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맞춤형화장품 베이스로서 나노에멀젼 앰플의 물성 평가 및 피부타입에 따른 만족도 평가

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Evaluation of Physical Properties of Nanoemulsion Ampoule as Customized Cosmetic Bases and Evaluation of Satisfaction According to Skin Type

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요 약: 맞춤형화장품은 사회환경 변화와 개성을 중시하는 트렌드에 따른 화장품으로서 지속해서 언급되고 있다. 이에 본 연구에서는 나노에멀젼 제형과 앰플 제형의 비율을 달리함으로써 피부타입에 대응한 나노에멀젼 앰플 4 종을 제조하여, 맞춤형화장품 베이스로서의 적용 가능성을 확인하고자 하였다. 휘발잔분량을 달리한 나노에멀젼 앰플 4 종에 대해, 90 일 동안의 시간에 따른 입자크기, 다분산지수, 제타전위 및 점도를 측정하였으며, 콜로이드 분산계의 안정성 평가방법으로 터비스캔을 측정하였으며, 마지막으로 인체 사용성 만족도를 평가하였다. 결과, 나노에멀젼 앰플 4 종은 지성용 시험품보다 건성용 시험품에서 휘발잔분량이 많음을 확인하였다. pH는 6.41 ~ 6.88 범위이며, 입자크기는 170 ~ 174 nm 범위로 90 일 경과 후 변화는 최대 1.2% 이내로서 입자크기 안정성에는 특이점이 없었다. 다분산지수는 모든 시험품에서 0.21 보다 작은 수치 내에서의 변화를 나타냄으로써 거의 일정하며, 단분산에 가까운 입도 분포를 보이는 것으로 확인하였다. 제타전위는 초기에 4 종의 시험품 모두 −63 mV 이상이며, 시간에 따라 약간 감소 경향을 보이나 최대 2.5% 감소하는 정도로 변화가 거의 없었다. 점도는 초기에 4,100 ~ 5,100 cps 범위로 시간에 따라 감소 경향을 보여 최대 37.7% 감소하였다. 터비스캔 측정에서는 안정성의 척도인 turbiscan stability index가 모두 1.0 이하로 분산 안정성을 보였다. 피부타입에 대응한 나노에멀젼 앰플 4 종의 사용성 만족도 평가(6 점법)에서는 지성용 시험품(5.42 ± 0.67 점) 〉 중지성용 시험품(5.36 ± 0.67 점) 〉 중건성용 시험품(5.15 ± 0.69 점) 〉 건성용 시험품(4.75 ± 0.75 점)의 순으로 평가되었다. 나노에멀젼 앰플 4 종은 물성적으로 안정하며, 피부타입에 따른 맞춤형화장품 베이스로서 적용 가능성을 확인하였으며, 다양한 방법으로 확장 가능성도 기대된다.

Abstract: Customized cosmetics are continuously mentioned as cosmetics in response to changes in the social environment and trends that emphasize individuality. Therefore, in this study, four types of nanoemulsion ampoules corresponding to

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skin types were prepared by different ratios of nanoemulsion formulation and ampoule formulation, and the applicability as a customized cosmetic base was checked. Particle size, polydispersity index, zeta potential, and viscosity according to time for 90 d were measured for four nanoemulsion ampoules with different volatile residues, and turbiscan was measured as a method for evaluating the stability of a colloidal dispersion system. Finally, human usability satisfaction was evaluated. As a result, it was confirmed that four kinds of nanoemulsion ampoules had a higher amount of volatile residue in the dry skin test product than in the oily skin test product. The pH was in the range of 6.41 to 6.88, and the particle size was in the range of 170 to 174 nm, and the change after 90 d was within 1.2% of the maximum, and there was no specificity in particle size stability. It was confirmed that the polydispersity index was almost constant, and showed a particle size distribution close to monodispersity by showing a change within a value smaller than 0.21 in all test products. The zeta potential was initially -63 mV or more for all four types of test products, and although it showed a slight decrease with time, there was little change to the extent of a maximum decrease of 2.5%. Viscosity was initially in the range of 4,100 to 5,100 cps and showed a decreasing trend with time, showing a maximum decrease of 37.7%. In the turbiscan measurement, the turbiscan stability index, a measure of stability, was all below 1.0, indicating dispersion stability. In the usability satisfaction evaluation (6 points) of 4 nanoemulsion ampoules corresponding to skin type, oily skin product (5.42 ± 0.67 points) > neutral oily skin product (5.36 ± 0.67 points) > neutral dry skin product (5.15 ± 0.69 point) > dry skin product (4.75 ± 0.75 points) in the order of evaluation. Four types of nanoemulsion ampoules are physically stable and have confirmed their applicability as a customized cosmetic base according to skin type, and are expected to expand in various ways.

Keywords: *customized cosmetics, nanoemulsion ampoule, turbiscan, skin type, satisfaction evaluation*

1. Introduction

The cosmetics/beauty industry is rapidly changing in recent years thanks to high demand and technological innovation[1]. One of the keywords driving this change trend is ‘customization’, and as consumers' need for personalized solutions increases, the number of products and services that actually meet them is increasing. The advent of ‘customized cosmetics’ is a sign of a major change in the existing cosmetics manufacturing and sales methods. Korea is the first in the world to legislate customized cosmetics and is taking the lead in improving related systems and building industrial infrastructure to strengthen industrial competitiveness. The customized cosmetics industry is accelerating its growth due to the personalized consumption trend of global consumers.

The concept of customized cosmetics includes ① selling products according to individual consumption preferences, ② choosing products according to their skin type by classifying products according to skin type, and ③ recommending or mixing products by experts through accurate skin diagnosis[2].

In the case of customized cosmetics, various products and services have been launched worldwide since the 2010s. If these are classified into four types in the skin evaluation method, the first ‘question-type customized cosmetics’, the second ‘skin diagnosis type customized cosmetics’, the third ‘gene diagnosis type customized cosmetics’, and the fourth ‘technology convergence customized cosmetics’, and there is also a type in which the four are properly mixed. If the process according to the sales of customized cosmetics is divided into 4 stages, stage 1 is ‘a process of identifying skin conditions and concerns’, stage 2 is ‘selection of products according to diagnosis’, and stage 3 is ‘mixing and subdividing products’, and finally, stage 4 is the ‘packaging and delivery method’[3].

According to the Korea Cosmetic Industry Institute's 2019 skin characteristics bank construction report by country, the skin moisture content, transepidermal water loss, and skin sebum amount were measured according to the age of 20 to 50 in the skin type survey of Koreans. There was a relatively large difference in the amount of skin sebum rather than the amount of percutaneous moisture loss[4]. For healthy skin, the amount of oil and moisture in the skin is important, and skin types can be classified based on these contents. In general, it is classified into four types; dry skin, neutral skin, oily skin, and combination skin according to the amount of oil and moisture in the skin. Problem skin types can be divided into sensitive skin, acne skin, aging skin, etc. These skin types can always change according to factors such as age, climate, season, sleep state, cosmetic use (side effects), and stress.

In the previous study, as the second stage of the customized cosmetic process, four types of liposome essences corresponding to skin types with different ratios of liposome base and essence base were manufactured by developing a customized cosmetic base related to 'selection of products according to diagnosis'. Applicability as a customized cosmetic base according to skin type was confirmed[5]. Based on this, in this study, 4 types of nanoemulsion ampoules corresponding to skin types were developed with different ratios of nanoemulsion base and ampoule base.

Nanoemulsion formulations generally refer to emulsions having a particle size of a nano level (usually 20 to 200 nm), they are classified as oil-in-water (O/W) or water-in-oil (W/O) emulsions[6]. In addition, nanoemulsions are known to be stable against sedimentation, creaming, aggregation and coalescence due to Brownian motion of the particles by minimizing the effect of gravity because the particles are very small[7]. In addition, due to various advantages such as differentiation of properties due to small emulsified particles, rapid skin absorption, and improved skin absorption of active ingredients, the importance of nanoemulsion as a carrier of physiologically active substances is gradually increasing[8,9].

In this study, the nanoemulsion formulation ampoule that can respond to skin types and can be easily mixed and provided on site is composed of a nanoemulsion formulation and an ampoule formulation, and by mixing them in a certain ratio, the product responds to 4 types of skin types (oily, neutral oily, neutral dry, dry) can create. Therefore, four types of nanoemulsion ampoules were prepared and the stability of the product was evaluated by measuring the change in physical properties over time, and the possibility of use as a customized cosmetic base for skin types was confirmed through the evaluation of human usability satisfaction.

2. Materials and Methods

2.1. Reagents and Instruments

The nanoemulsion ampoule in this experiment was composed of nanoemulsion bases using a PEG-free surfactant, ampoule bases, and active ingredients. First, polyglyceryl-10 stearate (Sunsoft Q-18Y-C, Taiyo Kagaku Co., Japan), stearic acid (Palm-Oleo Sdn. Bhd., Malaysia), glyceryl stearate citrate (Dermofeel PA-12, Dr. Straetmans GmbH, Germany), glycerin and inulin lauryl carbamate (Inutec SL1, CreaChem BVBA, Belgium), glycerin (Acid Chem Co., India), *Limnanthes alba* (Meadowfoam) seed oil (meadowfoam seed oil, Kerfoot, UK), octyldodecanol (Paester R-20SP, Patech Fine Chemicals Co., Taiwan), cholesterol (Cholesterol JP, Nippon Fine Chemical Co., Japan), glyceryl caprylate (Dermosoft GMCY, Dr. Straetmans GmbH, Germany), ethylhexylglycerin (Saskine 50, Sachem Co., USA), butylene glycol (1,3-butylene glycol, Daicel, Japan), 1,2-hexanediol (TW-HD, Twin Coschem, Korea), sodium stearoyl glutamate (Eumulgin SG, BASF, Germany) were used to prepare the nanoemulsion base, and water (purified water) prepared by a distilled water maker (Pure RO 130, Human Co., Korea) (< 3 μS/cm) was used.

In addition to the ampoule base manufacturing, functional whitening agent niacinamide (Niacinamide USP, Western Drugs, India), functional wrinkle improvement agent adenosine (Adenosine, Sharing Technologies, Co., China), betaine (Genencare OSMS BA, IFF Health & Bioscience, Netherlands) , glyceryl polymethacrylate and butylene glycol (creagel CG BG NP, CCW, France), ammonium acryloyldimethyltaurate/VP copolymer (Aristoflex AVC, Clariant, Switzerland), xanthan gum (Keltrol-F, C.P. Kelco, USA), carbomer (Carbopol 940, Lubrizol, USA) and arginine (L-Arginine, Ajinomoto Co., Japan) were used.

As active extracts, *Chrysanthemum indicum* flower extract as a moisture/moisturizing ingredient for skin moisturizing power, *Styrax japonicus* branch/fruit/leaf extract, *Saururus chinensis* extract and *Akebia quinata* extract as raw materials that can help improve wrinkles, *Acanthopanax koreanum* extract, *Styrax japonicus* branch/fruit/leaf extract and *Brassica napus* flower extract as anti-pigmentation raw materials, *Akebia quinata* extract and *Leonurus sibiricus* extract as raw materials for sensitive skin were obtained from Coseedbiopharm (Korea) and used. In addition, *Sasa quelpaertensis* extract was obtained from The garden of natural solution (Korea).

A homo-mixer (T.K. auto homomixer mark Ⅱ 2.5, Tokushukika, Japan) and a high-pressure homogenizer (nanodisperser, NLM1000, Ilshin autoclave, Korea) were used to prepare the nanoemulsion base, and an agi-mixer (overhead stirrer, SL 4000, Global Lab, Korea) was used to prepare the ampoule base.

Table 1. Formula for Nanoemulsion Base

Phase	Ingredient	wt%
Surfactant phase	Stearic acid	0.2
	Glyceryl stearate citrate	0.5
	Glycerin and inulin lauryl carbamate	0.5
	Glycerin	6.0
	Polyglyceryl-10 stearate	2.0
Oil Phase	*Limnanthes alba* (meadowfoam) seed oil	3.0
	Octyldodecanol	2.0
	Cholesterol	0.2
	Glyceryl caprylate	0.1
	Ethylhexylglycerin	0.05
Aqueous phase	Butylene glycol	6.0
	1,2-Hexanediol	1.0
	Sodium stearoyl glutamate	0.1
	Water	78.35

Table 2. Formula for Ampoule Base

Phase	Ingredient	wt%
Aqueous phase	Butylene glycol	3.0
	Glycerin	5.0
	1,2-Hexanediol	2.0
	Niacinamide	8.0
	Adenosine	0.2
	Betaine	3.0
	Ethylhexylglycerin	0.2
	Glyceryl polymethacrylate and butylene glycol	5.0
	Sasa quelpaertensis extract	0.5
	Vitex trifolia fruit extract	4.0
	Water	7.1
Thickener phase	Ammonium acryloyldimethyltaurate/VP copolymer	0.3
	Xanthan gum	0.1
	Carbomer	0.2
	Water	59.4
pH Adjuster phase	Arginine	0.2
	Water	1.8

2.2. Preparation of Nanoemulsion Base and Ampoule Base

To prepare the nanoemulsion base (Table 1), first, the surfactant phase, the oil phase, and the aqueous phase are each dissolved and dispersed by heating to 70 to 75 ℃, and mixed with a homo-mixer at 2,000 rpm for 10 min while adding the oil phase to the surfactant phase. After that the primary emulsion was prepared by emulsifying with a homo-mixer at 3,000 rpm for 5 min while adding an aqueous phase. The prepared primary emulsion was subjected to high pressure emulsification at 40 to 45 ℃ under the conditions of 800 bar and 2 passes, the final nanoemulsion base was prepared.

To prepare the ampoule base (Table 2), first, the aqueous phase is dissolved and dispersed by heating to 40 to 60 ℃, and the thickener phase is uniformly dispersed in advance using an agi-mixer, while adding the thickener phase to the aqueous phase. Then the mixture of the two phases was mixed by stirring with an agi-mixer, and then mixed by stirring sufficiently with an agi-mixer while adding the pH adjuster phase.

2.3. Preparation of Nanoemulsion Ampoule

Based on Table 3 formula, after mixing the nanoemulsion base and ampoule base prepared as in [2.2. Preparation of nanoemulsion base and ampoule base] with an agi-mixer, four kinds of nanoemulsion ampoules were prepared by stirring with an agi-mixer for 10 min while adding active extracts (Figure 1).

Nanoemulsion ampoule was used for oily skin (#1) when the content of the nanoemulsion base and the ampoule base was low, and it was used for dry skin (#4) when the content was relatively high. Medium is for neutral oily skin (#2) and

Table 3. Formula for Nanoemulsion Ampoule (unit: wt%)

Part	Ingredient	#1	#2	#3	#4
A	Nanoemulsion base	10.0	20.0	30.0	40.0
B	Ampoule base	45.0	48.0	51.0	54.0
C	Moisture ingredient	1.5	1.5	1.5	1.5
	Wrinkle improvement ingredient	1.5	1.5	1.5	1.5
	Anti-pigmentation ingredient	1.5	1.5	1.5	1.5
	Sensitive skin ingredient	1.5	1.5	1.5	1.5
	Water	39.0	26.0	13.0	-

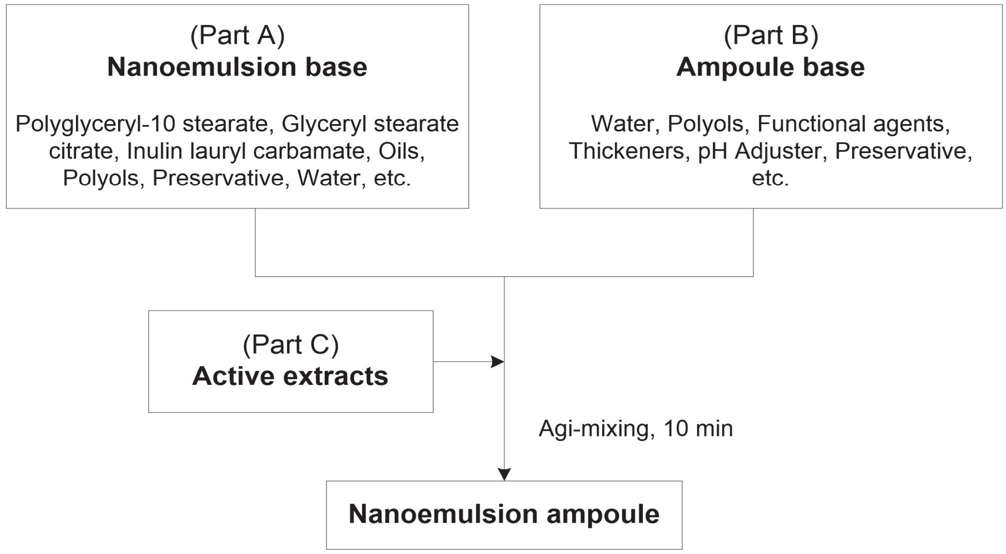

Figure 1. Manufacturing method of nanoemulsion ampoules contained active extracts.

neutral dry skin (#3), so that it can respond to four types of skin types.

2.4. Evaluation of Physical Properties of Nanoemulsion Ampoules

2.4.1. Stability Evaluation

While storing four nanoemulsion ampoules (#1 to #4) at room temperature (25 ℃) and constant temperature (40 ℃) for 90 d, respectively, changes in the properties over time were observed by day (1, 30, 60, 90 d).

2.4.2. Volatile Residue Measurement

The effect of volatile residue is due to surfactant, oil, powder (functional ingredients, thickeners, etc.) and some moisturizing ingredients in the test product. It is known that the higher the amount of volatile residue, the more residual feeling when used on the skin, and the moisturizing effect is known[9]. Therefore, an infrared moisture determination balance (FD-720, Kett, Japan) was used to measure / compare the amount of volatilization of the nanoemulsion ampoule, and measurements were carried out under the conditions of about 0.6 g of sample, 110 ℃, and bias < 0.01% (N = 3).

2.4.3. pH Measurement

A pH meter (orion star A111, Thermo scientific, USA) was used to measure the pH of the nanoemulsion ampoule. For pH measurement, 2 g of each sample was diluted with 30 mL of purified water and measured at 25 ℃ (N = 3).

2.4.4. Measurement of Particle Size, Polydispersity Index and Zeta Potential

A particle size analyzer (zetasizer nano ZS system, Malvern Instrument Ltd., UK) using a dynamic light scattering method to measure the particle size, polydispersity index (PDI) and zeta potential (ZP) of nanoemulsion ampoules was used. At this time, the temperature was kept constant at 25 ℃, and the test product was diluted with purified water to a concentration of 1% (N = 3)[10, 11].

2.4.5. Viscosity Measurement

A viscometer (DV-E viscometer, Brookfield, USA) and a spindle (helipath stand spindle, Brookfield, USA) were used to measure the viscosity of the nanoemulsion ampoule. Measurements were made after 1 d storage at 25 ℃, T-F spindle (#96), 30 rpm, 1 min conditions (N = 3).

2.4.6. Turbiscan Measurement

Turbiscan measurement is by measuring the intensity of backscattering and transmission for the sample using the multiple light scattering technique using the NIR light source

(880 nm). For various formulations, changes in dispersion stability against sedimentation, creaming, aggregation, and coalescence without dilution are evaluated[12-14]. The dispersion stability of the nanoemulsion ampoules was measured by scanning at 25° C. for 3 d at intervals of 1 h using turbiscan (turbiscan LAB, Formulaction, France). The measure of stability is expressed as the turbiscan stability index (TSI), and the smaller the TSI value, the more stable it is.

2.5. Usability Satisfaction Evaluation

As shown in Table 3, the primary human skin irritation evaluation test (KDRI-IRB-220216) was completed by Korean Dermatology Research Institute before the human usability satisfaction evaluation for four types of nanoemulsion ampoules divided into nanoemulsion base and ampoule base content. Afterwards, for the evaluation of usability satisfaction according to skin type, evaluation was conducted based on healthy adults in their 20's to 60's with oily (7 female / 5 male, SM-JU04-22A19-033), neutral oily ((11 female, SM-JU04-22A19-034), neutral dry (7 female / 6 male, SM-JU04-22A19-035), and dry (9 female / 3 male, SM-JU04-22A19-037) skin types from SkinMed Clinical Trial Center.

Prior to evaluation, in the case of test subjects who does not know their skin type accurately, according to the score of the ‘oily *vs.* dry’ questionnaire among Dr. Leslie Baumann skin type questionnaire[15,16], it was divided into four skin types of oily, neutral oily, neutral dry, and dry. Nanoemulsion ampoules, which are customized cosmetics for each skin type, were allowed to be used on the face for one week, and then evaluated.

The usability evaluation paper consists of 7 evaluation items of viscosity, spreadability when using the test product, moisturizing feeling (moisture) after use, absorption, non-stickiness, no irritation, and overall satisfaction after using the test product. Scores were given on a 6-point scale from very good (6 points) to very bad (1 point).

2.6. Statistical Analysis

All experiments were repeated three times, and the experimental results were expressed as mean ± standard deviation. Significance was performed by student's *t*-test, and was expressed as $^{*}p < 0.05$, $^{**}p < 0.01$ according to significance.

3. Results and Discussion

3.1. Evaluation of Physical Properties of Nanoemulsion Ampoules

3.1.1. Stability Evaluation

Four types of nanoemulsion ampoules (#1 to #4) were stored at room temperature (25 ℃) and constant temperature (40 ℃) for 90 d, respectively, and changes in the properties over time were observed by day (1, 30, 60, 90 d). As a result, all were white to pale yellow opaque liquids, and all were stable without separation (data not shown).

3.1.2. Volatile Residue Measurement

The amount of volatile residues of the four nanoemulsion ampoules (#1 to #4) divided by the content of the nanoemulsion base and the ampoule base was measured in the range of 8.4 to 14.7%. The oily skin product #1 (8.70 ± 0.24%) was the least and the dry skin product #4 (13.91 ± 0.80%) had the most (Table 4). The average of the measured values showed a difference of less than 4% when compared with the theoretical value.

3.1.3. pH Measurement

Four nanoemulsion ampoules (#1 to #4) were stored for 90 d, and the pH was measured three times per day (1, 30, 60, 90 d). As a result, the overall pH was measured in the range of 6.4 to 6.9. It slightly increased as the content of the nanoemulsion base increased, and it also showed a tendency to slightly increase with time, but showed only a change within 0.5 (Figure 2).

Table 4. Volatile Residue for Nanoemulsion Ampoule (unit: wt%)

Volatile residue	#1	#2	#3	#4
Measurement	8.70 ± 0.24	10.42 ± 0.95	12.07 ± 1.00	13.91 ± 0.80
Theoretical value	8.91	10.68	12.45	14.22

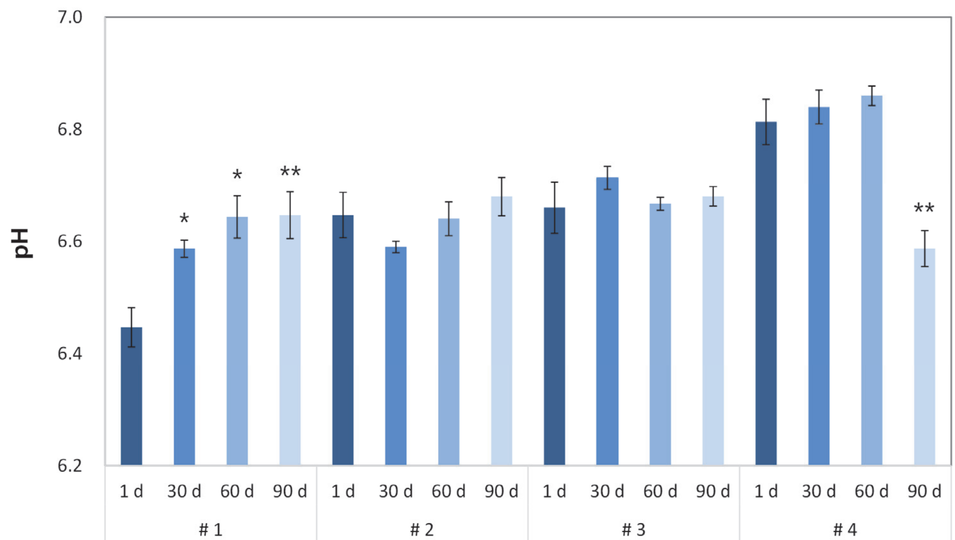

Figure 2. pH data of nanoemulsion ampoule #1 ~ #4 after 1, 30, 60, and 90 d at 25 ℃ (mean ± SD, N = 3). The results were expressed as the mean ± SD (N = 3), $^{*}p < 0.05$, $^{**}p < 0.01$ compared with each 1 d data.

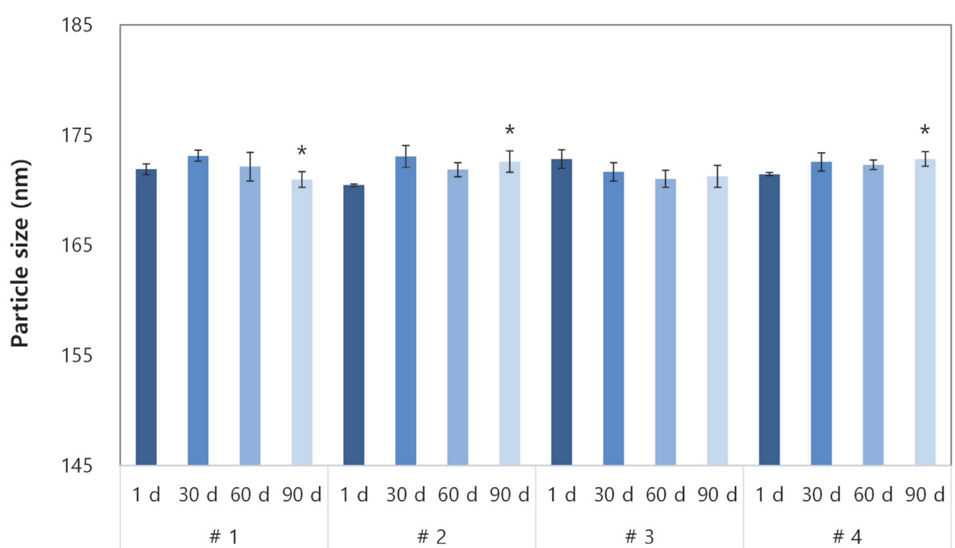

Figure 3. Particle size data of nanoemulsion ampoule #1 ~ #4 after 1, 30, 60, and 90 d at 25 ℃. The results were expressed as the mean ± SD (N = 3), $^{*}p < 0.05$, $^{**}p < 0.01$ compared with each 1 d data.

3.1.4. Measurement of Particle Size, Polydispersity Index and Zeta Potential

The initial particle size of the four types of nanoemulsion ampoules (#1 to #4) was in the range of 170 to 174 nm, and all four types of test products were measured with similar particle sizes (Figure 3).

It was measured that there was almost no difference in particle size in all the test products according to the increase in the nanoemulsion base content, and there was also little change in the particle size with time. The change in particle size decreased within 1% compared to 1 d in test products #1, #2, and #3 after 90 d, and increased by 0.8% in test product #4.

A change in particle size is expected due to the ostwald

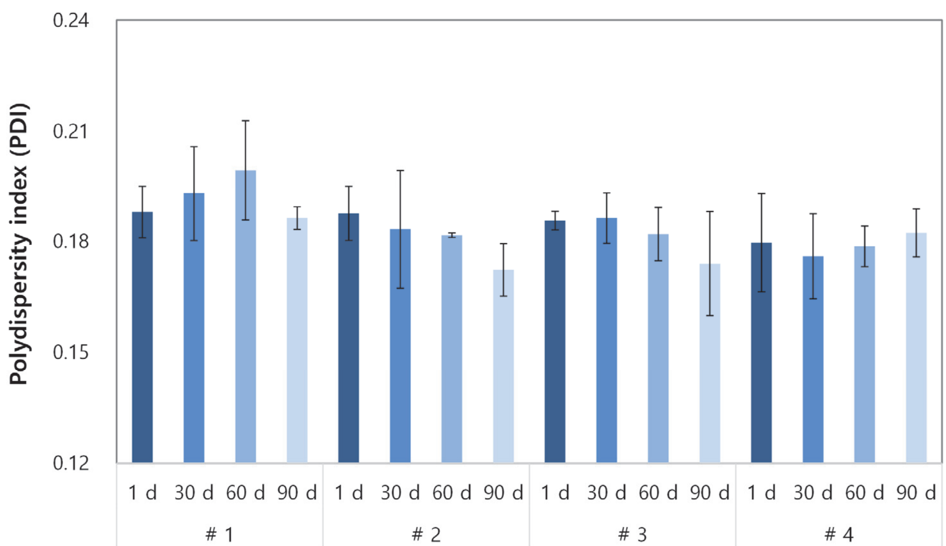

Figure 4. PDI data of nanoemulsion ampoule #1 ~ #4 after 1, 30, 60, and 90 d at 25 °C. The results were expressed as the mean ± SD (N = 3), $^{*}p < 0.05$, $^{**}p < 0.01$ compared with each 1 d data.

ripening phenomenon between nanoemulsion particles[17-19], but the value is within 0.8%, and the maximum particle size is 174.1 nm, so there was no singularity in particle size stability.

The PDI of the four nanoemulsion ampoules (#1 to #4) ranged from 0.15 to 0.22, and the overall average was measured to be 0.184 (Figure 4).

There was no difference in PDI in all test products according to the increase in nanoemulsion base content. The change in PDI with time decreased by 8.9% and 6.7% in test products #2 and #3, respectively, and increased by 1.5% in test product #4 compared to 1 d after 90 d. All showed changes within values less than 0.22, indicating that they were almost constant. All showed that the PDI was almost constant with the change within the value less than 0.22. From the average PDI value of about 0.184, it was confirmed that the particles of the nanoemulsion ampoules showed a particle size distribution close to monodisperse[20,21].

In general, not only physical stability but also electrostatic stability are important when improving dispersion stability for nanoparticle-sized dispersions, such as nanoemulsion-type products. Therefore, a method of measuring the zeta potential is used as a method of verifying the dispersion stability of a dispersion at the nanoparticle level. In DLVO theory, interactions between particles are expressed as electrostatic repulsion and attraction between particles. When the electrostatic repulsive force is large, the aggregation of particles decreases, and the electrostatic repulsive force is related to the charge on the particle surface when the particles move, which can be measured as the zeta potential[22,23]. The larger the absolute value of the zeta potential, the better the repulsive force between the dispersed colloidal particles, so that the colloidal state is relatively stable. In general, the stable range of zeta potential is known to be more than ± 40 mV[24].

The initial zeta potential of the four nanoemulsion ampoules (#1 to #4) was measured to have a good value in the range of -63.2 to 65.4 mV. There was almost no difference in the zeta potential according to the increase of the nanoemulsion base content. The absolute value of the zeta potential with time showed a tendency to decrease slightly. After 90 d, the zeta potential decreased by 2.5% for test products #1 and #2, decreased by 1.7% for #3, and decreased by 2.4% for #4. It was found that the four nanoemulsion ampoules were electrostatically stable at -61 mV or more even after 90 d (Figure 5).

3.1.5. Viscosity Measurement

The initial viscosity of the four nanoemulsion ampoules (#1

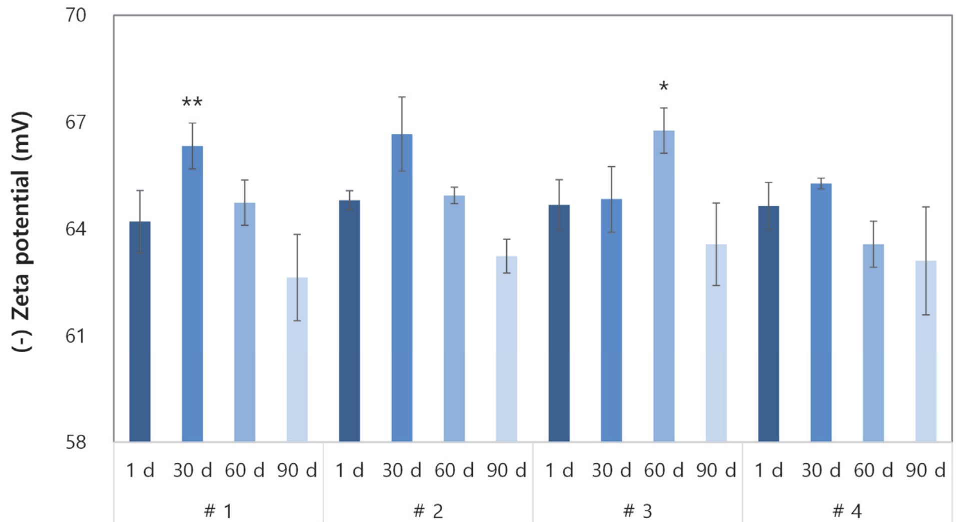

Figure 5. Zeta potential data of nanoemulsion ampoule #1 ~ #4 after 1, 30, 60, and 90 d at 25 °C. The results were expressed as the mean ± SD (N = 3), $^{*}p < 0.05$, $^{**}p < 0.01$ compared with each 1 d data.

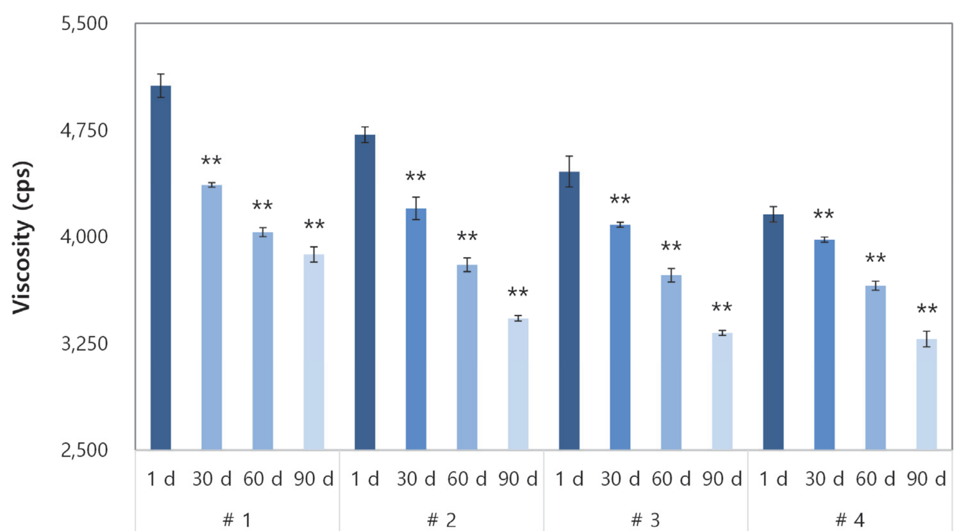

Figure 6. Viscosity data of nanoemulsion ampoule #1 ~ #4 after 1, 30, 60, and 90 d at 25 °C. The results were expressed as the mean ± SD (N = 3), $^{*}p < 0.05$, $^{**}p < 0.01$ compared with each 1 d data.

to #4) is #1 (5,062 cps), #2 (4,718 cps), #3 (4,458 cps), #4 (4,156 cps). As the content of the nanoemulsion base and the ampoule base increased, the viscosity decreased, and the effect seems to be due to the nanoemulsion base rather than the ampoule base. In a general emulsion (macroemulsion), the viscosity increases when the inner phase ratio increases[25], and it is expected that the viscosity increases when the emulsion content increases. However, since the nanoemulsion base in this paper is almost liquid, it is not thought that increasing the liquid content will affect the viscosity. It seems that the role of the thickener in the ampoule base is relatively decreased due to the increase in the polyol content according to the increase in the nanoemulsion base.

The viscosity with time showed a tendency to decrease slightly. This seems to be a characteristic of products that have been thickened with general water-soluble thickeners such as carbomer. After 90 d, the visosity decreased by 30.6% for test product #1, 37.7% for # 2, 34.2% for #3, and 26.7% for #4 (Figure 6). This phenomenon is considered to be an area that needs to be further investigated in the future.

3.1.6. Turbiscan Measurement

In general, dispersed colloidal formulations are thermodynamically unstable. That is, over time, it undergoes a process of reaching an equilibrium state (macroscopically separated state) that is no longer changing, which is a thermodynamically stable state. Turbiscan irradiates NIR light from the lower layer to the upper layer to the dispersion standing vertically. The transmittance is measured for samples with high transparency, and the scattering is measured for samples with high opacity.

All four nanoemulsion ampoules are white and opaque, so the scattering degree is measured. The TSI is calculated by dividing the sum for ΔBS by the height (height of the upper layer - height of the lower layer) of the total contents. When irradiated repeatedly over time (1 h interval, 72 times), △BS is the difference from the degree of backscattering (BS) for the previous light irradiation ($scan_{i-1}$ (h)) and the degree of BS for the current light irradiation ($scan_i$ (h)). If the difference in the degree of BS before and after is large in the middle part of the contents, not the lower layer and the upper layer, it is reported that the contents are relatively non- uniformly agglomerated, and these measures are expressed as the TSI values.

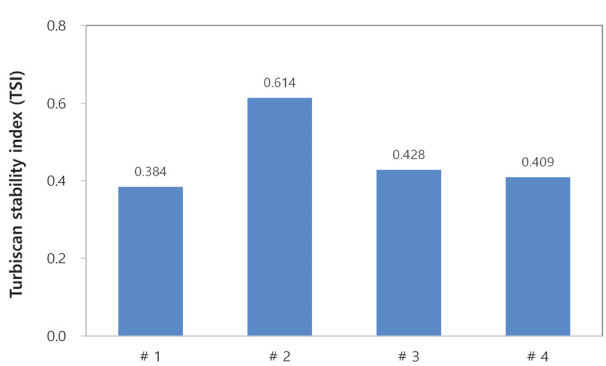

Figure 7. Turbiscan data of nanoemulsion ampoule #1 ～ #4 at 25 ℃ for 3 d at 1 h intervals.

The TSI values of the four nanoemulsion ampoules (#1 to #4) were all below 1.0, indicating good dispersion stability regardless of the content of the nanoemulsion base and the ampoule base (Figure 7).

3.2. Usability Satisfaction Evaluation

3.2.1. Overall Satisfaction Evaluation According to Skin Type

Before evaluating the usability satisfaction of four types of nanoemulsion ampoules (#1 to #4) according to skin type, subjects were classified into four skin types (oily, neutral oily, neutral dry, and dry skins) through a questionnaire (Dr. Leslie Baumann skin type classification method). According to each skin type, satisfaction evaluation was conducted with test product #1 for oily skin (12 persons), #2 for neutral oily skin (11 persons), #3 for neutral dry skin (13 persons), and #4 for dry skin (12 persons).

Overall satisfaction after using test products by skin types was highest for #1 (for oily skin) with 5.42 ± 0.67 points,

Table 5. Comparison of Overall Satisfaction Evaluation of Nanoemulsion Ampoule According to Skin Type

Skin type	Oily skin (#1)	Neutral oily skin (#2)	Neutral dry skin (#3)	Dry skin (#4)
Satisfaction	5.42 ± 0.67	5.36 ± 0.67	5.15 ± 0.69	4.75 ± 0.75

Table 6. Comparison of Satisfaction Evaluation by Item of Nanoemulsion Ampoule According to Skin Type

Skin type	Viscosity	Spreadability	Moisturizing	Absorption	Stickiness	Irritation
Oily skin (#1)	5.00 ± 0.85	5.17 ± 0.58	5.42 ± 0.67	5.25 ± 0.75	5.00 ± 0.95	5.25 ± 0.97
Neutral oily skin (#2)	5.45 ± 0.52	5.55 ± 0.52	5.55 ± 0.52	5.45 ± 0.69	5.36 ± 0.50	5.55 ± 0.52
Neutral dry skin (#3)	4.77 ± 0.60	5.00 ± 0.71	4.85 ± 0.80	5.00 ± 0.58	4.85 ± 0.99	4.92 ± 0.76
Dry skin (#4)	4.83 ± 0.83	5.00 ± 0.60	4.58 ± 1.24	5.00 ± 0.74	4.08 ± 1.38	4.83 ± 1.11

and relatively low for #4 (for dry skin) with 4.75 ± 0.75 points, but all four types of test products were positive. The overall satisfaction result was evaluated in the order of #1 (for oily skin) > #2 (for neutral oily skin) > #3 (for neutral dry skin) > #4 (for dry skin) (Table 5).

3.2.2. Evaluation by Item According to Skin Type

Out of the total 12 subjects of test product #1 for oily skin, 5 subjects in their 20s, 4 subjects in their 30s, 1 subject in their 40s, and 2 subjects in their 50s responded to the evaluation, and the average score for each evaluation item is shown in Table 6. All items showed high satisfaction with more than 5 points.

Out of a total of 11 subjects in test product #2 for neutral oily skin, 4 subjects in their 20s, 2 subjects in their 30s, 2 subjects in their 40s, and 3 subjects in their 50s responded to the evaluation, and the average score for each evaluation item is shown in Table 6. As with test product #1, satisfaction was high with a score of 5 or more in all items. In terms of evaluation items, test product #2 (for neutral oily skin) was rated higher than test product #1 (for oily skin).

Out of a total of 13 subjects in test product #3 for neutral dry skin, 2 subjects in their 20s, 6 subjects in their 30s, and 5 subjects in their 40s responded to the evaluation, and the evaluation results are shown in Table 6. In terms of spreadability and absorption, the score was 5 or higher. At 5 points or less, the viscosity was 4.77 points, the moisturizing feeling was 4.85 points, the stickiness was 4.85 points, and the irritation feeling was 4.92 points.

Out of a total of 12 subjects in test product #4 for dry skin, 2 subjects in their 20s, 2 subjects in their 30s, 3 subjects in their 40s, and 5 subjects in their 50s responded to the evaluation, and the evaluation results are shown in Table 6. As in test product #3 (for neutral dry skin), it was 5 points or higher in terms of spreadability and absorption. At 5 points or less, the viscosity was 4.83 points, the moisturizing feeling was 4.58 points, the stickiness was 4.08 points, and the irritation feeling was 4.83 points.

Overall, test products #1 and #2 were evaluated better than #3 and #4. In the case of #3 and #4, satisfaction with viscosity, moisture, stickiness, and irritation was low. In particular, the reason for the low overall satisfaction with test product #4 seems to be due to the lowest stickiness evaluation score in addition to the moisturizing feeling.

4. Conclusion

In this study, four types of nanoemulsion ampoules corresponding to skin types were prepared by varying the ratio of nanoemulsion base and ampoule base as a customized cosmetics.

For the four nanoemulsion ampoules, the amount of volatile residue related to skin moisture was measured in the range of 8.70 to 13.91%, test product #1 (for oily skin) was the least, and #4 (for dry skin) had the most. When compared with the theoretical value, both showed an error of less than 4%. The pH was overall in the range of 6.41 to 6.88, and slightly increased with the increase of the nanoemulsion base content. There was also a slight increase with time, but there was no significant change. The particle size was initially about 170 to 174 nm, and a change in the particle size was expected due to the ostwald ripening phenomenon between the nanoemulsion particles, but the change after 90 d was within 1.2% of the maximum, and there was no singularity in particle size stability. The PDI, as a whole, was measured to have an average of 0.184 in the range of 0.172 to 0.199, and it was confirmed that the particle size distribution was almost constant and close to monodisperse by showing a change within a value smaller than 0.21 in all test products. The zeta potential, which is a measure of electrostatic stability, was initially measured to be -63 mV or more for all four types of nanoemulsion ampoules, and was measured to be -61 mV or more after 90 d, confirming that it was electrostatically stable.

In addition, the viscosity initially showed 4,100 to 5,100 cps, and the viscosity decreased as the content of the nanoemulsion base and the ampoule base increased, and the effect seemed to depend on the nanoemulsion base rather than the ampoule base. The viscosity value with time showed a tendency to decrease slightly, and it was measured to decrease up to 37.7% (test product #2) after 90 d. In the turbiscan measurement, which can evaluate the stability of the dispersed colloidal formulation, all TSI values were 1.0 or less, indicating good dispersion stability regardless of the nanoemulsion base content and the ampoule base content.

In the human usability satisfaction evaluation of 4 nanoemulsion ampoules corresponding to skin types, overall satisfaction after using the test product was the highest in #1 (for oily skin) with 5.42 ± 0.67 points, and the lowest in #4 (for dry skin) with 4.75 ± 0.75 points. Satisfaction was evaluated in the order of #1 (for oily skin) > #2 (for neutral oily skin) > #3 (for neutral dry skin) > #4 (for dry skin). In the average score for each evaluation item, test products #1 and #2 showed high satisfaction with 5 points or more in all items, and #3 and #4 showed 5 or more points in spreadability and absorption, but the items of viscosity, moisture, stickiness, and irritation were less than 5 points, indicating relatively low satisfaction. In particular, the reason for the low overall satisfaction in test product #4 was that it had the lowest stickiness evaluation score in addition to the moisturizing feeling.

By varying the ratio of the nanoemulsion formulation and the ampoule formulation, the four types of nanoemulsion ampoules corresponding to skin types confirmed the possibility of application as customized cosmetics in the future, and the possibility of expansion is also expected.

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