures. Additionally, natural and safe processing agents including cyclodextrins, collagen, sericin, and alginate are progressively being replaced by bio-based alternatives. Governments are looking for ways to address the issue of trash generation as a result of the rise in the manufacturing of nonrenewable and nonbiodegradable oil-based plastics globally. [1-5]

A new range of economically feasible smart textile materials called biopolymers is derived from petroleum, agricultural, or animal sources. [6-13] Microorganisms in the environment, such as fungus and bacteria, break down biopolymers; cotton fiber is an example of a complex biopolymer. [2, 14]

Many standardized testing protocols have been developed by researchers to assess the compostability and biodegradability of polymers through the use of mixed cultures. [1] The primary determinants of the market size and breadth of biodegradable polymers, taking environmental dangers into account, are material qualities and cost. The most prevalent protein in the animal kingdom, collagen is essential to the extracellular matrix. Resources both natural and manmade are used to make collagen.

The finest resources are those found in nature. [14] Due to its availability, affordability, and intriguing physical and chemical properties—particularly its biocompatibility and biodegradability—collagen has garnered significant interest across a number of industries. Nevertheless, collagen has poor chemical and physical properties (enzyme resistance, thermostability, and mechanical strength). [1] Collagen must thus be altered throughout the processing procedure. Collagen is a sustainable material that may be utilized to create biodegradable, recyclable, biocompatible, and multipurpose materials that are perfect for emerging technologies in environmental remediation, biomedicine, and materials science. [2, 14]

Collagen

The most prevalent protein in your body is collagen. It makes up around 30% of the total protein in your body. The main component of your body's tendons, ligaments, muscles, skin, and other connective

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tissues is collagen. It's also present in the lining of your intestines, blood vessels, and organs. [8, 13, 15, 16]

Amination and digestion produce proteins. Collagen is primarily composed of three amino acids: hydroxyproline, glycine, and proline. These amino acids come together to create triple-helix protein fibrils. To form the triple helix, your body also need the appropriate concentrations of zinc, copper, manganese, and vitamin C. [8, 13, 15-17]

Some 28 types of collagen types have been identified. They differ by how the molecules are assembled, the cell components that are added and where the collagen is used in your body. All collagen fibrils have at least one triple helix structure.

What the five primary forms of collagen accomplish are as follows:

- **Type I.** Ninety percent of the collagen in your body is this type.Type I is tightly packed and gives your skin, bones, tendons, and ligaments structure.
- **Type II.** Elastic cartilage, which supports joints, contains this kind.
- **Type III.** This kind is present in organs, arteries, and muscles.
- **Type IV.** Your skin's layers contain this kind.
- **Type V.** This kind is present in the placenta's tissue, hair, skin, and cornea of your eyes. [18]

Collagen Structure

In mammals, collagen is the most prevalent type of protein. The three polypeptide chains that make up collagen form a triple-helix protein. The polypeptide chains consist of two (α1) chains that are exactly the same and a second (α2) chain that differs slightly chemically. [19]

Each of the three left-handed peptide chains that make up a collagen's right-handed triple helix is connected by hydrogen bonds and has roughly 1000 amino acids. The smallest amino acid, glycine, occurs every third amino acid in peptide chains, which are made up of sequences that repeat regularly. Proline and hydroxyproline make up the majority of the remaining amino acids. The peripheral places of the triple helix include structurally bigger amino acids, while all glycine residues are located in the center axis.[20]

29 distinct types of collagen have been identified; these are categorized into various families based on their structural and functional characteristics. Physicochemical, densitometric, and spectroscopic properties of collagen, such as molecular organization within and across polypeptides, stability, and elasticity, vary based on the source. [21]

There are currently 40 vertebrate collagen genes known to exist, which produce 29 distinct homo-and/or heterotrimeric molecules. Greek letters stand for the chains, bands, and higher molecular weight components, whereas Roman numbers represent the kind. [19-21]

Functional properties of collagen

The most significant characteristics of collagen, aside from their basic hydration characteristics like swelling and solubility, can be categorized into two groups: those linked to their gelling behavior, such as gel formation, texturizing, thickening, and water binding capacity, and those linked to their surface behavior, such as stabilization and formation of emulsions and foams, adhesion and cohesion, protective colloid function, and film-forming capacity. [22]

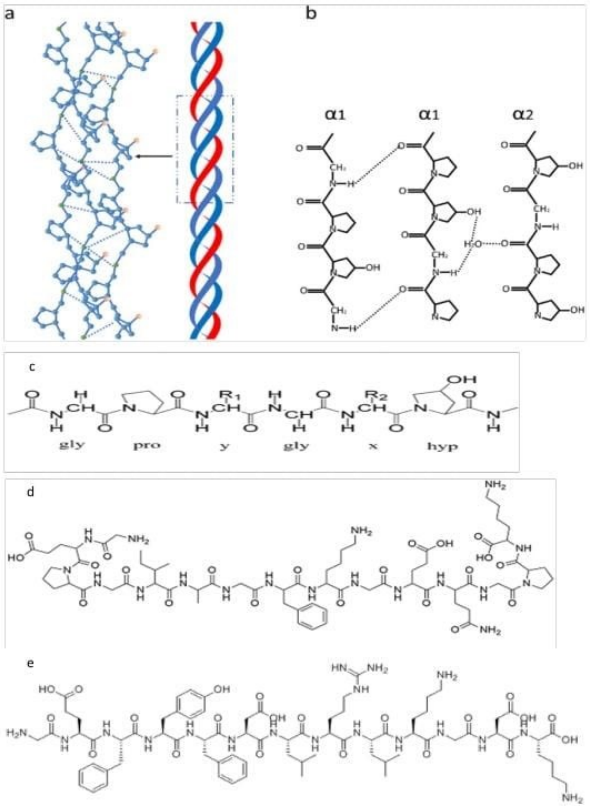

Fig.1. Structure of Collagen

Gelling and water binding properties

The structure, molecule size, and temperature of the system play a major role in determining the closely linked qualities of gel formation, viscosity, and texture. Changes in temperature, pH, and ionic strength cause collagen molecules to aggregate and form fibrils during the collagen gelation process. The main aggregates, or dimers and trimers of collagen molecules, are nucleated during a lag phase of the collagen gelation process. After then, subunits begin to agglomerate lateral to begin microfibrillar aggregation, which continues until equilibrium is established. Collagen gels melt by lowering the temperature, and the self-assembly process of type-I collagen from vertebrates happens when the gelation temperature is elevated from 20 to 28ºC. [23, 24]

Gelatin hydrogels, as they are generally called, are matrices that may swell in the presence of aqueous solutions when collagen strands in solution are covalently cross-linked. Hydrogels can swell to an equilibrium

volume while maintaining their shape. They are distinguished by their hydrophilicity and insolubility in water. Chemical cross-linkers such as polyfunctional macromolecules like glutaraldehyde or relatively tiny bifunctional molecules can be employed. [24]

Surface properties

The presence of charged groups in the side chains of proteins and certain regions of the collagen sequence that include hydrophilic or hydrophobic amino acids determine the surface properties of collagen. Both hydrophobic and hydrophilic components have a tendency to migrate towards surfaces, which lowers the aqueous systems' surface tension and forms the necessary equally charged film around the dispersed phase's constituent parts. Gel formation can further reinforce this film. [22, 25]

Collagen is an insoluble protein, may be presumed to have little significance as an emulsifier. Nonetheless, a 1973 study noted that using collagen offered benefits in relation to milk proteins when it was properly digested. Because of this, isolated or partially pure collagen must be soluble (acid-soluble or pepsin-soluble collagen) in order to exhibit its surface-active characteristics, which can vary greatly depending on the source material. When compared to the equivalent muscle connective tissues, the emulsifying ability of acid-soluble collagen from hake skin was found to be higher than that of trout skin. The acid-soluble collagen from the Pacific Whitting Surimi Refiner discharge was discovered to present in a subsequent research. [22, 25]

Collagen sources

Collagen is produced from both natural and synthetic resources. Plant and animal sources are both good sources for collagen. The most common animal sources of collagen are sea organisms, pigs, humans, and cows. Sternal cartilage is one of the additional landed animal sources.[26]

from domestic birds, lamb, equine, porcine, ovine, and rabbits; from chickens (broiler and laying hens), turkeys, quails, ducks, and geese; and from the skin, tendon, and bones of cows.[17]

The biochemical and physical properties of collagen obtained from marine sources, like scale fish and fish skin, are compara\ble to those of collagen from pigs and cows. Therefore, marine invertebrates and/or teleosts from freshwater and marine environments are viable resources. [25, 27]

Even though these sources are easily obtained and reasonably priced, prolonged use of them might result in allergies and a host of other health problems. Marine collagen is another natural source that doesn't seem to spread disease. Collagenous biopolymers derived from marine invertebrates, cartilaginous fish, and teleost fish have physicochemical and spectroscopic properties similar to:

- Larger ontogenetic gap between humans and fish (lower chance of disease transmission compared to collagen from mammals).
- lack of obstacles based on religion or culture.
- simpler extraction techniques (often assisted by new technologies, such sonication).
- adequate levels of glutamic acid, arginine, and glycine; also, the material has good flexibility, bioresorbability, and glycine and alanine content.
- Lack of toxicity (fish) or little toxicity (marine invertebrates).
- little reaction of inflammation.
- low viscosity and melting point
- favorable homeostatic characteristics. [26-28]

Collagen Extraction from Various Waste Bovine Hide Sources

The primary application of hide, a byproduct of the manufacturing of meat, is in the manufacture of leather. The primary protein found in animal skin, cartilage, and connective tissue is collagen. By extracting collagen from waste hide off-cuttings, collagen can be added value to these materials. Five distinct hide sources were treated with three different extraction techniques. The age, sex, nutrition, and environment of the animal as well as the hide sources varied, which affected the yield of collagen extractables and, thus, the financial benefit of extraction. The highest dry collagen content was from cow hides using the AES2 method (75.13%), followed closely by bull hides at 74.45%. On the other hand, the lowest collagen content was from cow hides (3.80%) with the AS extraction method and the AS method proved to be inefcient for collagen extraction from bull, cow, face-piece and ox-hide sources. Analysis concluded that all the samples were of Type I collagen with α, β, and γ chains. [29]

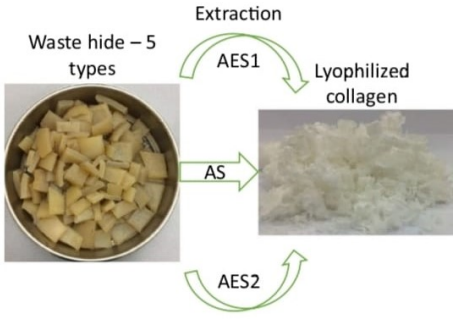

FIG.2. Extracting Collagen from a Range of Waste Bovine Hide Sources

Pretreatment

Before size reduction, hide off-cuttings were dehaired and bleached in NaOH for a whole day. After being cut, samples were cleaned with distilled water. The pre-treated hides were kept cold, at 4 °C, until one of three techniques was applied (Fig.1). Each method's extraction temperature, acetic acid concentration, and

pH are displayed in (table.1). Acid-Soluble (AS) Collagen Extraction

To eliminate non-collagenous material, prepared hide portions were soaked in NaOH for a duration of 6 hours. After the tissue reached a neutral pH, it was rinsed with distilled water. The chunks were acid-dissolved in acetic acid for 24 hours after being soaked in butyl alcohol for 18 hours to defat them. NaCl was used to precipitate collagen, and centrifugation was used to gather the precipitation. Before the pellet was put in the dialysis tubing and dialysed against distilled water, it was dissolved in acetic acid for a whole day. [29, 30]

OR 2. Acid-Enzyme Soluble (AES1) Collagen Extraction

Every step was completed while constantly stirring. Samples of hide were defatted in 20 volumes of 0.1 M NaOH and NaCl for a full day. After that, they were rinsed with distilled water until their pH was neutral. The samples underwent a 24-hour demineralization process in HCl before being neutrally pH-washed with distilled water. After being defatted, the samples were floated for 24 hours while suspended in acetic acid and pepsin. Centrifuging was done after utilizing NaCl to precipitate the collagen in the filtrate and letting it sit at 4°C for 24 hours. After rinsing with distilled water, the collagen-containing pellet was frozen for an entire night and then freeze-dried for 48 hours. [29, 30]

OR 3. Modified Acid-Enzyme Soluble (AES2) Collagen Extraction

A more complete method was created by integrating all of the helpful extraction techniques that have been documented in the literature (AES2). Temperature, length of extraction steps, extraction step repetition, chemical concentration, and purification processes were all adjusted in the AES2 process. Every step was completed while constantly stirring. Pre-treated hide portions were combined with NaOH and NaCl for six hours to defat them. After doing these three more times, the samples were cleaned with distilled water until their pH was neutral. For two hours, the materials were demineralized in HCl and NaCl. To solubilize the collagen, the tissue was immersed in acetic acid and pepsin for 48 hours. Filtered supernatant was used. After using NaCl to precipitate the collagen in the filtrate, it was centrifuged and kept at 4°C for 24 hours. The pallet was dialyzed in acetic acid for 24 hours, and then it was dissolved in distilled water for another 24 hours. Every two hours, the dialysate was changed. After being purified, the extractables were freeze-dried for an entire night. [29, 30]

Lyophilization

LabServ plastic cups containing a predetermined quantity of purified collagen were frozen for an entire night. Following that, the samples were kept in a Freezone 2.5 Labcono freeze drier for 48–72 hours at −52°C and a vacuum of 42.0 Pa. Controlling the temperature is a crucial aspect of collagen extraction. The temperatures employed in this investigation for each extraction process are listed in Table 1. Most researchers employ low temperatures (4°C) for collagen extraction in order to protect the collagen from potential contamination and deterioration. Microbial deterioration or the hydrolysis of enzymes can cause contamination. Nonetheless, extraction has been done at room temperature in certain publications. To see how temperature affected the differences in the characteristics of the collagen, extractions were done both at 4 and 21℃. [29-31]

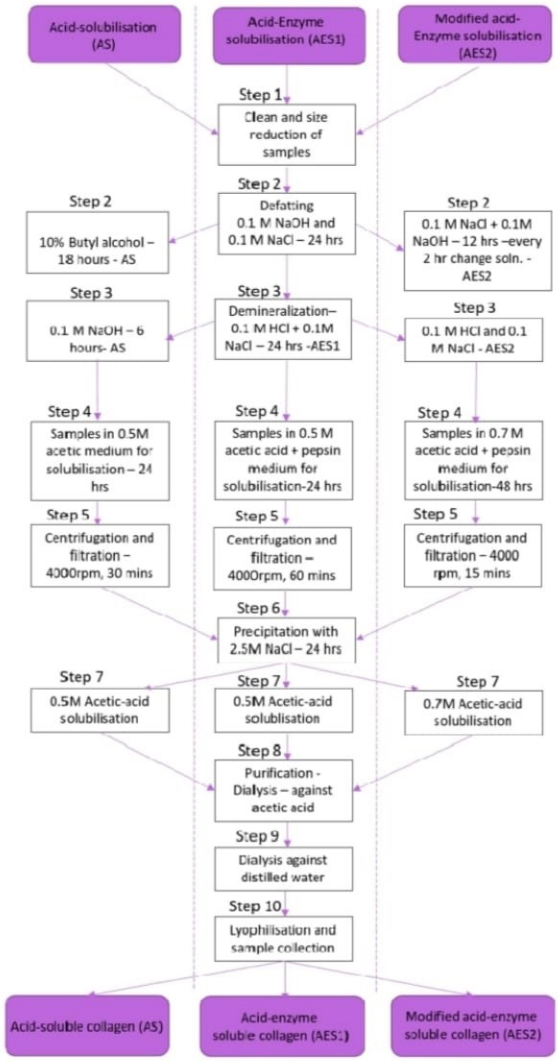

Table.1. Three Methods of Collagen Extraction [29, 30]

Collagen Extraction from animal skin

The collagen extraction process depends on the source material. The aim is to remove all the non-collagenous matter and recover collagen as the final product. The recovery process typically involves pre-treatment of the source tissue, collagen extraction, and further purification. For recovery from skin, the pre-

treatment steps are generally preceded by washing the skin by soaking in cold water for a few days while replacing the water every few hours. This is followed by cutting the skin into more manageable pieces. Typically, skin is cut into small 1 cm2 pieces.[32]

Pretreatment

The goal of pretreatment is to dissociate the covalent bonds that hold collagen molecules together. These crosslinks help collagen perform its mechanical and structural roles in tissues and organs in vivo. Even in boiling water, these crosslinks break down very slowly. [21] Several gentle chemical processes are employed to disrupt the covalent bonds. For partial hydrolysis of the collagen, diluted acids and alkalis are usually utilized. [22] This breaks down the crosslinks but preserves the collagen chains. The pretreatment phase may also involve the use of certain enzymes. [33]

Acid Pretreatment

Skin parts that have been cleaned and cut are submerged in diluted acid at a regulated temperature for acid treatments. [13, 34] The epidermis is penetrated by the acid, which hydrolyzes the crosslinks and causes it to inflate to two or three times its original volume. [35] Skins from fish and pigs that are relatively delicate and have less fiber entwinement are good candidates for acid pretreatment. [36]

Alkaline Pretreatment

For pretreatement, diluted alkalis such calcium hydroxide ($Ca(OH)_2$) and sodium hydroxide (NaOH) are utilized. [32] The thickness of the material to be treated determines how long the pretreatment will take. Collagen may be extracted from thick and hard materials very well with alkalis. The NaOH pretreatment process can take a few days to many weeks to finish. [35] Despite the drawn-out nature of the treatment, alkaline therapy using NaOH is frequently recommended because it causes the skin to expand significantly, which guarantees that the alkali diffuses deeply into the tissue matrix. The undesirable non-collagenous proteins, lipids, pigments, and other organic materials are hydrolyzed by alkalis. The temperature, length of time, and alkali concentration during treatment all have a big influence on how well the undesired non-collagen material is removed. [35] NaOH is adequate for the preparatory step. As long as the treatment temperature remains between 4 and 20°C, a significant portion of the acid soluble collagen and its original structure are preserved in the tissue within this concentration range. [32] A significant loss of acid-soluble collagen may result from a high concentration of NaOH (e.g., ≥0.2 kmol m−3). Collagen that is soluble in acid may lose its original structure when exposed to 0.5 kmol m−3 NaOH. [32]

Skin-Specific Pretreatments

Pretreatments particular to the skin, such as fleshing, dehairing, cutting, and soaking, may be required depending on the source or the type of skin. For instance, different pretreatments could be needed for skins with fur and feathers. You can employ mechanical slicing to get rid of part of the fat stuck to the hide. [36, 37] It is possible to solubilize fat and pigments from the skins of chickens and cows using alcohols such butyl alcohol. Additional pretreatment procedures could involve hot water rinses, heating, detergents, and solvents like hexane and petroleum ether. [38, 39] The application of chelating compounds like ethylene diamine tetra acetic acid (EDTA) may be a phase in the demineralization process. [32, 36, 38]

Extraction Process

Acid Hydrolysis

The most popular method for removing collagen from skin is hydrolysis, which uses either acids or alkalis. Collagen may have its bonds successfully broken by both organic and inorganic acids, allowing the fibrils to be extracted. Collagen molecules undergo a net positive change in acidic environments, which leads to an electrostatic repulsive force between them that promotes molecular separation. [40, 41] Acetic, chloroacetic, citric, and lactic acids are the frequently utilized organic acids. There are numerous reports of acetic acid being used to remove collagen. The most often utilized inorganic acids are nitric, sulfuric, and hydrochloric acids. Compared to mineral acids, organic acids appear to be more successful at cleaving collagen crosslinks and produce a higher extraction yield. [42] Collagens without crosslinks are also soluble in organic acids. for acetic acid extraction while constantly stirring. [32, 40]

Alkali Hydrolysis

Collagen can also be extracted using alkaline hydrolysis, but calcium oxide, calcium hydroxide, and sodium carbonate are other possible extractants. Aqueous sodium hydroxide or potassium hydroxide are the most frequently utilized in this process. [40, 43] Collagen fibrils are often hydrolyzed by alkalis, which may result in the destruction of the amino acids cysteine, histidine, serine, and threonine. Although collagen extracted from leather production waste appears to be the main application for alkali hydrolysis, collagen derived by alkaline extraction of otherwise untreated calf skin has been used to generate a collagen-based flame retardant.[20],[36] [32]

Salt Solubilization

Salt solubilization is a less often employed technique. Neutral salt solutions are widely employed in extraction because they effectively solubilize collagen. [40, 44] When extracting with salts, as opposed to alkaline and acid hydrolysis, careful control is needed. Ex-

amples of the salts employed are citrates, phosphates, sodium chloride, and Tris-HCl. [32]

Enzyme Hydrolysis

Collagen extraction involves the use of proteolytic enzymes. These enzymes can come from microbes, plants, or animals (trypsin, pepsin, bromelain, papain, ficin, etc.). Animal-derived pepsin is most frequently utilized in collagen extraction processes. [40, 44] Only the non-helix (ends) section of the collagen peptide chain is affected by pepsin, trypsin, and papain; the structurally significant helical portion remains unaltered. [44, 45] Furthermore, as the enzyme effectively hydrolyzes the non-collagenous proteins, the recovered pepsin-soluble collagen often has a greater purity. Collagen's acid solubility is also increased by pepsin treatment. [45]

Ultrasound-Assisted Extraction

Applying ultrasound during the collagen extraction process shortens the extraction time and increases yield. [46, 47] Intense turbulence produced by ultrasound increases mass transfer and chemical reaction rates in a liquid. Although sufficiently powerful ultrasonic treatment has the potential to alter protein structure, the structure of the collagen extracted from sea bass skin after acid extraction with ultrasound assistance remained intact. [32, 48]

Table.2. Skin as percentage of total body mass.

Animal	Skin (% *wt/wt*)
Cattle	5.1–8.5
Sheep	11.0–11.7
Pig	3.0–8.0
Goat	~9.0
Chicken	8.0–20.0

Fish Collagen

During fish processing, 50–70% of the waste materials produced are scales, fins, bones, and skin. These waste products are becoming more and more popular as sources of collagen due to their high collagen content. There are numerous extraction techniques mentioned for collagen derived from fish waste. [49, 50]

Collagen Extraction

Pretreatment

To eliminate non-collagenous protein, the source material is chopped, combined with NaOH, and stirred for 24 hours. The treated mass is then filtered through a coarse sieve and cleaned with chilled distilled water. [50, 51]

Extraction

Stir and homogenize for 24 hours while using acetic acid. After centrifuging, gather the supernatant. Using acetic acid, extract the residue once again as before. Collagen that is soluble in acid is the mixed supernatant. Stir the residue and formic acid together for a full day to homogenize it. Stir the pepsin enzyme in and let it sit for 24 hours. After centrifuging, gather the supernatant, which contains pepsin-digestible collagen. For 24 hours, add NaCl and stir. Keep the precipitate suspended in the tris-glycine buffer. Centrifuge after dialyzing against the same buffer. For pre-collagen powder, dry. [50, 51]

Collagen as dyeing improvement agent*:*

Due to the use of numerous chemical compounds, the textile industry is experiencing serious environmental issues, particularly in the wet processing sector. Salts, artificial dyes, and other additives that are frequently used to improve the dye's attachment on fabric are among these goods. Despite the fact that modern dyes have a better affinity for fibers, there are still restrictions on how completely the cloth may be exhausted. The textile sector uses the hydrolyzed proteins to mitigate the harmful effects of chemical agents.

Effect of hydrolyzed collagen in the dyeing of wool

An investigation was conducted into the impact of hydrolyzed collagen during wool dyeing. The major goal of the study was to use hydrolyzed collagen as a dyebath ingredient to increase the reactive and acid dyes' fatigue on wool. [52] Prior to optimizing the amount of hydrolyzed collagen to be added to the dyebath, the ideal dyeing parameters were ascertained. Additionally, research was done to clarify the dyeing process and identify the most suitable percentage of hydrolyzed collagen that could guarantee high dye affinity to wool. The hydrolyzed collagen is a natural and biodegradable product; therefore, the findings are encouraging and help "green" the wool dyeing process. Hydrolyzed protein-treated wool is noticeably softer and is more elastic and tensile strong. [52]

Preparation of hydrolyzed collagen

In order to facilitate the enzymatic action, cowhide waste were first denatured by heat treatment. In a bioreactor, the enzymatic hydrolysis was completed. It was discovered that alkaline protease enzyme worked best at pH 9.5 and 50–60°C for two hours. [52, 53] The enzyme was rendered inactive upon process completion by increasing the temperature to 90°C for a duration of 20 minutes. In order to preserve the hydrolyzed protein, the pH was further increased to 4.5. the entire proportion as well as three distinct fractions (high, medium, and low) determined by the obtained molecular weights. [53]

Dyeing of wool

Conventional process

The acid dye and the three reactive dyes were used to color the wool samples. Acetic acid was used to bring the dyebath's pH down to 4.5, and a material to

liquid ratio of 1:20 was set. An Ugolini dyeing machine was used, and the dyeing was done at 85°C and 40 rpm. [54]

Hydrolyzed collagen based dyeing process

The wool samples were dyed using three different ratios of water to collagen (95:05, 90:10, and 80:20) along with the red, blue, and yellow reactive dyes (Realan Red EHF, Realan Blue EHF, and Realan Amber EHF) and the red acid dye (Telon Red AFG) at two different pHs (pH 4.5 and 5.6). All four hydrolyzed collagen fractions (complete, high, medium, and low) were used in the investigation. The remaining parameters remained unchanged from traditional dyeing. [54]

The colored samples underwent five cycles of 40°C household washing. The K/S (color intensity) values of the cleaned and unwashed samples were measured using the Minolta CM-3600d spectrophotometer.

When dyeing wool with hydrolyzed collagen, the impact of the dyebath pH was investigated; the findings are displayed in Fig. 2. Both cleaned and unwashed samples' K/S values have been established. The sample colored at pH 4.5 had a greater K/S value than the sample dyed at pH 5.6, as was observed. [54]

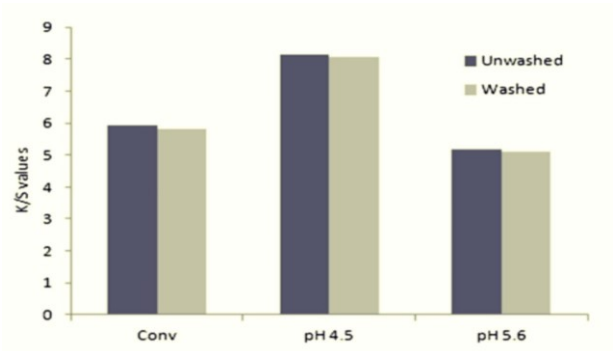

Fig.2. Effect of the dyebath pH in the hydrolyzed collagen process

The ideal ratio of water to hydrolyzed collagen was ascertained. Fig.3 displays the outcomes in terms of K/S values both before and after washing. When compared to the conventionally dyed sample and the other samples dyed even after washing, the sample dyed with the 90:10 percentage demonstrated the highest K/S value, as was expected.

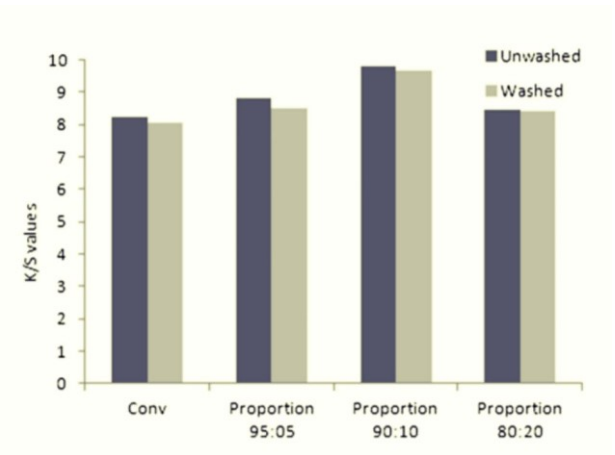

Fig.3. Study of the effect of the hydrolyzed collagen proportion

The K/S values of the wool samples colored with various hydrolyzed collagen fractions, both before and after washing, are displayed in Fig. 4. As was seen, every collagen fraction that had been hydrolyzed performed better than the sample that had been traditionally colored. Furthermore, out of all the dyed samples, the sample that was dyed with the entire proportion of hydrolyzed collagen produced the greatest results. [54]

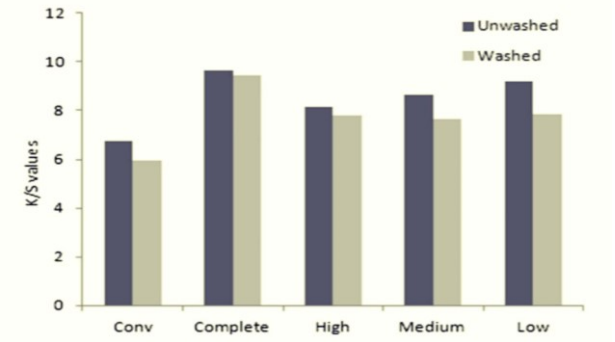

Fig.4. Study of the influence of the hydrolyzed collagen fraction

effect of hydrolyzed collagen in the dyeing of cotton

Compatibility study

A thorough analysis was conducted to determine the total proportion of hydrolyzed collagen's compatibility with each chosen direct and anionic dye. In order to conduct the study, a solution of 95:05 water: hydrolyzed collagen was prepared at pH values of 3, 5, 7, and 9, and then mixed with different dyes. After a 24-hour period, the samples were preserved, and the compatibility was visually assessed. To compare the outcomes, blank research was also conducted without the hydrolyzed collagen.

Conventional cotton dyeing process

Red direct dye (Sirius Red K-BE sodium chloride) was used to dye the cotton samples. The dyeing procedure started with the addition of sodium chloride to the

dyebath. The material to liquor ratio was fixed at 1:20 and the dyeing was done in a Ugolini dyeing machine for 30 minutes at a speed of 40 rpm and 80°C. [55, 56]

Hydrolyzed collagen based dyeing process

In the case of direct dyes, the preliminary screening test revealed that the optimal water:collagen ratio was 90:10. Thus, this ratio of Sirius Red K-BE was used to dye the cotton samples, and hydrochloric acid was used to bring the pH down to 4.7. The full, high, medium, and low fractions of hydrolyzed collagen were used in the investigation. The material to liquor ratio was fixed at 1:20 and the dyeing was done in a Ugolini dyeing machine for 30 minutes at a speed of 40 rpm and 80°C. No salt was applied during the hydrolyzed collagen dyeing process, and the results were compared to a control sample that was dyed using a traditional manner. [55, 56]

The color strength has decreased due to the use of collagen. When colored with hydrolyzed collagen, the low molecular fraction produced the best results out of all the samples. This same pattern persisted even after five washing cycles. Even though the hydrolyzed collagen dye uptake values are lower than in the traditional method, salt-free dyeing is still possible since the hydrolyzed collagen and cotton coordinate at pH <5. Cotton's negative charge is decreased by the electrostatic fixation of the hydrolyzed collagen. Additionally, adding salt to the dyebath is avoided when using hydrolyzed collagen in the dyeing process. [56]

Conversely, it is evident that the dye would not adhere to cotton at pH levels higher than 7, given the repulsion of charges between cotton, dye, and the hydrolyzed collagen. However, it was intriguing to see that direct dyes could be used to color cotton at an acidic pH without the need for salt. [56] Therefore, the hydrolyzed collagen can act as salt to lessen the repulsion of comparable charges and aid in dye fixing, resulting in effluents devoid of salt. Since hydrolyzed collagen is a natural product, there are no environmental problems and it degrades naturally. [55]

the cotton samples dyed with different fractions of hydrolyzed collagen and their washing and rubbing fastness in comparison to traditional dyeing methods. The washing fastness of samples dyed with hydrolyzed collagen is comparable to that of conventional samples. [55] Thus, it demonstrates that the inclusion of hydrolyzed collagen in the dyebath has no detrimental effects on the samples' ability to wash quickly. On every sample, dry and wet rubbing fastness tests have also been performed. Every sample exhibits satisfactory dry rubbing fastness and mediocre wet rubbing fastness results. Thus, hydrolyzed collagen has no effect on the samples' ability to rub together. [55, 56]

Collagen as textile finshing agent

Collagen's impact on cellulosic fibers

In this work, a surface treatment technique is used to functionalize regenerated cellulose fibers using hydrolyzed collagen derived from marine and bovine sources. [57] Fibers infused with collagen undergo a range of characterization techniques, including water-holding capacity investigations, Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and nitrogen estimates. Additionally, performance studies were conducted to assess their advantages. marine collagen made from bone marrow. [57] Collagen infusion significantly improves the material's water-holding capacity, antistatic, and UV protection factor, making it a premium and sustainable option for functional textiles. An analysis of the fabric qualities shows that the freshness and shelf life of the goods have improved. Utilizing collagen derived from animal or aquaculture waste demonstrates the possibility of monetizing waste for textiles. The product's biodegradability complies with the green, sustainable strategy. In conclusion, collagen-modified viscose fibers offer a fresh approach to technological advancement in the textile sector that will have long-term advantages. [57]

Fig.5. Collagen's impact on cellulosic fibers

Production of bacterial cellulose/collagen membranes

These days, a growing number of biomaterials—particularly bacterial cellulose (BC)—have being researched to speed up the healing of wounds. In addition to having perfect qualities, pure BC is now faced with the demands of contemporary wound dressings (antibacterial and anti-inflammatory characteristics, etc.). [58]

Despite earlier attempts to functionalize BC, there is still a strong need for effective and efficient processes to produce composite forms of functional BC wound dressings. In this work, the textile padding method using Collagen, Lactic Acid, Tannic Acid, and Tween 80 has been used to investigate functional fabric-like BC/Collagen membranes for wound dressing. The resulting BC/Collagen has an amazing absorptive capacity (within 30 minutes) and an acidic pH (2.9). [58] It also has an innovative grid-embossing surface morphology, high antibacterial activity (for Escherichia coli and Staphylococcus aureus within just two minutes of contact), hydrophilicity (contact angle of less than 15 within the first second), and compatibility with water and wound exudate. These characteristics have demonstrated that the BC/Collagen membranes that resemble fabric can meet the demands of contemporary wound dressings. [58]

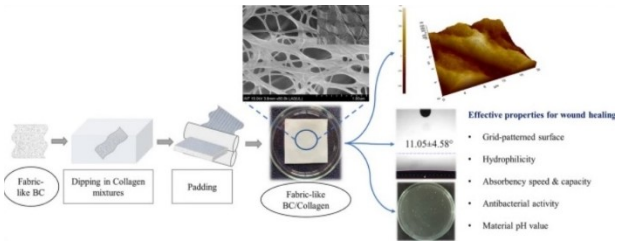

Fig.6. Production of bacterial cellulose/collagen membranes.

Collagen Methacrylamide Microcapsules for modifying nonwoven polyamide fibers

Collagen microspheres with "-CH≐CH_2" (CMAs) were created using waste leather collagen and the emulsification cross-linking process. The resulting modified nonwoven polyamide fibers (PA-CMAs) were subsequently inserted into a nonwoven polyamide fiber material using the "thiol–ene" click chemistry method. [59]

The results of the experiments indicated that the grafting rate could reach 25.83% at a CMA concentration of 6%, an initiator concentration of 0.008%, and an irradiation time of 5 hours. The effective grafting of CMAs onto nonwoven PA materials is verified by means of an X-ray photoelectron spectrometer (XPS) and a scanning electron microscope (SEM). [59]

The results of the stability and fastness test demonstrate the good stability, acid, alkali, organic solvent resistance, and rubbing resistance of PA-CMAs. The results of the contrast test showed that PA-CMAs had superior moisture absorption and permeability than nonwoven polyamide/polyurethane (PA/PU), a synthetic leather-based material that is thought to be one of the standard goods. Furthermore, PA-CMAs kept PA's natural elastoplastic and softness. [59]

Collagen as bioprinting agent

Collagen and chitosan in 3D-bioprinting

Chitosan and collagen are commonly used as biomaterials, especially in 3D bioprinting. Collagen and chitosan (col:chi) mixtures are still not widely used as bioinks, nevertheless. This study examined the rheology of several hydrogel precursors (0.5–1.50% w/v chi: 0.18–0.54% w/v col) at various shear rates and using frequency and strain sweeps. Blends of Col:chi exhibited a shear-thinning characteristic, with viscosity values ranging from 0.35 to 2.80 Pa s at low shear rates. Precursor viscosities during extrusion were in the range of 0.5–0.8 Pa s, taking into account the strain rate ascertained by the applied flow in a 3D bioprinter. [60, 61]

Using photo analysis, printability (Pr) was calculated by comparing photos of the printed meshes with the matching CAD grid design. [60, 61] Col:chi 0.36:1.00 was selected for the printing of mono-layered scaffolds for tissue engineering (TE) due to its appropriate polymer ratio composition, printability, and viscosity. Hydrogels were produced by nebulizing NaHCO3 and incubating it at 37°; NHS/EDC was then added to produce scaffolds with better mechanical behavior. After 44 hours in PBS containing physiological levels of collagenase, they were stable and had no cytotoxic effects on NIH-3T3 fibroblasts. [60, 61]

Collagen: Chitosan (col: chi) Inks

To prepare solutions, low molecular weight powder chitosan (Sigma-Aldrich, 92% deacetylation degree and 46 cps viscosity for the 1% solution) was used. By magnetic stirring at room temperature, a 2% w/v solution was obtained using 0.10 M acetic acid as the solvent. [61]

The final pH was approximately 4.50. Various volumes of chi 2 percent w/v and chi 0.72% w/v stock preparations were used to create col:chi blends, which resulted in the following percentages of w/v: col:chi 0.36:0.50; col:chi 0.54:0.50; col:chi 0.24:1.0; col:chi 0.36:1.0; col:chi 0.18:1.5, and col:chi 0.45:1.5. The final blends displayed excellent miscibility and had a pH of 4.50. They were all kept at 4º and employed as hydrogel precursors, or inks. [60, 61]

3D-Bioprinter

Printing was done using a low-cost bioprinter (3-DonorRes, trademark LIFE SI, Argentina) that included two syringes-one of which was thermostatized. The ejection time, the amount of material in each dot, and the spacing between dots could all be controlled by software settings; these two initial factors were varied in Printability experiments to produce various flows. A 25G needle was utilized in each instance, and there was roughly 1 mm of space between the needle and the bed. Both the deposit bed and the ejection chamber were at room temperature during the extrusion operation. [60, 61]

Conclusion

The most common protein in animals and the primary building block of their skin and bones is collagen. It is one of the many Matrices that are extracellular. Collagen's availability, affordability, and unique physical and chemical properties-such as its biocompatibility and biodegradability-have attracted interest from a wide range of industries. In the textile business, collagen is utilized in a variety of applications, including improving printing, dyeing, and finishing.

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Conflict of Interest

There is no conflict of interest in the publication of this article.

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