Application of Multiple-light Scatterer to Evaluate the Effect of Different Emulsification Technology on Emulsion Stability

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Abstract

Background: The properties and stabilities of emulsion rely greatly on the emulsification methods and emulsifiers. Usually we need to evaluate the reliability of the process through stability testing. Turbiscan Lab multiple-light scatterer is an analytical instrument used to vertically scan concentrated systems to determine their stability. It can quickly reflect the changing trend of the emulsion system and shorten the stability test period.

Methods: In this study, different emulsification methods were employed for the preparation of emulsions firstly. Then we prepared creams with the same formula above by changing the adding method of different active ingredients using the same low-energy emulsification technology. The stabilities of all the creams prepared by different processes were investigated by multiple-light scatterer.

Results: Compared with the traditional emulsification process, the cream prepared by the low-energy emulsification process had better stability overall, but the internal particle dispersion uniformity was poor, and its particle size changed more significant under different test conditions. However, different ingredient's adding method showed different stability in all aspects.

Conclusion: The effect of different emulsification processes and different ingredient's adding methods on the stability of the system were studied using multiple-light scatterer. Compared with traditional evaluation methods, the application of multiple-light scatterer can not only obtain the product system change information simply and objectively, but also improve the screening efficiency of formula development and process development. These results will be helpful for selecting an appropriate emulsification method and emulsifier to improve the stability of emulsions.

Keywords: Different emulsification technology; Multiple-light scatterer; Stability

Introduction.

Emulsification of immiscible two-phase fluids, i.e., one condensed phase dispersed homogeneously as tiny droplets in an outer continuous medium[1], represents a large part of the products of the cosmetics industry. They are extremely important both for commercial and scientific reasons and are a frequent object of research[2]. The traditional process of cosmetic emulsion is to first heat and melt or dissolve the raw materials of the inner phase and the outer phase in two containers, and then mix the two phases to combine them to form an emulsion. Add actives and other raw materials at 40-50 °C, and finally cool the emulsion to room temperature. In the production of lotions and creams by the traditional process, the hot water phase used is excessive, so the excess water will consume more heat energy during the heating process. However, low-energy emulsification method is an energy-saving emulsification process, which can improve the efficiency of emulsified products and shorten the batching time, and because the use of LEE can greatly reduce cooling water, effectively reduce the burden of processing and cooling, and greatly reduce production costs[3]. Meanwhile, the previous research results in our laboratory showed that the cream prepared by the low-energy emulsification process was easier to be absorbed with a smaller particle size and a better skin feeling, and it was more popular with consumers, compared with samples from the traditional method.

Stability evaluation is an important aspect of cosmetic quality assurance. Recently, multiple light scattering technique has received increasing attention from the research and industrial communities thanks to its ability to detect physical aggregation phenomena based on the scattering and transmission of light through a sample[4]. The multiple light scattering instrument uses near-infrared light as the light source, and has a transmitted light device and a backscattered light detector. The light source, the transmitted light detector and the backscattered light detection detector form a measuring probe. The measuring probe measures every 40μm from the bottom of the sample cell to the top of the sample cell, and the measurement from the bottom to the top of the sample cell is called a scan. Then, both the transmitted light and the backscattered light will change due to the instability of the sample over time, which means that the particle size and/or concentration of the sample particles have changed. Through this way, we can infer the stability of the product. Many active ingredients used in cosmetics are sensitive to temperature or high-speed shearing, so when using traditional methods to prepare emulsions, we often add these active ingredients after homogenization at low temperature, but how these additions affect emulsions' stability is worth exploring.

Based on this background, the present work aims to investigate the difference in stability by different emulsification methods using multiple light scattering techniques. In this study, we selected the water-soluble active ingredient sodium hyaluronate and the oil-soluble active ingredient α-bisabolol as the research objects to evaluate their effects of addition on system stability before homogenization or after homogenization and cooling.

Materials and Methods.

Materials

The materials used in this study were at least cosmetic grade, and deionized water was used for all experiments.

Methods

Samples preparation by different emulsification methods. The traditional emulsification process and the low-energy emulsification process were used to prepare oil-in-water creams with the same formula to compare the stability differences in these different emulsification methods. Then we used low-energy emulsification method to make emulsions using the same formula above with the oil-soluble active ingredient α-bisabolol (0.3%) and the water-soluble active ingredient sodium hyaluronate (0.05%) feded in different steps (low-temperature addition after homogenization, and high-temperature addition before homogenization) to evaluate their influences.

Stability evaluation by multiple light scattering technique. A Turbiscan (Formulaction, L'Union, France) was used to observe changes in the emulsions studied. This device uses the backscattering and transmission principle of multiple light scattering. This method not only allows the identification and monitoring of instabilities occurring in emulsion systems but also allows their numerical visualisation. It also allows rapid assessment of the stability of emulsion systems without the need for additional sample dilution[2]. Test as follows: Put the product into the 20 mL measuring cell, then the sample cell was placed in a multiple light scattering instrument (AGS) for measurement, and the measurement parameters were: 25 °C and 50 °C and the freeze-thaw were scanned every hour for 24 hours. The stability was evaluated from the following three aspects: Absolute value intensity evaluation of backscattered light in the middle part, variation in backscattered light intensity at the top or bottom of the sample and dispersion uniformity index evaluation.

Determination of α-bisabolol content in the emulsions. α-bisabolol is a active component existing in chamomile flowers who has a good antibacterial effect. However, due to the characteristics of its left-handed structure, α-bisabolol is easy to lose its activity at high temperature. Therefore, in the preparation process of cosmetics, α-bisabolol is generally added to the system at low temperature. Using α-bisabolol as a marker, by measuring the content of α-bisabolol in different processes, the destructive effect of different processes on active substances can be evaluated, helping us to screen a more suitable emulsion preparation process. In this study, the content of α-bisabolol in the emulsions were tested by Agilent liquid chromatograph (LC-1260).

Results.

Change in intensity of backscattered light (∆BS) over time. From the variation of backscattered light intensity in the middle part and at the top or bottom of the sample to evaluate the stability of emulsions. The test patterns of different emulsification process samples are as follows.

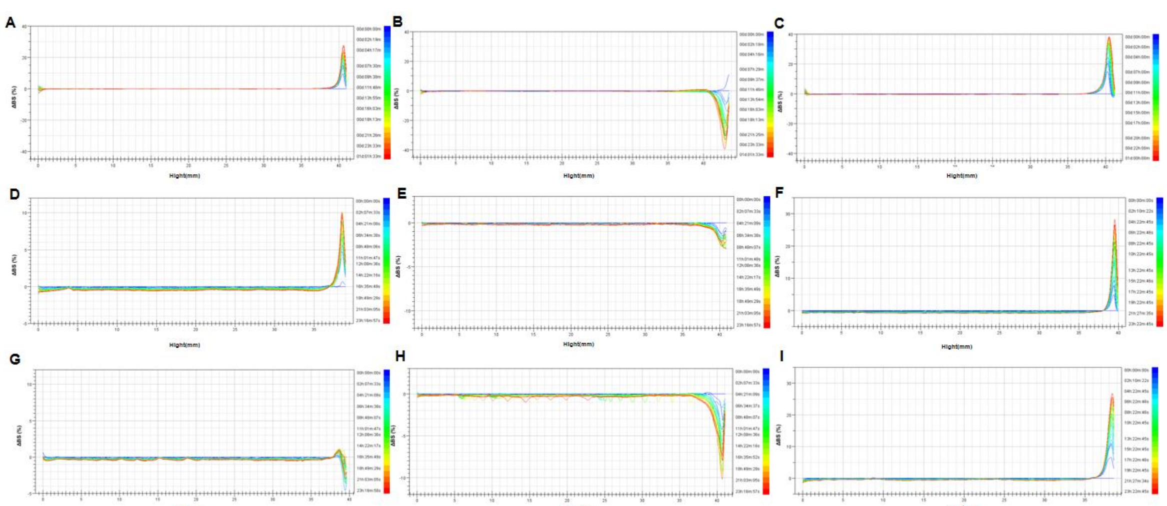

Figure 1. Change in intensity of backscattered light (ΔBS) over time for emulsions A-I. Blue line-first measurement, red line-last measurement. A-C: samples by traditional emulsification process; D-F: samples by low-energy emulsification process with active ingredients added before homogenization; G-I: samples by low-energy emulsification process with active ingredients added after homogenization and cooling. A/D/G are samples' 25 °C scan patterns, B/E/H are samples' 50 °C scan patterns, C/F/I are freeze-thaw samples' scan patterns.

The absolute value of the backscattered light intensity in the middle part of the spectrum is jointly determined by the particle size, concentration and the formed thickener molecular network structure. If the wight of solids added to the sample is the same, the intensity of the backscattered light is determined by the particle size and the molecular network structure of the thickener.

From the data in figure 1, backscattered light intensity values of the three samples decreased after high temperature treatment, indicating the size of the emulsion droplets increased in the samples at high temperature and the particles agglomerated at high temperature. The samples obtained by the low-energy emulsification process have a greater degree of variation. It was speculated that when using low-energy emulsification process to make emulsions, only a part of the water could participate in the homogenization process, so the emulsions shared more homogenization energy. The huge homogenization energy could not only help the emulsions got better particle sizes but also destroy partial structure of high molecular polymers leading to a greater degree of variation in stability.

The change value of the low-energy process with active ingredients added after homogenization and cooling was larger than that of the traditional emulsification process, indicating that the low-energy process destroyed part of the molecular network of the thickener, and the particle size became larger. When the active substance added before homogenization by low-energy process, the light intensity change value was small comparing to low-energy emulsification process with active ingredients added after homogenization and cooling, indicating that the active substance participating in the homogenization could make the product disperse more evenly and improved the stability.

Meanwhile, from the above figure, the changes of light intensity value of all the creams by different emulsification process under freeze-thaw conditions were relatively small, indicating that the creams had a relatively strong low temperature resistance. The change of the low-energy process was larger than that of the conventional process, indicating that the internal structure of the low-energy process cream changed more.

Changes in the backscattered light intensity at the bottom and top of the samples characterized the extent to which the sample floats or settles. By comparing the conventional emulsification process and the energy-saving process, it was found that the low-energy process improved the degree of sample floating or sedimentation and increased the stability of the formulation. Does not delaminate but the inner particle size of the cream became larger.

Dispersion uniformity index evaluation

The uniformity index is calculated by taking all the backscattered data points in the middle to calculate the relative standard deviation (RSD), Relative Standard Deviation (RSD) = Standard Deviation (SD) / Arithmetic Mean of Calculated Results (X).

The dispersion uniformity index characterizes the degree of dispersion uniformity of each dispersed component in the sample in the system. The larger the index, the worse the dispersion uniformity of the sample. When the particle size distribution of the dispersed particles in the system is relatively large or the colloidal dispersion is not uniform, the uniformity index will become higher. This index can be used as a basis for the selection of the dispersion process.

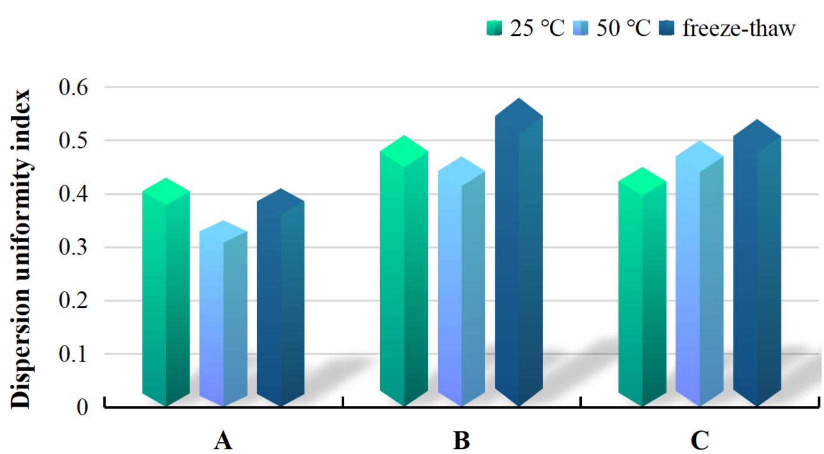

Figure 2. Dispersion uniformity index from samples by different emulsification methods. A: samples by traditional emulsification process; B: samples by low-energy emulsification process with active ingredients added after homogenization and cooling; C: samples by low-energy emulsification process with active ingredients added before homogenization.

Dispersion uniformity of all the samples improved in various degrees by traditional emulsification process after high temperature or freeze-thaw treatments. We speculated that the high temperature might cause the polymers in the formulation to swell better and the freeze-thaw treatment might distribute the free water in the emulsions more uniform. The uniformity of the emulsions by low-energy emulsification process were relatively poor. It was speculated that the reason was that the low-energy process destroyed the network structure of the thickener and decreased the supporting force.

Determination of α-bisabolol content in the emulsions.

Chromatography was used for detection, and the external standard method was used for quantitative calculation. The content of α-bisabolol in sample by traditional emulsification process was 0.30%, the content of α-bisabolol in sample by low-energy emulsification process with active ingredients added after homogenization and cooling was 0.30%, and the content of α-bisabolol in sample by low-energy emulsification process with active ingredients added before homogenization was 0.23%. High temperature treatment during homogenization period caused 23% loss of α-bisabolol activity.

Discussion.

Emulsion is a heterogeneous system. According to the second law of thermodynamics, emulsions are inherently unstable and will eventually separate into two phases. In the case of an O/W-type emulsion, in which water and oil are mixed, particle collapse occurs owing to various physical factors, such as the size of oil particles dispersed in the water phase. The phase separation of O/W-type emulsions is directly related to the size distribution of the oil particles in the emulsion, and the particle size and its distribution determine the emulsion stability[5]. The degree of emulsion instability and the rate of change are affected by the formulation ingredients and the manufacturing process. Understanding the changing process of emulsions can help us to better optimize formulations and processes, improve product stability, and extend shelf life. Multiple light scattering instrument can assist in stability analysis by revealing the distribution of particles inside the emulsion at different times and under different test conditions. It can help us analyze the reasons that may lead to product instability. As a consequence, multiple light scattering can be considered as a valuable and reliable tool for the stability detection at the early stage of the product research. Although this technology has been relatively widely used in the field of cosmetics, no one has yet used this technology to compare the difference in stability between the low-energy emulsification and the traditional emulsification process. This study provides ideas for better guidance of production by comparing the effects of different emulsification processes on formulation stability.

Conclusion.

In this study, the stability analysis of products with different emulsification processes was carried out using multiple light scattering instrument. The results show that, compared with the traditional emulsification process, the emulsified particles obtained by the low-energy process were smaller and tightly arranged. The emulsions had fine feelings to the skin and the products were more stable. The low-energy process could increase the stability of the formulation, but it would damage the structure of the thickener and reduce the uniformity of the system. The oil-soluble active substance α-bisabolol which is not resistant to high temperature, could improve the stability of the product when added to the system before homogenization with 23% lossing of the activity. Therefore, oil-soluble active substance that is resistant to high temperature should be selected as far as possible in the oil-in-water emulsions. Otherwise, we should increase the amount of active substances according to the needs of efficacy.

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Conflict of Interest Statement. NONE.

References.

1. Deng H, Peljo P, Huang X, Smirnov E, Sarkar S, Maye S, Girault HH, Mandler D. Ionosomes(2021) Observation of Ionic Bilayer Water Clusters. J Am Chem Soc

143(20):7671-7680.

2. Kowalska M, Żbikowska A, Woźniak M, Amanowicz A(2022). Quality of Emulsions Based on Modified Watermelon Seed Oil, Stabilized with Orange Fibres. Molecules 27(2):513.
3. Lin,T.J., Low Energy Emulsification: Beyond Energy Conservation(2001). C&T 116(5):61-66.
4. Ramezani M, Ferrentino G, Morozova K, Scampicchio M(2021). Multiple Light Scattering Measurements for Online Monitoring of Milk Fermentation. Foods 10(7):1582.
5. Seon-Ae Hwangbo, Seung-Yul Lee, Bu-An Kim, Chang-Kwon Moon 3. Preparation of Surfactant-Free Nano Oil Particles in Water Using Ultrasonic System and the Mechanism of Emulsion Stability(2022). Nanomaterials 12, 1547.