Natural Moisturizing Materials and their Nanoparticles

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Abstract. Moisturizing is one of the most important and fundamental functions in the skincare process, and the moisturizing effects of hyaluronic acid, ceramide, and collagen have been widely validated in the skincare field. Hyaluronic acid has excellent water-retention properties, ceramide strengthens the epidermal barrier to reduce water loss, and collagen enhances skin hydration and elasticity. This article combines the development of nanotechnology, first constructing a nanostructure of hyaluronic acid through emulsification, polyelectrolyte complex formation, and gel formation. To further optimize their synergistic effects and delivery efficiency, this study employs the film dispersion method to prepare ceramide-collagen liposomes, encapsulating the active ingredients within the lipid bilayer, significantly improving stability and bioavailability. Meanwhile, the study also explores hyaluronic acid-collagen electrospinning technology to enhance long-lasting moisturization and structural integrity. These innovative technologies not only amplify the inherent moisturizing advantages of the core ingredients but also provide new ideas for the development of multifunctional skincare systems. This research offers a forward-looking strategy for designing next-generation skincare formulations.

Keywords: Natural moisturizing ingredients, Hyaluronic acid, Ceramide, Collagen, Nanotechnology.

1. Introduction

According to studies, the water content of a healthy skin stratum corneum should be maintained at 10% to 20%. The moisture in the stratum corneum can nourish the skin and maintain its health. Insufficient moisture in the stratum corneum can lead to dry skin. When the humidity in the air decreases, the stratum corneum cannot timely adjust enough moisturizing factors, and the activity of sebaceous glands also decreases, resulting in reduced oil on the face. Consequently, the skin can easily feel tight, and fine lines may appear around the eyes and nose[1]. In addition to external environmental factors, the skin can also sustain damage to the stratum corneum due to prolonged exposure to ultraviolet radiation or aging, leading to skin aging.

The different effects of cosmetics mainly target human skin. And water is an extremely important nutrient, the most basic substance of the skin, which can promote healthy, full and radiant skin. Therefore, moisturizing is the most basic requirement of the skin, and cosmetics with corresponding effects are one of the most basic and widely used cosmetics. The primary tasks of moisturizing cosmetics are to maintain and repair the skin's ability to absorb and retain water, as well as to sustain and repair the barrier function of the skin's stratum corneum. However, while striving for effectiveness, it is also crucial to place greater emphasis on the safety of the ingredients in cosmetics. Some traditional chemical moisturizers, such as propylene glycol, have been associated with allergic reactions and other skin issues during use. As a result, the development of moisturizers has shifted towards natural moisturizing substances[2]. At the same time, natural additive cosmetics demonstrate advantages in terms of biodegradability, showcasing more eco-friendly characteristics. Researching and developing natural additive cosmetics has become a significant trend in the cosmetic industry.

Modern natural moisturizers come in a wide variety, including marine polysaccharides, aloe vera, sorbic acid, collagen, ceramides, and hyaluronic acid, all of which can provide moisturizing effects. Among them, ceramides and hyaluronic acid are particularly notable for their moisturizing efficacy. These substances are water-soluble and can engage in hydration reactions, allowing them to enter the skin through the pores, carry moisture, or encapsulate moisture that hasn't yet been lost from the skin to prevent further loss, thus achieving moisturizing effects. In addition to their moisturizing properties, ceramides and hyaluronic acid can also help alleviate skin aging and treat skin inflammation by repairing or filling the stratum corneum.

At the same time, with the application of nanotechnology in moisturizing cosmetics, the utilization efficiency of moisturizing agents has been significantly enhanced. Nanotechnology reduces the size of natural molecules, increasing their skin permeability and enhancing the hydrating effects of moisturizers within the skin. This not only improves the moisturizing effects but also allows for more targeted treatment of related inflammatory symptoms in sensitive skin patients[3].

This article studies three common natural moisturizing materials: hyaluronic acid, ceramides, and collagen, and provides a review of the corresponding nanotechnologies and related composite innovation techniques. Although the use of these nanotechnologies may increase the cost of cosmetic production, the results and economic benefits they bring should not be underestimated, offering significant potential for development.

2. Introduction to Natural Moisturizing Materials

2.1. Hyaluronic Acid

Hyaluronic acid (HA) is a natural polysaccharide and a major component of the extracellular matrix in epithelial and neural tissues. It is widely present in the epidermis and dermis of human skin. Due to its exceptionally high water-binding capacity, it plays a crucial role in skin hydration and is therefore widely used as a moisturizer in cosmetics[4]. HA was first discovered by Meyer and Palmer in the vitreous body of cattle's eyes. It was later found in many prokaryotic and eukaryotic systems. The functions of skin, eye fluid, synovial fluid, and connective tissues largely depend on the amount and aggregation of hyaluronic acid. In the 1950s, the chemical formula of HA was determined, and it was first isolated under physiological conditions as an acid. HA is a non-branching, non-sulfated glycosaminoglycan composed of N-acetyl-D-glucosamine and D-glucuronic acid, which are alternately linked through β-(1→4) and β-(1→3) glycosidic bonds.

The long molecular chains of HA intertwine to form a network structure, with water molecules binding to the HA molecules within this network through hydrogen bonds and polar bonds, creating a hydration film that helps retain moisture. HA has a theoretical water retention capacity of over 500 mL/g, and its actual water retention in connective tissues can reach 80 mL/g. HA has a longer-lasting moisturizing effect compared to other moisturizers and has a higher moisture absorption rate at lower relative humidity (30%) and a lower absorption rate at higher relative humidity (70%). Therefore, it can meet the skin's hydration needs in different seasons and environments. Among all water-binding moisturizers, HA is internationally recognized as the best moisturizing agent in the cosmetic industry[5].

2.2. Ceramides

Ceramides, cholesterol, and free fatty acids are the key components of the stratum corneum. They form a highly organized lipid layer that fills the spaces between the corneocytes. The composition and structure of this lipid layer are critical for the skin's permeability barrier function, forming an effective waterproof barrier[6].

In normal skin, the lipid components in the stratum corneum form a stable orthogonal structure. However, in dry skin, both the quality and quantity of ceramides are reduced, leading to the formation of abnormal hexagonal packing arrangements between cells, which disrupts the lipid layer's homeostasis and impairs the skin barrier function. Ceramides have two hydrophobic chains (LCB and FA), and LCB and LA bind in different combinations, making the amide bond at the binding site amphipathic, with one end hydrophilic and the other hydrophobic. These structural properties enable the formation of tightly packed, mesh-like lipid structures through non-covalent intermolecular forces, thus providing excellent moisturizing effects. Therefore, the exogenous supplementation of ceramides can promote the formation of an orthogonal arrangement of keratinocytes, alter the skin barrier function, and achieve moisturizing and repair effects[7].

Among the various types of ceramides, ceramide 1 and ceramide 3 can repair the lipid barrier and assist in the renewal of the skin's natural protective layer, enhancing the barrier function of the skin's surface and reducing moisture loss, resulting in a moisturizing effect. Ceramide 2 helps maintain the lipid barrier while inhibiting the active secretion of sebaceous glands, balancing the skin's oil and moisture levels, and enhancing the skin's self-protection. Ceramide 6II is a skincare agent that helps repair the skin barrier[8].

The efficacy of cosmetics relies on the active ingredients' ability to effectively penetrate the skin's surface, concentrate at high levels in the skin tissue, and remain in the skin for an extended period, thereby achieving targeted delivery of skincare active ingredients. However, ceramides are highly moisturizing crystals with low solubility, poor water dispersion, and a tendency to crystallize in cosmetic formulations, which limits their application. Currently, ceramides are primarily incorporated into cosmetics in the form of liposomes, microcapsules, and emulsified complexes, allowing ceramide-based moisturizers to fully exert their skin barrier repair functions, thereby achieving moisturizing effects and improving the skin barrier.

2.3. Collagen

Collagen is an important structural protein typically composed of three polypeptide chains, which are connected by hydrogen bonds in a triple helix structure. It contains a large number of polar functional groups such as hydroxyproline, glycine, and aspartic acid, which can bind water in the skin. The network structure formed by the crosslinking of collagen fibers helps maintain skin tension, withstand pulling forces, and preserve skin elasticity. It is an abundant protein, accounting for 30% of the total body protein, and is mainly classified into collagen type I and collagen type III. Collagen type I is the major collagen in skin, tendons, cornea and stromal tissues, accounting for 80-85% of the extracellular matrix of the dermis, and is a kind of fibrillar collagen. Collagen type I is thicker and stiffer, and mainly helps to support the skin and provide the necessary mechanical strength. Type III collagen is the main collagen found in the skin of infants and young children[9]. Like Type I collagen, it is also a fibrocollagen. Compared to Type I collagen, Type III collagen is more delicate and is mainly found between the dermal epidermis, making the skin tissue finer and smoother.

As infants grow into adults, Type III collagen gradually breaks down and decreases, while Type I collagen increases. Due to the differences in the thickness and toughness of the two types of collagen, adult skin is more supportive but less delicate than infant skin. Over time, the body produces less collagen and breaks down existing collagen in the skin at a faster rate, resulting in a decrease in overall collagen levels. This causes the skin to gradually sag and wrinkle. To replenish the collagen in the skin, Type III collagen is often added to daily skincare products. However, due to the relatively high molecular weight of Type III collagen (often in the tens of thousands), it exceeds the skin's transdermal absorption limit, resulting in limited absorption and utilization in cosmetics[10]. Collagen itself has a general moisture retention capacity, but its strong biocompatibility allows it to play a significant supporting role in the formulation of substances like hyaluronic acid and ceramides, enhancing the potential for research and application of these products.

3. Application of Nanotechnology in Moisturizing

3.1. Micro and Nano-structured Formulations of Hyaluronic Acid and Collagen

Polysaccharides are widely used in cosmetics due to their abundance and chemical versatility. Between these two natural polymers, proteins often exhibit high yield and protective costs due to stability limitations. Currently, only collagen, silk, and milk proteins show a sustainable and favorable approach for nanostructured formulations in the cosmetics industry. Thanks to the development of innovative, efficient, and environmentally friendly extraction technologies, the isolation and purification of polysaccharides have become cost-effective, leading to direct and economically advantageous industrial applications.

Polysaccharide-based nanostructures for cosmetic applications are usually realized by exploiting the chemical properties of polysaccharides in interaction with various substances. Linear or branched polysaccharides (e.g., hyaluronic acid) can be categorized into three groups: amphoteric polysaccharides, anionic polymers, and polyelectrolyte polysaccharides. Amphoteric polysaccharides interact with oily compounds, with the hydrophilic groups of the polysaccharide aligned toward the water phase and the hydrophobic groups aligned with the oil phase. Emulsification is then achieved by a high or low-energy homogenization process. Anionic polymers interact with cationic polymers to form micro/nanostructured complexes. Polysaccharides also interact with other synthetic or natural polymers such as proteins. Oppositely charged macromolecules form polyelectrolyte complexes. The addition of small molecule cross-linking agents interacts with polyelectrolyte polysaccharides to form micro/nanostructured hydrogels. Depending on the charge of the polysaccharide, the crosslinking agent can be anionic or cationic[11].

3.2. Ceramide Liposome - Film Dispersion Method

Ceramide nanotechnology is often manifested in the form of liposomes. Ceramide liposomes (cerosomes, CS) are liposomes composed of phospholipids, ceramide, cholesterol, and other components, with a lipid bilayer structure. These liposomes can efficiently deliver encapsulated active ingredients through the skin, offering excellent stability and skin tolerance[12].

The commonly used methods for preparing liposomes include the thin-film hydration method, reverse evaporation method, and ethanol injection method. However, the most widely used method is the thin-film hydration method, which can be used to prepare both water-soluble and lipophilic drugs. When encapsulating lipophilic drugs, the drug is mixed with membrane materials such as phospholipids and cholesterol in an organic solvent, while water-soluble drugs, they are added to a phosphate-buffered solution. The specific process is as follows: phospholipids, cholesterol, and lipophilic drugs are dissolved in an organic solvent, and then the organic solvent is removed by rotary evaporation. Once a transparent thin film appears on the inner wall of the flask, a phosphate-buffered solution containing the water-soluble drug is added and stirred continuously. When the transparent film is completely dissolved, a translucent solution is obtained, which is then filtered to yield the liposome preparation[13,14].

The preparation of ceramide/collagen liposomes also uses the thin-film hydration method[15]. Specifically, egg phosphatidylcholine, cholesterol, and ceramide are weighed, added to anhydrous ethanol, and dissolved by ultrasonic treatment for 10 minutes. The solution is then transferred to a round-bottom flask, and under reduced pressure at 40°C using a rotary evaporator, the anhydrous ethanol is removed, leaving behind a uniform lipid film. Collagen solution and 1% Tween-80 are added to the round-bottom flask, and hydration is performed at 40°C for 1 hour until the film completely detaches, forming a milky white suspension. The suspension is then treated by ultrasonic waves for 10 minutes at 60W power. The resulting collagen suspension is filtered through a porous water-based membrane to obtain a collagen ceramide liposome suspension, which is stored in a dark place at room temperature.

When using the thin-film method to prepare liposomes, the rotation speed during the film formation process should be fast. This not only helps form a thinner, more uniform membrane but also ensures more complete evaporation of the organic solvent. During hydration, the rotation speed should be slow, which facilitates better hydration and is more conducive to obtaining the final product.

4. Electrospinning of Collagen/Hyaluronic Acid Nanofibers

Electrospinning can be used in cosmetics for the preparation of facial masks. Electrospun masks offer advantages such as high surface area and porosity, as well as the ability to load active functional substances. Therefore, HA electrospun facial masks possess excellent water absorption and moisturizing properties, alongside great biocompatibility and biodegradability[16].

HA electrospinning can form gel-like structures due to its strong water-binding capacity. However, the application of electrospinning is limited by its high viscosity and surface tension under conventional conditions. This drawback can be mitigated by mixing HA with other polymers. Collagen has excellent biocompatibility and biodegradability but has the disadvantages of low adsorption capacity, poor selectivity, and inability to withstand high temperatures. Therefore, a nanofiber form of collagen/HA mixtures has been developed, which is well-suited for biomedical and skin care applications. This mixture combines the structural advantages of collagen with the hydration ability of HA.

Electrospinning is the most commonly used method for preparing nanofibers. The needleless electrospinning technique used in the experiment reduces the complexity of the experimental parameters, overcoming the low production efficiency and time-consuming issues associated with traditional single-needle electrospinning. It also avoids common limitations of multi-need array spinning devices, such as poor fiber uniformity and needle blockage. The polymer solution droplet produces a narrow polymer jet in the electric field, and as the solvent evaporates, the jet undergoes stretching forces induced by the electric field to form fiber jets. Finally, the dried nanofibers are deposited on the collector, forming a uniform nanofiber mat[17].

Collagen/HA nanofibers are non-toxic and have excellent skin moisturizing properties. With regular use, this product quickly improves skin hydration and function. Compared to pure collagen, this product exhibits improved tensile strength and elongation. Collagen/HA nanofibers have an advantage over traditional skincare products in maintaining cell growth and vitality without the need for preservatives, offering a healthier and more efficient method for delivering active ingredients. The formulation of collagen/HA mixture provides an eco-friendly alternative to traditional methods by eliminating the need for preservatives and reducing residual waste, thus addressing environmental issues and potential health risks associated with preservatives.

5. Conclusion

Hyaluronic acid, ceramide, and collagen, as natural moisturizing agents, not only have moisturizing capabilities but can also repair the stratum corneum to some extent, helping to reduce skin inflammation. However, natural molecular materials often come with larger molecular structures, which makes it difficult for them to penetrate the stratum corneum effectively when applied topically for optimal moisturization. To improve skin penetration and achieve more efficient moisturizing, nanotechnology is required for preparation. Hyaluronic acid, the most widely used moisturizing material, can form a nanostructure through techniques like polyelectrolyte complex formation, emulsification, and ion gelation. Ceramides can also enhance their skin penetration ability through liposome technology. Collagen itself has moderate moisturizing ability, but due to its strong biocompatibility, it can improve moisturizing and biocompatibility when incorporated into ceramide liposomes, and can also enhance the electrospinning technology of hyaluronic acid, allowing natural moisturizing agents to continually innovate towards the cosmeceutical field. However, due to the low stability of natural materials and the underdeveloped nanotechnology processes, the cost of related chemical products tends to rise. Nonetheless, the increased functionality of moisturizers brings substantial economic benefits. Yet, the preparation of highly efficient moisturizers can only be achieved in small-scale laboratories, and the technical barriers to industrial-scale production have yet to be overcome. Making advanced moisturizing technology accessible to the general public remains a key direction in modern cosmetic research and development.

References

[1] Tao Qinqian, Yan Erping. Research and Application of Wheat Natural Moisturizing Ingredients in Cosmetics[J]. Guangdong Chemical Industry, 2024, 51(04): 40-43.

[2] Hou Yaoyong, Chen Gang, Yang Xiaoling, et al. Research on Moisturizing Cosmetics and Natural Moisturizing Agents[C]//Chinese Academy of Engineering. Proceedings of the 5th China Daily Chemical Industry Symposium. Qingdao Jiurun Fine Chemical Co., Ltd.; 2005: 8.

[3] Zhao Xiaojing, Hong Yanhang, Liu Wei. Nanocarrier Technology - From Transdermal Drug Delivery to Functional Cosmetics[J]. Journal of Daily Chemical Science, 2021, 44(07): 12-16.

[4] Review of Hyaluronic Acid. China Cosmetics, 2021, (S1): 34-35.

[5] Shi Jing, Feng Yun, Bao Jie, et al. Preparation, Properties, and Applications of Natural Biomass Materials (III) — Glycosaminoglycans for Medical and Cosmetic Use: Hyaluronic Acid. Daily Chemical Industry, 2022, 52(03): 237-244.

[6] Watanabe Daisuke, Ishida Koichi, Kaizu Kazuhiro, et al. Physiological Characteristics of Skin in Chinese Women with Sensitive Skin and the Improvement Effect of Low-Irritation Ceramide Cosmetics[C]//Proceedings of the 2023 National Academic Conference on Dermatology and Venereology of Integrated Chinese and Western Medicine. Kao Corporation; Kao (China) Research & Development Center Co., Ltd.; Shanghai Skin Disease Hospital; 2023: 8.

[7] Zhao Bingyi, Yang Hongqin, Pan Qicheng, et al. Evaluation of the Moisturizing and Repairing Effects of Ceramide Complexes in Formulations. China Daily Chemicals Industry, 2022, (08): 70-77.

[8] Luo Dan, Chen Jialing, Wu Yutong, et al. Repairing Effects of Composite Ceramide Nanocarriers on the Skin Barrier. Fragrance and Flavour Cosmetics, 2022, (05): 24-29.

[9] Zhu Yuxin, Mu Yujie, Sun Yang, et al. Analysis of Current Application Status of Common Moisturizers in Cosmetics and Outlook on Research Trends[J]. Chinese Cosmetics, 2022, (11): 80-83.

[10] Yun Xinru, Lu Yangyan, Zhang Guodong. Study on the Skincare Effects of Hydroxy Acids and Type III Collagen. Yunnan Chemical Industry, 2024, 51(09): 61-64.

[11] Massironi, A., Morelli, A., Puppi, D., & Chiellini, F. (2020). Renewable Polysaccharides Micro/Nanostructures for Food and Cosmetic Applications. Molecules, 25(21), 4886.

[12] Kong Weiyi, Li Rongting, Yuan Huanxiang. Application of Nanocapsulation Technology in the Formulation of Active Ingredients for Cosmetics[C]//Cosmetic Industry Branch of the China Anti-Aging Association, CBE Hangzhou International Beauty Expo, China Educational Film and Television Association Education Committee, Beijing National Cosmetic Science and Technology Innovation Research Institute. Proceedings of the 2nd Academic Forum on Anti-Aging Cosmetics in China. School of Light Industry Science and Engineering, Beijing Technology and Business University; Hangzhou Zhiyuan Research Institute; 2024: 5.

[13] Liu Liming. Optimization and Screening of Liposome Preparation Technology and Formulations [D]. Qingdao University of Science and Technology, 2015.

[14] Şahin Bektay, H., Sağıroğlu, A. A., Bozali, K., Güler, E. M., & Güngör, S. (2023). The Design and Optimization of Ceramide NP-Loaded Liposomes to Restore the Skin Barrier. Pharmaceutics, 15(12), 2685.

[15] Tang Chunhui, Zhang Zhenbo, Wu Dongqin, et al. Preparation and Quality Evaluation of Collagen Ceramide Liposomes[J]. Shandong Science, 2024, 37(03): 18-26.

[16] Tören E., Mazari A. A. Needless electrospun collagen/hyaluronic acid nanofibers for skin moisturization: Research [J]. Polymers for Advanced Technologies, 2024, 35(6): e6434.

[17] Partheniadis, I., Nikolakakis, I., Laidmäe, I., & Heinämäki, J. (2020). A Mini-Review: Needleless Electrospinning of Nanofibers for Pharmaceutical and Biomedical Applications. Processes, 8(6), 673.