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"Development of Multifunctional Hydrogel-Coated Illite Microparticles as a Cosmetic Ingredient"

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Abstract

Illite is one of the clay minerals with a plate-like layered structure found in nature. Illite is buried in approximately 500 million tons in Yeongdong, Chungcheongbuk-do, South Korea, known as the world's largest reserve site. In addition, it possesses various functions, including antibacterial effects, negative ion emission, far-infrared ray radiation, harmful substance adsorption, UV blocking, and skin tone-up effect. Due to its beneficial features, it has been used across various fields, such as wastewater treatment, agriculture, food, pharmaceuticals, and cosmetics. However, its more active utilization in the cosmetic industry is limited due to the following disadvantages. Illite may cause discoloration when exposed to light, and the sharp edges of the particles can irritate the skin. Moreover, the heat generated by exposure to light can cause moisture evaporation, making it more difficult to retain moisture over time, which may result in skin dryness. To overcome these issues, the particles were coated by hydrogels. As known, hydrogels with a three-dimensional network structure exhibit excellent biocompatibility, high water absorption and retention capacity, reduced friction, and softening properties. In this talk, the development and characterizations of the hydrogel-coated illite microparticles, for which a patent has been filed, as a cosmetic ingredient will be discussed. First, the control of illite particle size and the optimization of its coating process will be explored. Through coating the particles, skin irritation can be minimized, higher moisture content and longer moisture retention can be achieved, and the possibility of discoloration can be reduced, while maintaining their original functions, such as antibacterial effects, UV blocking, and skin tone-up effects. To confirm their potential as a cosmetic ingredient, the moisture evaporation content over time and the change in roughness were determined. Moreover, sunscreen cream formulations containing the coated illite microparticles were fabricated and characterized. Their sensory properties and biocompatibility through quantitative evaluations performed using rheological measurements and cell viability tests, respectively, will be discussed. As a result, the potential of hydrogel-coated illite microparticles as a highly promising cosmetic ingredient will be discussed.

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1. Introduction

Illite is a clay mineral with an alternating aluminosilicate layered structure of one octahedral layer sandwiched between two tetrahedral layers [1,2]. The 2:1 layered structure, in which potassium ions in the interlayer space induce strong bonds that prevent swelling. Illite, along with kaolinite and smectite, is widely found in clay-rich sedimentary rocks and is considered one of the most abundant clay minerals in the Earth's crust [3,4]. In addition, approximately 500 million tons of illite are buried in Yeongdong, Chungcheongbuk-do, South Korea, known as the world's largest reserve site [5,6]. Illite has non-toxicity, abundance in nature, UV shielding effect, tone-up effect, and ability to absorb pollutants and heavy metals [7-10], it has attracted increasing attention in many industrial fields, including agriculture, food, construction, and cosmetics [11-14].

Hydrogels are hydrophilic polymer materials that possess a three-dimensional crosslinked network structure. Hydrogels have biocompatibility, excellent water absorbency and retention capacity, reduced friction, softening properties and similar mechanical properties to extracellular matrix, stimuli-responsiveness and so on [15-17]. Due to these diverse properties, hydrogels have attracted significant attention in various biofields, such as tissue engineering, agriculture, pharmaceuticals, and cosmetics [18-20]. Hydrogels are generally classified into two types. One is physical hydrogels of which network is formed by non-covalent bonds, as crosslinks, such as hydrogen bonds, ionic bonds, and van der Waals interactions. The other is chemical hydrogels with a chemically cross-linked network structure formed via covalent bonds between polymer chains [21,22]. Depending on the target application, one of the two types is designed and fabricated.

In this study, we aim to treat illites, abundant in South Korea, to promote their more active use as cosmetic raw materials. As mentioned above, illites have various advantages for use in cosmetics; however, they still have some limitations as follows. Illite may cause discoloration when exposed to light, the sharp edges of the particles can irritate the skin, and the heat generated by light exposure can cause moisture evaporation from the skin, resulting in dryness. To overcome these issues, the illite particles were coated with hydrogels. First of all, the size of illite particles was controlled. Then, the size-controlled illite particles were coated by hydrogels in optimized processing conditions. The structural and morphological characteristics of the hydrogel-coated illite particles were investigated. In addition, their moisture retention and surface roughness were measured. Moreover, their biocompatibility was evaluated through cytotoxicity tests. Furthermore, the sunscreen cream formulations containing the hydrogel-coated illite particles were fabricated. Their sensory properties were quantitatively evaluated through rheological measurements and their tone-up performance was checked to confirm their potential as cosmetic raw materials.

2. Materials and Methods

2.1. Size control of illite particles by ball milling and their characterizations

The size of Illite particles was controlled using a ball milling process. Illite and zirconia (ZrO_2) balls (diameter: 2mm) were added in a 500 mL high-density polyethylene (HDPE) container and milled for various durations (2 h, 6 h, and 10 h) The weight ratio of the balls to the milling medium was set to 1:6, and distilled water was used as the medium. All processes were conducted at room temperature conditions. The size and morphology of the size-controlled illite particles were examined by SEM. Based on the SEM images, the size and size distribution of the particles were determined using ImageJ software.

2.2. Fabrication and characterization of hydrogel-coated illite particles

After obtaining the size-controlled illite particles, the particles were coated with hydrogels. First, the homogeneous mixture of monomer, crosslinker, and illite particles was prepared in distilled water and mechanically stirred. Then, an initiator was added to the mixture and the polymerization was carried out for 1 h. Once the reaction was completed, the resulting product was washed to remove unreacted species and dried to obtain hydrogel-coated illite particles.

Various characterizations of the hydrogel-coated illite particles were performed. The surface morphology of the illite particles before and after the hydrogel coating process was observed using a scanning electron microscope (SEM). The chemical structure of the raw and hydrogel-coated illite particles was observed using Fourier transform infrared (FTIR) spectroscopy. Additionally, the moisture content and moisture retention capacity of the illite particles before and after the hydrogel coating were measured using a moisture analyzer. The surface roughness of the illite particles before and after coating was measured using a 3D surface profilometer. Finally, their cytotoxicity was evaluated through cell viability tests using human adult low calcium temperature (HaCaT) keratinocytes.

2.3. Fabrication of sunscreen formulations with hydrogel-coated illite particles and their sensory property and tone-up effect

The sunscreen formulations containing raw or hydrogel-coated illite particles at 8-15 wt% were prepared to check their potential as cosmetic materials. The rheological measurements of the sunscreen formulations containing raw or hydrogel-coated illite particles were performed using a rheometer to assess the flow behavior and sensory properties in order to predict the product's application performance, stability, and user satisfaction. Moreover, the tone-up effect of the illite particles was evaluated to assess their potential to enhance skin brightness.

3. Results & Discussion

3.1. Control of the particle size of illite using ball milling

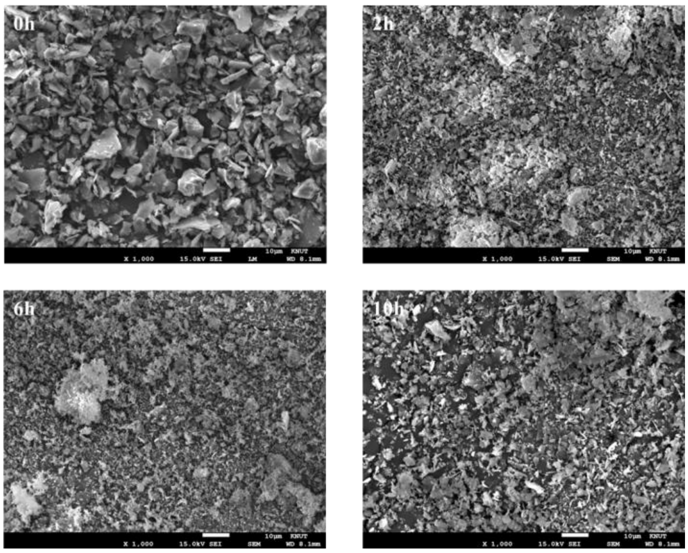
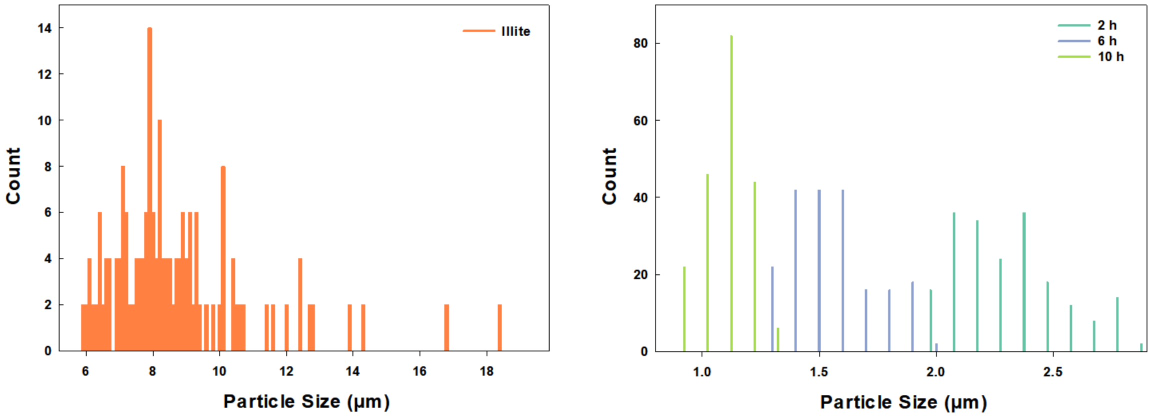


Figure 1. SEM images of illite particles before and after ball-milling for 2 h, 6 h, and 10 h.

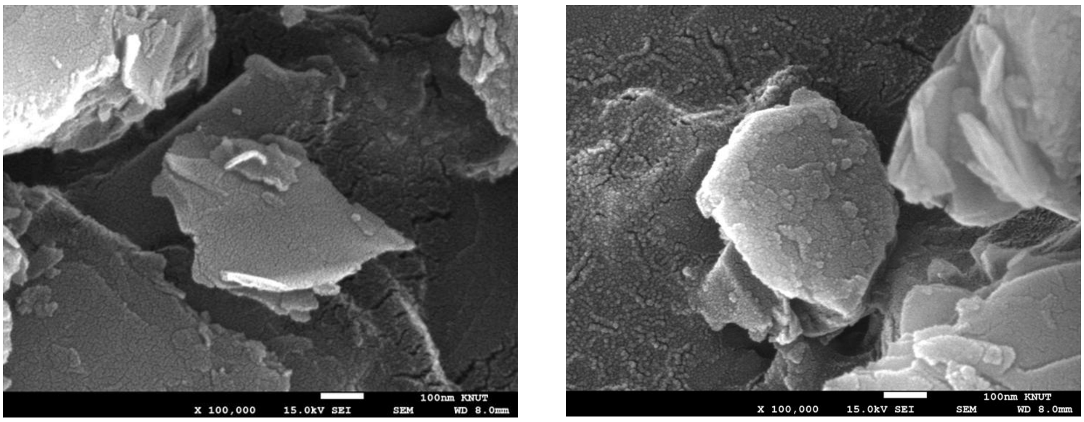


(**a**) (**b**)

Figure 2. Size distribution of illite particles (a) before and (b) after ball milling for different durations (2 h, 6 h, and 10 h).

As shown in Figure 1, the morphology of raw illite particles observed by SEM exhibited sharp edges and a wide range of particle sizes. After their size was adjusted over time through ball milling at room temperature, a significant decrease in particle size was observed over time. Specifically, the size of the untreated illite particles was approximately 8.7 ± 2.2 μm, while the sizes of the illite particles milled for 2 h, 6 h, and 10 h were 2.3 ± 0.2 μm, 1.6 ± 0.2 μm, and 1.1 ± 0.1 μm, respectively. In addition, the size distributions of untreated (0 h) and ball-milled illite particles for different durations (2 h, 6 h, and 10 h) are presented in Figures 2(a) and 2(b), respectively. With increasing ball milling time, the size distribution of the particles became narrower, and the mean particle size decreased. This indicates that the particle size was effectively refined with ball milling.

3.2. Fabrication and characterization of hydrogel-coated illite particles



(**a**) (**b**)

Figure 3. SEM images of (a) raw and (b) hydrogel-coated illite particles.

Once the size and size distribution of the illite particles were adjusted, the particles were coated with a hydrogel to enhance their moisture content and retention, prevent discoloration upon light exposure, and improve their surface smoothness to minimize their potential for skin irritation. The success of the hydrogel coating on the illite particles was evaluated using SEM and FT-IR analyses. Figure 3 shows the SEM images of illite particles before and after hydrogel coating. The raw illite particles (Figure 3a) exhibit sharp edges. In contrast, the hydrogel-coated illite particles (Figure 3b) display rounded and smooth corners, probably due to the hydrogel shell layer coating the illite particles.

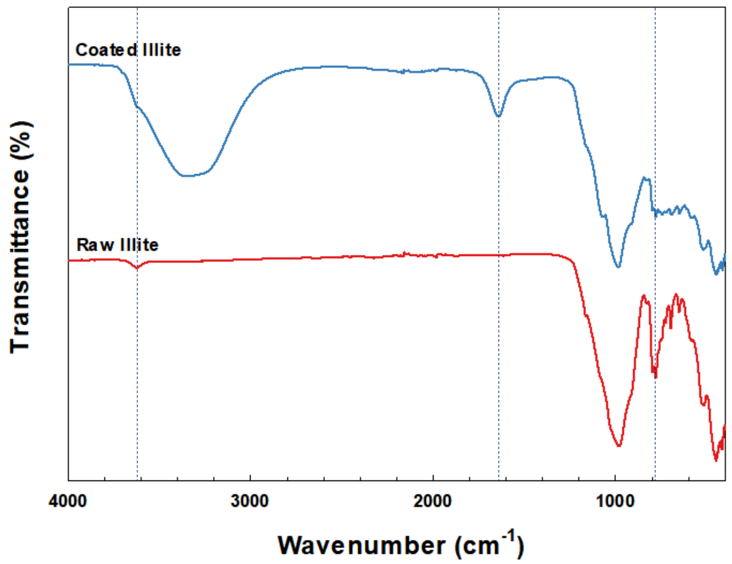


Figure 4. FT-IR spectra of raw and hydrogel-coated illite particles.

Figure 4 shows the FT-IR spectra of raw illite and hydrogel-coated illite particles. The peak at 1638 cm^{-1}, corresponding to the C=O bond originating from a component of the hydrogel, was observed in the hydrogel-coated illite particles, whereas no such peak was identified in the raw illite particles. This finding also confirms that the hydrogel was successfully coated onto the illite particles.

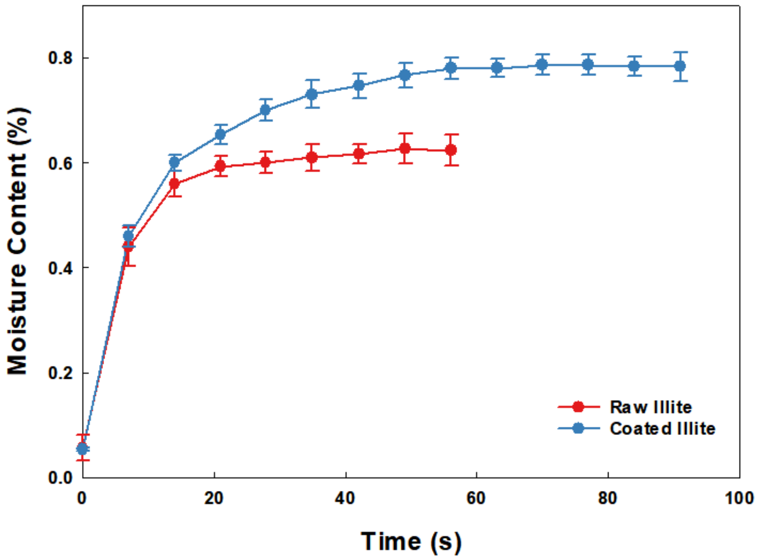


Figure 5. Moisture contents over time for raw and hydrogel-coated illite particles.

In addition, the moisture content over time for the raw illite and hydrogel-coated illite particles was measured to evaluate the effect of the hydrogel coating layer on the moisture content and retention. As shown in Figure 5, the raw illite particles contained up to 0.62% moisture and retained it for up to 57 s. On the other hand, hydrogel-coated illite particles contained up to 0.78% moisture and maintained moisture retention for up to 96 s. These results indicate that improved moisture-holding capacity was due to the hydrogel coating.

Table 1. Comparison of roughness values of raw and hydrogel-coated illite particles

Roughness	Raw Illites	Hydrogel-Coated Illites
Ra	0.92	0.04
Rz	5.16	0.20

Moreover, the determined surface roughness of raw illite and hydrogel-coated illite particles is listed in Table 1. The raw illite exhibited an arithmetic mean roughness average (Ra) value of 0.92, suggesting that the particle surfaces had distinct protrusions and irregularities. On the other hand, hydrogel-coated illite particles had a significantly lower Ra value of 0.04, indicating a flatter and smoother surface, with substantially reduced roughness. The average maximum height of the profile (Rz), representing the average distance between the highest and lowest points on the particle surface, for raw illite was 5.16 μm, whereas that of hydrogel-coated illite particles was reduced to 0.20 μm. This decrease in Rz indicates that the variation in surface height was reduced after hydrogel coating. Collectively, these results confirm that the hydrogel coating effectively reduced the surface roughness of the illite particles.

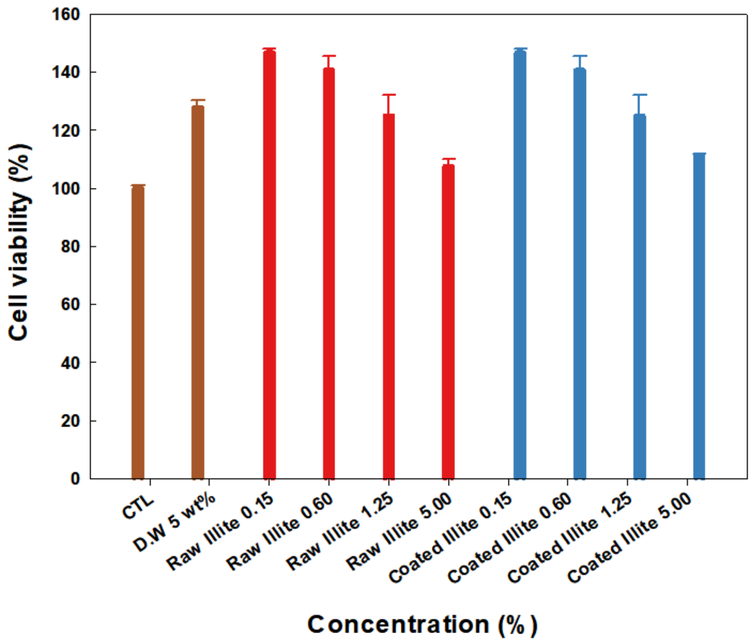


Figure 6. Cell viability of raw and hydrogel-coated illite particles.

To evaluate the safety of raw illite and hydrogel-coated illite particles, cell viability was assessed using HaCaT cells, as shown in Figure 6. According to the ISO 10993-5 standard, dissolution solutions of the particles were treated with HaCaT cells to assess cytotoxicity. Both raw illite and hydrogel-coated illite particles exhibited high cell viability at treatment concentrations ranging from 0.15 to 5.00 wt%, indicating no cytotoxicity and excellent biocompatibility.

3.3. Sunscreen cream formulations containing hydrogel-coated illite particles: Sensory properties and tone-up effect

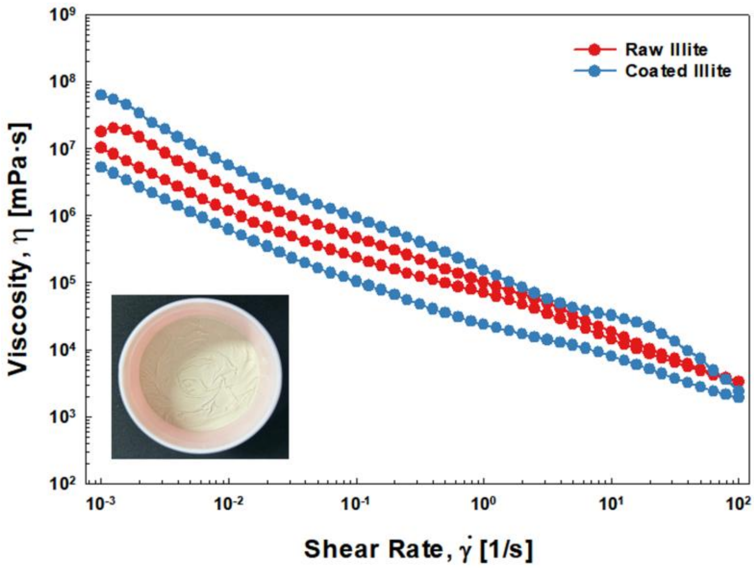


Figure 7. Time-dependent viscosity profiles of the sunscreen formulations containing raw and hydrogel-coated illite particles. Inset image: Tone-up formulation containing 15 wt% of hydrogel-coated illite particles.

To compare the sensory properties of raw illite and hydrogel-coated illite particles, sunscreen cream formulations containing 15 wt% of each illite particle were prepared and their rheological characterization was performed. Figure 7 shows the time-dependent viscosity profiles of the sunscreen cream formulations containing hydrogel-coated illite particles (red solid line with dot markers) and those containing raw illite particles (blue solid line with dot markers). With increasing shear rate, the viscosity values of both formulations decreased, demonstrating shear-thinning behavior. Additionally, the sunscreen cream formulation containing hydrogel-coated illite particles exhibited more pronounced thixotropic behavior compared to that containing raw illite particles. This behavior of the formulation containing hydrogel-coated particles is attributed to the easier breakdown of the internal structure under prolonged shear, leading to a more rapid decrease in viscosity. These results suggest that the greater thixotropic behavior of the formulation containing hydrogel-coated particles are more desirable for cosmetic uses, as it enhances spreadability and sensory properties during application. Overall, hydrogel-coated illite particles contribute to superior rheological and sensory performance in sunscreen cream formulations.

4. Conclusion

This study demonstrated the successful fabrication of hydrogel-coated illite microparticles under optimized coating conditions to enhance their suitability as cosmetic raw materials. Through size control and surface modification via hydrogel coating, the intrinsic limitations of illite for cosmetic use, such as sharp edges, light-induced discoloration, and poor moisture retention were addressed without compromising their original properties. The hydrogel-coated illite particles exhibited improved moisture content and retention capacity, significantly reduced surface roughness and edge sharpness, and excellent biocompatibility. When incorporated into sunscreen cream formulations, they enhanced the thixotropic behavior of the formulation compared to raw illite particles, leading to improved spreadability and sensory performance, while maintaining tone-up functionality. Collectively, these findings demonstrate that hydrogel-coated illite particles are highly promising multifunctional cosmetic raw materials for next-generation cosmetic formulations.

5. References

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