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Review

Utilization of Natural Polymers in Beauty Product Materials and Evaluation Technology

Tomoyuki Kawasoe

Shiseido Research center
2-2-1, Hayabuchi Tsuzuki-ku, Yokohama, Kanagawa 224-8558 Japan

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A variety of natural polymers such as biologically derived proteins, lipids, and functional polysaccharides are blended as materials for functionality and safety in beauty products. Of these natural polymers, we developed the polysaccharide curdlan (β-1, 3-glucan), which forms an irreversible gel through heating at a certain temperature or higher, as a beauty product material that has a hairstyling function of memorizing a hairstyle when heat from a dryer is applied. We also used a curdlan gel obtained by heating and appropriately molding this curdlan as a substitute for conductive adhesive paste that is generally used to secure electrodes for measuring brain waves to the scalp. On the other hand, in the research and development of beauty products, efforts are also actively underway to develop a technique to objectively evaluate the effectiveness and functionality of beauty products. We also realized a simple, high precision method that uses keratin film fabricated from a protein solution extracted from hair to detect initial hair degradation, which is ordinarily difficult to measure with high precision due to variations such as individual differences and damage history.

Key words: curdlan, β-1, 3-glucan, electrode, keratin film, initial hair degradation

Introduction

A variety of natural polymers are blended as materials in beauty products including biologically derived proteins, lipids, and functional polysaccharides. For example, collagen and elastin, which are the main components of skin, and hyaluronic acid, which is a

Corresponding author: Tomoyuki Kawasoe: +81-45-590-6038, E-mail: tomoyuki.kawasoe@to.shiseido.co.jp

mucopolysaccharide present in joints are often blended in skincare products for purposes of skin protection and moisture retention. In addition, high molecular weight polysaccharides such as carrageenan and xanthan gum, which are also used as food additives, provide a moisture retention effect that retains moisture in the skin and hair, and are also blended as thickening agents to impart thickness and viscosity to product formulations. In some cases, natural polymers are also used in techniques to objectively evaluate the effectiveness, functionality, and safety of beauty products. For example, a three-dimensionally cultured dermis model fabricated using human skin fibroblast cells and collagen is used to evaluate the safety against cytotoxicity and other areas [1].

Of the various natural polymers used in the research and development of beauty products, in this paper, I introduce development and applications of two natural polymers in which I was involved. Polysaccharide curdlan has a unique property of forming an irreversible gel through heating at a certain temperature or higher, and therefore it was developed as a material for beauty products that have a hair styling function. We also examined a curdlan gel obtained by heating and appropriately molding curdlan for using as a substitute of the conductive adhesive paste that is generally used for securing electrodes for measuring brain waves to the scalp. Furthermore, we used a keratin film fabricated from a keratin protein solution extracted from hair to detect hair degradation from everyday ultraviolet light. This type of hair degradation is ordinarily difficult to measure with a high precision due to variations in individual difference and damage history.

Curdlan as a Hairstyling Material [2]

Curdlan, which is used as a food additive such as gelling agent, stabilizer, and thickening agent, is a straight chain β-1,3-glucan having a molecular weight of about 500,000 and β-1,3-linked glucose residues (Fig.1). It is produced from glucose in a culture medium using a bacterium of the microorganism

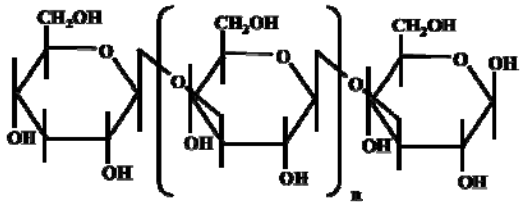

Fig. 1. Structures of curdlan

agrobacterium genus. The solubility of curdlan in water is low in the neutral pH range, and therefore an aqueous solution of sodium hydroxide is added so that the final concentration is 20 mM. After the curdlan is uniformly dissolved under the alkaline condition, the solution is similarly neutralized with a solution of hydrochloric acid to fabricate a dispersed solution.

When the curdlan dispersion solution is exposed to a temperature of about 55°C, a moisture retaining gel begins to form, and in the temperature range of 80°C or higher, the gel exhibits temperature-dependent strength. A low-set gel, which is formed when the curdlan dispersion solution is heated to 55-65°C followed by cooling to ambient temperature or lower, exhibits a thermally-reversible property, while a high-set gel, which is formed when the curdlan dispersion solution is heated to 80°C or higher, is stable with respect to temperature and exhibits an irreversible property [3]. Figure 2 shows a 1% curdlan dispersion solution and a curdlan gel formed by heating at 90°C for 5 minutes.

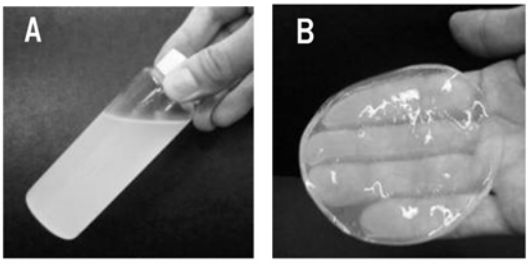

Fig. 2. Ability for gelation of curdlan
A: 1% curdlan dispersion solution
B: curdlan gel formed by heating

The mechanism for curdlan gelation through heating is presumed to be the formation of a triple helix structure by the molecular chain through the formation of hydrogen bonds between the molecules.

In everyday activities, it is inconceivable that living organisms would be exposed to temperatures of 80°C or higher, but when hair is dried and styled after being shampooed, it is heated to temperatures of 80°C or higher using a dryer. Therefore, it was expected that a hairstyle will be immediately fixed through the heat of the dryer by using curdlan which promptly forms an irreversible gel through heating. Polymers that are ordinarily blended in beauty products for hair for providing a hair styling function have often been copolymers of vinyl pyrrolidone and vinyl acetate, copolymers of methacrylic acid alkyl ester and acrylic acid alkyl ester, and other synthetic polymers. Each of these synthetic polymers provides a hard coating after being dried, and therefore when used as a beauty product for hair, they exhibit a hard setting force. On the other hand, a problem with these polymers was that the hair becomes sticky when a coating is formed while the product is applied and dried, and the finished hair is hard and loses its natural texture. In contrast to these conventional materials, a dried curdlan gel film formed by heating at 80°C is flexible and exhibits resistance against elongation stresses (Fig. 3). Moreover, a film formed

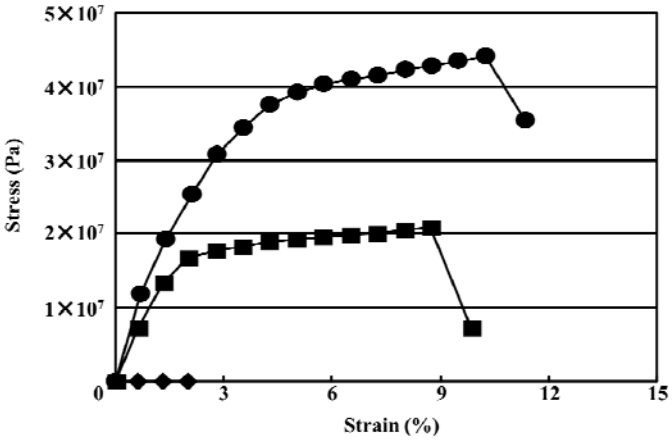

Fig. 3. Stress-strain curve of curdlan film
●: curdlan film after heating
■: curdlan film without heating
◆: vinyl pyrrolidone / vinyl acetate

through heating is insoluble in water, and therefore, an effect of maintaining a hairstyle under high humidity conditions was also confirmed. Figure 4 shows the test results [4] of evaluating curl hold strength at a temperature of 30°C with 90% humidity both with and without heating of the hair coated with curdlan.

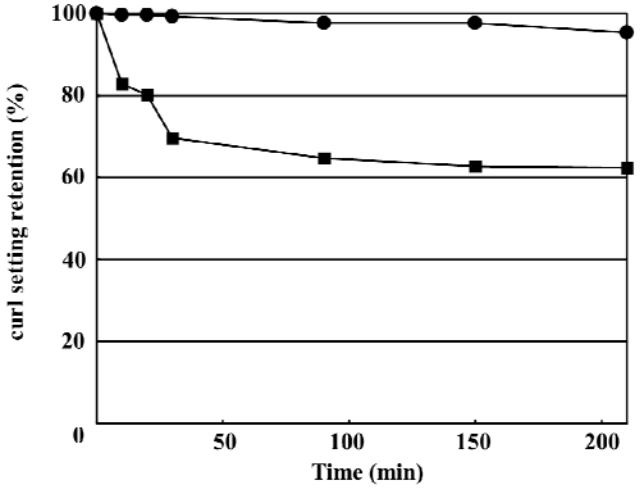

Fig. 4. Curl setting retention of curdlan film
●: curdlan film after heating
■: curdlan film without heating

This curdlan was actually blended in a foam type styling product and marketed as a product with a copy, "memorizing a hairstyle by dryer heat", and became a topic of conversation. While the product does have a disadvantage of not allowing to be subject to a temperature of 55°C or more in the manufacturing process at the factory, it did successfully create a new trend of sustaining a natural finish of hair.

Curdlan as a Material that Contacts the Scalp for Brain Wave Measuring Electrodes [5]

The curdlan gel formed by applying heat exhibits superior ultrasonic wave characteristics and mechanical strength, and therefore it have also been developed as contact medium of high safety for probes of ultrasonic diagnostic equipment [6]. Therefore, we focused on the moderate elasticity and electrolyte-originated conductivity exhibited by the curdlan gel obtained by heating a 5% curdlan gel dispersion solution, and examined use of the curdlan gel in place of the conductive adhesive paste that is used to secure electrodes to the scalp when measuring brain waves. Conventionally, when brain waves are measured, an adhesive base called a paste is used to secure the electrodes to the scalp (Fig. 5A), but after the brain waves have been measured, the paste must be washed off, which is a nuisance. On the other hand, an alternative method is known in which a helmet is worn on the head to measure brain waves without the use of the paste [7]. In this technique, a felt piece impregnated with a saline solution or other electrolyte is used as the contact material between the electrodes and the scalp, but when a helmet is worn for an extended period of time, a headache attributable to the hardness of the felt can occur, and the normal saline solution impregnated in the felt easily evaporates, resulting in a decrease in measurement precision. Therefore, we examined use of the curdlan gel in place of the felt by utilizing the

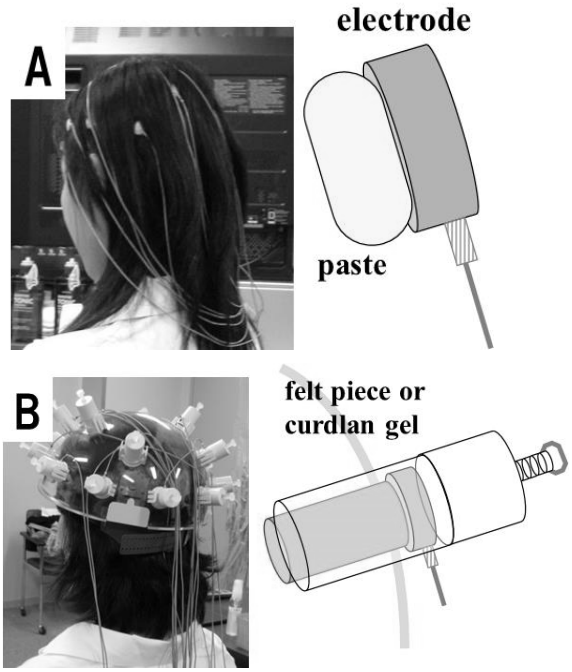

Fig. 5. The illustration of electrode unit for electroencephalography
A: conventional method using paste
B: alternative method without the use of paste

excellent moldability of the curdlan gel (Fig. 5B). As a result, we found that the curdlan gel obtained by heating a 5% curdlan dispersion solution at 80°C for 20 minutes had an elastic modulus of 7.8×10^5 Pa and an electrical resistivity of 3×10^4 Ω·m, no pain was generated by contacting the gel with the scalp, and sufficient conductivity for measuring brain waves was obtained. By using curdlan as a contact material between the scalp and electrodes, we found that the material "does not dry out even when used for an extended period of time," "pressure on the head is minimal," and the "contact surface between the scalp and the electrodes is stable," and thus burdens during brain wave measurements can be significantly reduced. We were able to be involved in this application research because we had participated in the development of curdlan as a hairstyling material.

System for Evaluating Hair Damage Using a Keratin Film

Keratin film is a sheet-shaped material (Fig. 6A) derived from hair protein and produced by casting, to the bottom of a plastic dish. This protein solution is derived in a high concentration from the human hairs of numerous people using a reducing agent solution characterized by thiourea [8]. Like hair, the keratin film is configured by keratin and keratin related proteins, and a fibrous structure accompanied by a granular structure is

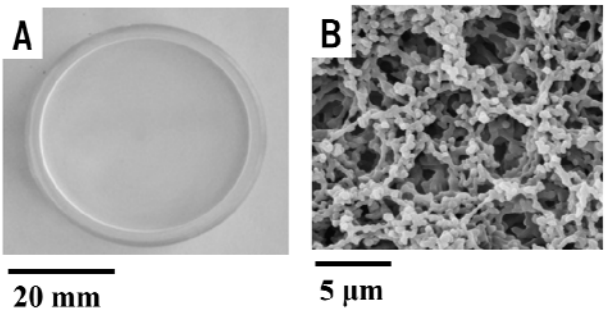

Fig. 6. Morphological observation of keratin film
A: photography, B: SEM image

confirmed through an observation with a scanning electron microscope (Fig. 6B). Because the film exhibiting the same properties can be produced in a large quantity, it was expected that slight hair degradation due to exposure to daily ultraviolet light could be stably measured

with a high precision. Until now, detecting this slight hair degradation was difficult due to individual differences in hair and to variations in the damage history.

Hair is a biological sample of which physical properties can be easily measured, and it is suited for researches because it can be easily sampled and can withstand storages for a long period. Measurements of the tensile strength of a sampled hair in its axial direction are generally used to detect hair degradation, and hair degradation due to hair coloring, perms, and long-term continuous exposure to ultraviolet radiation can be quantitatively determined accordingly [9, 10]. However, hair degradation caused by sunlight exposure through everyday activities without a decrease in tensile strength was difficult to be detected using this technique. In a prior research, we found that hair proteins are non-specifically carbonylated in proportion to exposure time to daily ultraviolet light, and that this phenomenon can be quantitatively determined by using a fluorescent reagent (fluorescein-5-thio-semicarbazide, 5-FTSC) that bonds specifically to carbonyl groups [11]. However, as a trade-off for the high-precisions measurement technique, variations in data due to individual differences in hair and the damage history are emphasized, and thus the problems of individual differences in hair, which is the test substance, and the damage history must be dealt with while maintaining the characteristics of hair such as the production of carbonylated protein.

Therefore, we examined the application of a keratin film in place of hair samples to detect hair degradation from light exposure during everyday activities. We used a keratin film exposed to artificial sunlight for a certain amount of time to detect the carbonylated proteins generated in the film using 5-FTSC, and as a result, we confirmed the increase in the carbonylated proteins in proportion to the

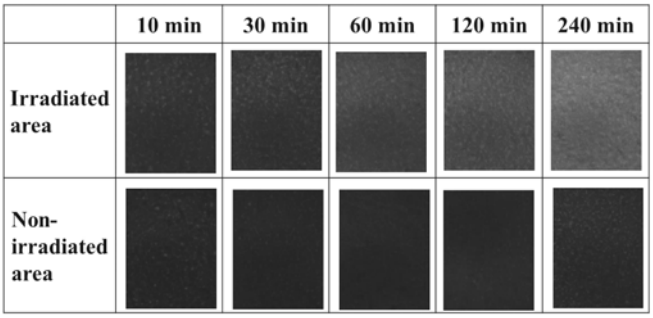

Fig. 7. Fluorescence images of the keratin films reacting with 5-FTSC after artificial sunlight irradiation

light exposure time (Fig. 7). This indicates that the keratin film also undergoes the same oxidation as hair. Moreover, when the film was exposed to light for 10 minutes or longer, the fluorescence intensity increased significantly compared to that of a keratin film not exposed to light (Fig. 8), suggesting a highly sensitive measurements were possible [12]. In contrast to hair of which characteristics easily vary due to individual differences, the keratin film is effective at improving testing precision and reproducibility

because the film shows a similar reaction to hair, which produces carbonylated

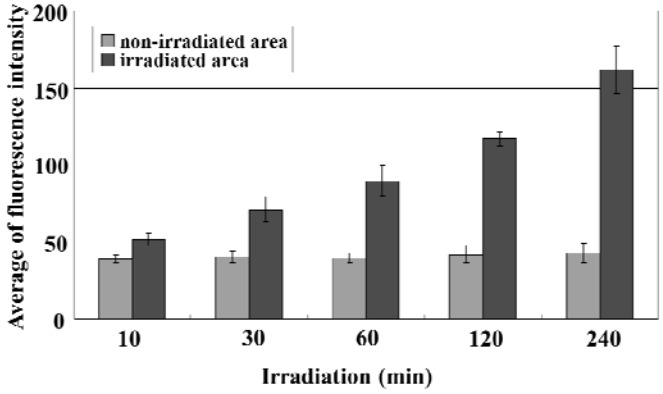

Fig. 8. Average of fluorescence intensity of the keratin films reacting with 5-FTSC after artificial sunlight irradiation

proteins, and the film with the same properties can be produced in a large quantity.

In addition to the light exposure test, because the keratin film can reproduce the same changes occurring to the hair protein when subjected to bleaching, perm applications, and the like with high sensitivity, it has been actively utilized to develop materials to confirm changes due to hair damages and minimize the damages. With respect to the impact of oxidation from bleach treatments, even with a slight oxidation condition, which could not be confirmed with hair samples, cysteic acid could be detected with FT-IR [13]. Moreover, in applications in perm agent treatments, we confirmed that proteins that are eluted during a reducing agent treatment are keratin-related proteins, which suggests that they are indicators of damage due to perm agents [14]. Furthermore, the surface structure of keratin film is sensitive to oxidation-reduction reactions, and its fine morphology changes to smooth when subjected to a reducing agent treatment. Then when an oxidation treatment is performed, a fibrous structure which is accompanied by a granular structure is restored. This unique property of having

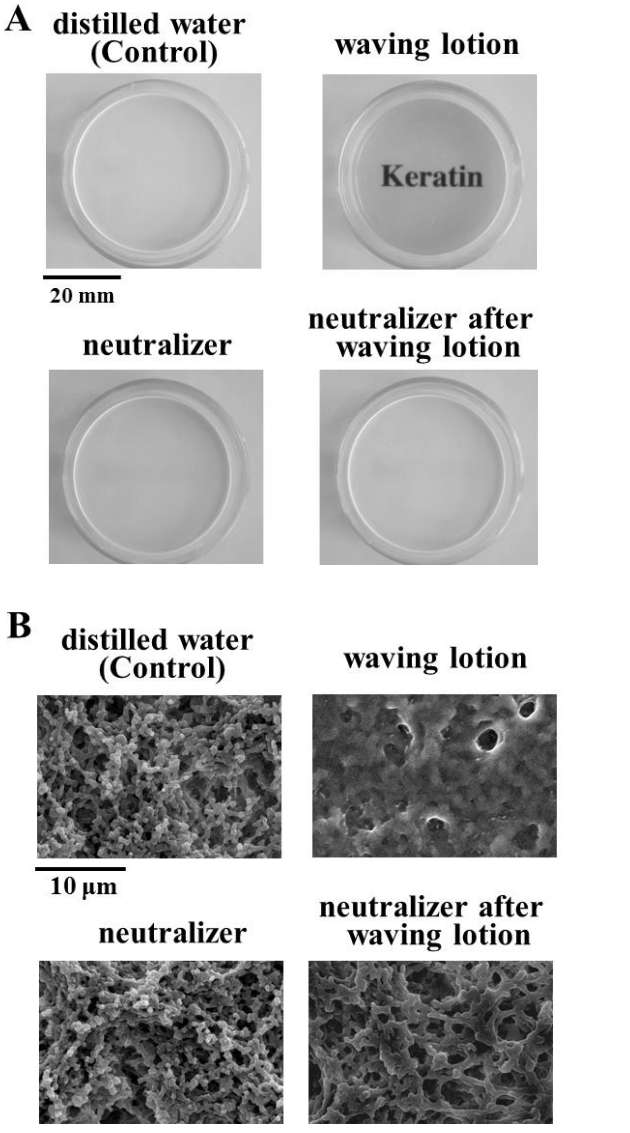

Fig. 9. Morphological observation of the hair keratin films treated with permanent wave solutions
A: photography, B: SEM image

the reversible structural change was confirmed (Fig. 9).

Recently, use of a keratin film to evaluate the frictional properties of shampoo and conditioner has been reported [15] Treatment effects of shampoo and conditioner can be confirmed by measuring a keratin film, to which these products were applied, using a friction sensitivity tester (from Kato Tech Co., Ltd.) Because absorption of silicon compounds, similar to that of hair, can be confirmed, the keratin film was effective for examining conditioner formulations and the tactile sensation of the shampoo. While keratin film does not have a cuticle structure, because an increase in cysteic acid and carbonyl groups resulting from damage can be confirmed, keratin film is also thought to be effective for examining the adsorption of components that can improve tactile sensation on damaged hairs.

Conclusion

The research and development of beauty products consists of elemental technologies from numerous different academic fields. When the characteristics of beauty products are considered, it becomes necessary to integrate these different technologies to find effectiveness in the three areas: functionality, safety, and sensitivity. In utilization of natural polymers in beauty product materials and evaluation technologies, the polymers should be considered not from cost or quality stability perspective, but be positioned as alternatives to biological samples, which have unique functionality that cannot be realized with synthetic polymers. We demonstrated in this paper; a new functionality of curdlan was developed by utilizing its unique property; and a keratin film was applied in a technique to objectively evaluate functionality and sensitivity. Moreover, because curdlan that was developed as a material for beauty products can also be used as the contact material of electrodes for the scalp to measure brain waves, we expect that the keratin film can be widely used in a variety of fields in the future.

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