Synthesis of Damaged Hair Protective Agents using Nanocellulose extracted from Rice Husk and Application of Hair Care Products

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1. Introduction

This study is about the development of a cellulose cationic surfactant using natural cellulose derived from rice husk, and nanofibers made from this raw material. As an application of this, we developed a prescription for shampoo and hair tonic essence, and reported the results of clinical evaluations. Usually, cellulose fibers are classified into various types such as rayon, viscose, acetate, riocell, modal, etc. [1-3]. Cellulose includes microcrystalline cellulose (MCC), hydroxypropyl cellulose, and carboxymethyl cellulose [4-6]. Cellulose is used in paper, fibers, plastics, adhesives, films, and biofuels [7-9]. Cellulose is widely used as an absorbent, a voting agent, a thickener, a film-forming agent, and a filling agent in the cosmetics industry [10-11]. However, its use as a coating agent or as a damaged hair protection agent in the skin or hair has not yet been found. In this study, natural cellulose derived from rice husk is extracted as a recycling material in Korea to discover new materials. This cellulose was nanofibered and studied to be used as a moisturizer or soothing effect. It also aims to develop new raw materials by synthesizing an anionized alkyl chain using this nanocellulose as a hydrophilic group. Finally, by applying this, a prescription for shampoo and hair tonic essence was developed, and the coating power and protective function of damaged hair were studied. In addition, we report the results of a clinical evaluation on the improvement of scalp cleansing power and scalp condition and the increase in moisturizing power.

2. Materials and methods

2.1. Materials

The reagents and materials used in this study are as follows. Cellulose (green growth, Korea), glycidyltrimethylammonium chloride (GTAC), sodium hydroxide (Daejung Chemicals, Korea), trifluoroacetic acid (Duksan General science), SLES, cocamidopropyl betaine (Miwon Corporation, Korea), dipropylene glycol, 1,3-butylene glycol, sodium C14-16 olefin sulfonate (Miwon, Korea), cocamidopropyl betaine (Dongnam Chemicalsynthetic, Korea), sodium chloride (Daejung Chemicals, Korea), disodium EDTA (Daejung Chemicals, Korea), sodium chloride (Duksan General Science, Korea), sodium benzoate (Ducksan Science, Korea), etc. All raw materials used in this study were used as cosmetic grade without any purification.

2.2. Device

Synthetic reactors (Donglim Science, Korea), centrifuges (ROTOFIX 32A, Matech Trading, Korea), microfluidizer (Micronox, Korea), dispensing mixer (K Corporation, Korea), homomixer (K Corporation, Korea), pH meter (Human Corporation, Korea), AramoTS (Aram Hubis, Korea), JANUS Pro (Pie, Korea), Viscomete (Burukufield, Korea), bubble force meter (NabiMRO, Korea), particle meter (Microtrac, Korea), microscope (Olympus, Japan) [12].

2.3. Cellulose extraction and nanocellulose manufacturing methods

5 wt% of rice husk is put in a trifluoroacetic acid solvent and stirred at 70 to 90 °C at 200 to 900 rpm for 48 hours. The residue is removed and the precipitated solid is removed. The solution is separated by a filter to obtain a cellulose solution. It is dried to extract cellulose powder. After dispersing and wetting 3 g of the dried cellulose in 300 mL distilled water, the mixture was stirred with a homomixer at 5,000 rpm for 30 minutes to prepare nanocellulose by passing the mixture 3 to 5 times at 10,000 to 20,000 psi and 25 ° C through a high pressure microfluidizer [13].

2.4. Synthesizing method of cationic cellulose surfactant

In 1 g of nanocellulose, 400 g of 1 M NaOH was added and dispersed for 1 h at 2,000 rpm with a homo-mixer. This was adjusted to 70 °C and reacted for 2 h by adding 45 mmol of glycidyltrimethylammonium chloride. The supernatant was removed and centrifuged, and cellulose hydroxypropyltrimonium chloride was synthesized through washing and pH control [14].

2.5. Performance evaluation of scalp and hair

Prescriptions of shampoo and tonic essence containing a coating agent having cationic cellulose surfactant power were developed and their performance was evaluated. The gloss evaluation through the coating power of hair was visually evaluated through microscopic analysis. The skin condition of the scalp and the effect of improving sebum were measured through high-magnification camera photography. The hair improvement effect was measured through the measurement of the tensile strength of the hair [15].

2.6. Measurement of the moisturizing effect of scalp

The moisturizing effect of the scalp was measured by applying the sample twice a day for 4 weeks to 10 volunteers to improve the moisturizing effect before and after application. In order to minimize the error between the subjects, the lowest and highest measured values were excluded and, the remaining values were averaged. The moisturizing effect of the 5 %-containing hair tonic essence was clinically evaluated by dividing participants into a placebo group and a treatment group before the application. [16].

Table 1. Formula composition of shampoo containing a coating agent with cellulose cationic surfactant.

Phase	Ingredient Name	Control Wt%	Functions
A	Water	62.22	Solvent
	Sodium C14-16 Olefin Sulfonate	11.20	Surfactant
	Lauryl Hydroxysultaine	4.94	Surfactant
	Alcohol	0.96	Solvent
	Sodium Chloride	0.78	Stabilizer
	Sodium Benzoate	0.50	Preservative
	Menthol	0.40	Cooling agent
	C12-13 Alketh-9	0.30	Surfactant
	Caprylyl Glycol	0.20	Preservative
	Disodium EDTA	0.10	Chelating agent
B	Cellulose cationic surfactant*	5.00	Conditioning agent
	Water	10.00	Solvent
C	Citric acid	0.20	Stabilizer
	Water	2.00	Solvent
D	Dipropylene Glycol	0.70	Moisturizer
	Fragrance (Citrus)	0.50	Perfume
Total		**100.00**	

* Cellulose cationic surfactant ; Cellulose hydroxypropyltrimonium chloride

Table 2. Prescription composition of tonic essence containing a coating agent with cellulose cationic surfactant activity.

Phase	Ingredient Name	Control Wt%	Functions
A	Dipropylene Glycol	3.00	Moisturizer
	Alcohol	20.00	Solvent
	C12-13 Alketh-9	1.10	Conditioning agent
	Caprylyl Glycol	0.30	Preservative
	Sodium citrate	0.03	Buffer solution
	Citric acid	0.05	Buffer solution
	Water	73.00	Solvent
B	Cellulose cationic surfactant*	5.00	Conditioning agent
	Water	1.00	Solvent
C	Menthol	0.30	Cooling agent
D	Fragrance (Citrus)	0.15	Perfume
Total		**100.00**	

* Cellulose cationic surfactant ; Cellulose hydroxypropyltrimonium chloride

3. Results

3.1. Cellulose extracted from rice husk

Rice is a staple food in Korea, and rice husks obtained from rice are abundant resources. This rice husk is mainly used for livestock feed or compost of crops, and the rest is a resource that is discarded by nature. The method of extracting cellulose from this rice husk is partially known, and extraction was performed using this method [17]. Fig. 1 shows a photograph of cellulose obtained from rice husk. It has a light specific gravity like cotton, is not soluble in water, and is floating. Dried cellulose is composed of a light yellow fiber, and in order to synthesize a cationic alkyl chain, it must be processed into nanocellulose to easily react, and the performance we want to obtain can be obtained.

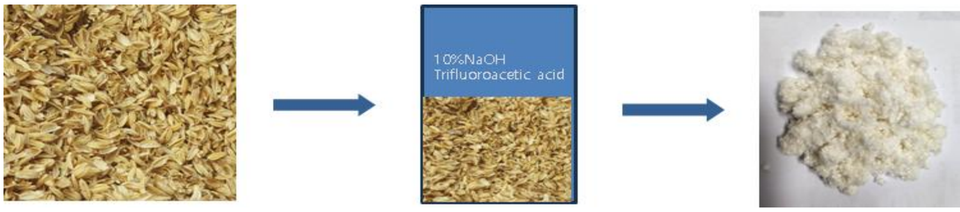

Fig. 1. A schematic diagram of Nano-liposome explaining the skin absorption pathway.

3.2. Development of nanocellulose fiber

Cellulose nanofibers typically have a diameter range from 10 to1000 nm and a length of several to tens of microns and are mainly manufactured using mechanical crushing treatment. It is usually made by crushing from non-wood biomass, which is a wood lump, to a smaller size. Since these raw materials form a rigid structure by combining substances such as hemicellulose and lignin in addition to cellulose [18], various methods are being studied to efficiently crush them. A cellulose fiber-distilled water mixed suspension at a concentration of 1 to 2 wt% is homogenized by placing it in a high-pressure homogenizer. At this time, due to the high pressure, the fibers pass through the thin slit at high speed and receive strong shear and impact forces to nanoize, producing cellulose nanofibers. Fig. 2 shows a photograph of a nanocellulose dispersion. As shown in the picture, it is a transparent or translucent viscous liquid and can be used for various purposes in cosmetics. In this study, we focused on the synthesis of cationic alkyl chains to more advanced nanocellulose head groups.

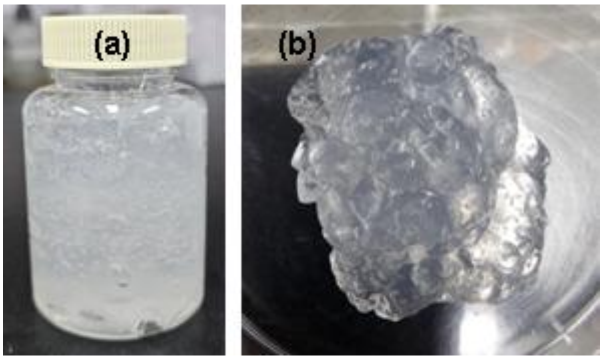

Fig. 2. The picture of nano-cellulose using microfluidizer from rice husk extract.
(a); Bulk, (b); nano-gel

3.3. Synthesis of cationic cellulose surfactants

Synthesis of bonding a cationic polymer was performed using nanocellulose for use as a major coating agent in the hair care market. Figure 3 illustrates the results of introducing glycidyltrimethylammonium chloride onto the cellulose moiety. As depicted in the figure, cellulose exhibits a substantial distribution of hydrophilic -OH groups, and glycidyltrimethylammonium chloride is observed to react with one of these -OH groups, forming a cationic cellulose surfactant. The synthesized cellulose can be referred to as cellulose 2-hydroxy-3-(trimethylammonio) propyl ether chloride and cellulose hydroxypropylmethylammonium chloride. The resulting cationic cellulose demonstrates spontaneous self-assembly at oil-water interfaces via charge-directed assembly. Increased surface cationic charge density enhanced its emulsifying poweras a surfactant.

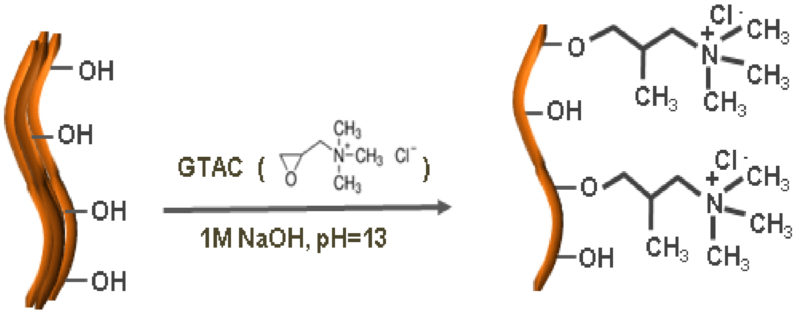

Fig. 3. Synthesis method of cellulose hydroxypropyltrimonium chloride.

In addition, it is expected that it can be widely used for coating power due to its amine group and cationic properties that easily adhere to objects with anionic charge. Cellulose can be moisturized, anti-inflammatory relief, and sedation, and because the alkyl chain with amine charge exhibits a softening effect and a moist and smooth texture, it can be used as a hair care or cosmetic softener.

3.3 Protective effect of damaged hair

Using the cellulose hydroxypropyltrimonium chloride, shampoo and hair tonic essence were applied to the damaged hair to improve the effect. The results are shown in Fig. 4. As shown in the picture, the damaged hair before application showed that the surface of the cuticle of the hair was cracked and rough (a), and the coated state after use was a photograph confirming that the surface of the cuticle was smoothly and uniformly coated to improve the hair in a clean state (b).

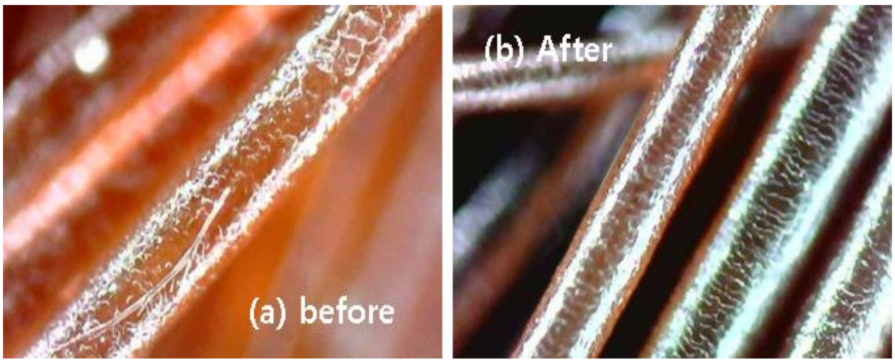

Fig. 4. Photos of damaged hair improvement effects; (a) cuticles before use, (b) cuticles after use.

Fig. 5 is a graph that measures whether the friction coefficient of hair changes according to the amount of shampoo used. As shown in the graph, the hair index before application showed a high value because of its roughness, and the finishing coefficient decreased as the number of uses of Sampo increased. In particular, when shampoo was used 5 times, the friction coefficient was 0.199, which was significantly lower than 0.277 before use. This can be seen as a phenomenon in which the surface of the uncoated hair before use is cracked and rough, and it is considere as a phenomenon in which the friction number of the cuticle increases, and is reduced because it is smoothly coated on the surface after shampooing.

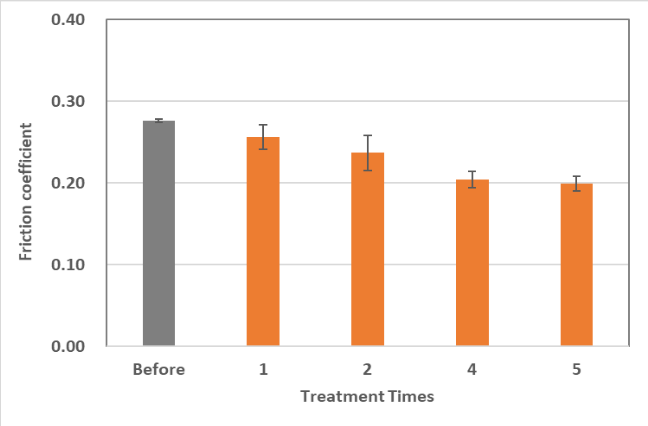

Fig. 5. Friction coefficient of hair according to changes in the number of shampoo uses; before, use 5 times

3.4 Hair tonic essence moisturizes the scalp

Fig. 6 shows the *in-vivo* clinical evaluation results of the moisturizing effect of the scalp with hair tonic essence containing cellulose hydroxypropyltrimonium chloride. Moisturization evaluation was evaluated by applying the most common evaluation method to cosmetics. Ten men and women in their 20s and 60s were selected, and a certain point at the top of the scalp was selected to minimize the error in evaluation. As shown in Fig. 6, the moisturizing power before application was 6.8±1.5%, and the moisturizing power after application was 17.0±3.2%, resulting in an increase of about 10.2% compared to before application. The reason for this was considered that in the sample containing cellulose hydroxypropyltrimonium chloride, the scalp barrier was strengthened and increased by acting on the surface of the scalp.

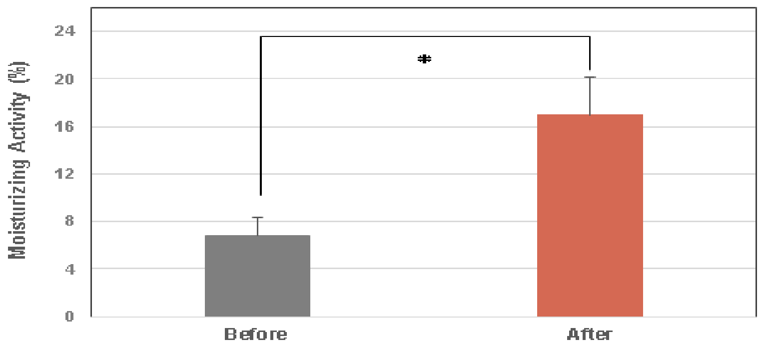

Fig. 6. Moisturizing improvement effect of scalp: Evaluate scalp moisturizing power before and after application.

In addition, the results of observing the scalp condition after 5 uses with a scalp meter are shown in Fig. 7. As shown in the picture, it was found that a lot of sebum was deposited around the pores of the scalp before use, and it was found that the scalp condition after using shampoo 5 times was cleaned.

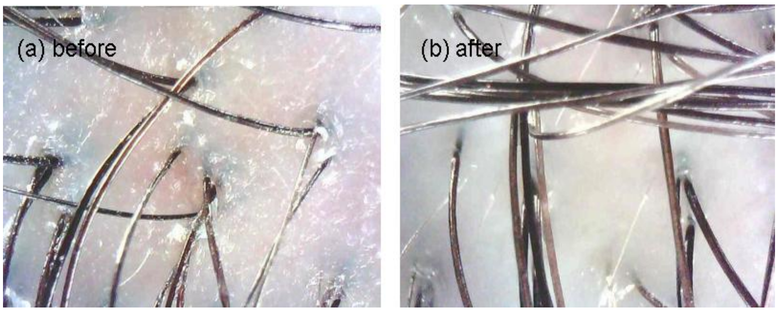

Fig. 7. Improving the barrier enhancement effect on the surface of the scalp

This result was considered to be because the cellulose cationic surfactant not only has a reinforcing effect through hair coating, but also has characteristic performance that contributes to the moisturizing effect and improvement of the scalp.

4. Discussion

The process of extracting and upcycling cellulose extracted from rice husk is of great significance in terms of ESG environment management. It is also considered valuable as a study with high added value by recycling discarded natural materials. In addition, nanocellulose is a fiber with a diameter of 5 to 100 nm and a length of several to tens of micron and is mainly prepared using mechanical crushing treatment. Usually, it is made by crushing it into smaller sizes from non-wood biomass, which is a wood lump. In addition to cellulose, these raw materials combine with materials such as hemi-cellulose and lignin to form a solid structure, so various methods are being studied to crush them efficiently, but developing nanocellulose from rice husk is also expected to be widely applicable in the cosmetics industry in various ways. The most commonly used method for manufacturing cellulose nanofibers in large quantities is. It is a mechanical treatment using a high-pressure homogenizer. The cellulose fiber-distilled water mixture at a concentration of 1 to 2 wt% was homogenized by putting it in a high-pressure homogenizer. At this time, it can be explained that due to the high pressure, the fibers pass through the thin slit at high speed, receive strong shear and impact force, and nanoize to produce cellulose nanofibers. It is expected that by synthesizing cellulose hydroxypropyl trimethyl ammonium chloride, it can exert surfactant activity, has various effects on hair and scalp, and that can be applied to various formulations.

5. Conclusion

The purpose of this study is to extract cellulose derived from rice husk, modify it with nanofibers, discover new materials, and apply them to make healthy skin. A new material with added performance was developed by combining this nanocellulose with a cationic alkyl chain and synthesizing it. A pre-scription for shampoo and hair tonic essence using this was developed and the clinical results for this were summarized. The fiber powder of cellulose was light yellow in a long chain of fibers like thread. A microfluidizer was used to modify it into nanofibers. The product was transparent or translucent and viscous. The particle size of nanocellulose was 50 to 500 nm, forming bulky particles. This nanocellulose was used as a hydrophilic group and a cationic alkyl chain was combined to synthesize a new raw material. The chemical name is cellulose hydroxypropyltrimonium chloride or cellulose 2-hydroxy-3-(trimethylammonio) propyl ether chloride. As a clinical result of shampoo prescription, it was found that damaged hair had a coating effect and a protective effect. In addition, smoothness was improved as the coefficient of friction was reduced. The moisturizing effect of hair tonic essence increased by 10.2% compared to before use. In addition, it was confirmed that the surface of the scalp was removed from the sebum and improved to a healthy scalp. Nanocellulose and cationic surfactants developed based on these research results are expected to be widely applied to the cosmetic industry and hair care products.

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Keywords: *cellulose, cationic surfactants, scalp moisturizing, hair protection, hair care*

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