Polymer(Korea), Vol. 42, No. 2, pp. 223-229 (2018)
https://doi.org/10.7317/pk.2018.42.2.223

ISSN 0379-153X(Print)
ISSN 2234-8077(Online)

양친매성 전분이 리포좀 에멀젼에 미치는 영향 및 안정화에 관한 연구

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(2017년 7월 28일 접수, 2017년 8월 31일 수정, 2017년 9월 14일 채택)

Effects of Amphiphilic Starch and Its Stabilization for Liposome Emulsion

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(Received July 28, 2017; Revised August 31, 2017; Accepted September 14, 2017)

초록: 본 연구는 전분을 함유한 천연 화장품 에멀젼 제조를 위해 수행되었다. 천연 원료의 성분비가 높은 화장품을 제조하기 위해서 일반적으로 활용되고 있는 제형 안정화에 용이한 화학적 안정화제는 사용할 수 없었다. 따라서 우리는 양친매성 전분이 리포좀 에멀젼에 미치는 영향 및 안정화에 관해 조사했다. 양친매성 전분의 호화와 노화에 영향을 주는 요인을 찾기 위해, 여러 종류의 검들과 혼용 시 전분 결정화 연구를 XRD, DSC와 Cryo-FE-SEM 분석을 통하여 수행했다. 화학적으로 가공되지 않은 전분을 가지고도 화장품에서 리포좀 에멀젼 안정화 제형을 만들 수 있었다.

Abstract: The objective of this work was to make emulsion with starch for natural cosmetics. For the cosmetic product with the high portions of natural grade ingredients, we could not use chemical stabilizers. Thereby, we investigated the effects of the amphiphilic starch and its stabilization for liposome emulsion. In this study, we conducted a starch crystallinity study to find the effect of gelatinization and retrogradation of amphiphilic starch with various types of gums using XRD, DSC and Cryo-FE-SEM techniques. To the best of our knowledge, there has been no report on the stabilization of liposome emulsion for cosmetics with native starch.

Keywords: starch crystallinity, gelatinization, gum, liposome, emulsion stability.

Introduction

Starch is completely biodegradable, nontoxic and renewable natural raw material, which is a semicrystalline polymer that can be found in most plants. Most starches are heterogeneous materials of polysaccharides: amylose is a mixture of linear D-glucose units linked α(1-4), and amylopectin is a mixture of branched D-glulcose units linked α(1-4) and 5% α(1-6) branch linkages. The glucose residues have various average numbers from 250 to 5000 for amylose, and from 10000 to 100000 for amylopectin.[1] The relative proportions of amylose to amylopectin depend on the plant source.[2] We used tapioca starch, which has the ratio of 18:82 of amylose to amylopectin.

Tapioca starch (TS) from cassava roots, is used as thickener in food industries for its high viscosity, clear paste, and low cost, compared to other starches.[3] In cosmetic industries, especially natural cosmetics, TS has been used for oil absorption and lubricant function with powder. However, we invented it as the emulsion stabilizer by gelatinization. Precisely, the shape of starch granule and the degree of crystallinity varies with its source. The relative proportions of amylose to amylopectin are the major determinants for physicochemical properties of starch.[4] This amylose is known to form a helix with different lipophilic ligands. These structural characteristics are important because lipid-amylose complex influences its interaction with the other components in food[5] and cosmetic systems.

After gelatinization, we were able to make more stable emulsion. Nevertheless, we needed to control the degradation of starch because native starch generally became crystallized

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by degradation after gelatinization.[6,7] Because crystallization makes the emulsion unstable, we researched the method that makes more stable emulsion with TS. In the food industry, we found that the miscibillity of starch with other gums, especially xanthan gum, that could affect the pasting and gelatinization of TS.[8-11] For natural cosmetics we used guar gum and arabic gum, and tested the effects from the gelatinization properties of TS. Guar gum, among natural gums, was used as effective viscosity increasing agent. Guar gum made from ground endosperm of Cyamopsis tetragonolobus is an edible thickening agent that contains galactomannan which forms hydrocolloid. It is mainly used as a gelling agent, natural thickener, soil stabilizer, bonding agent, hydrocolloid, natural fiber, fracturing agent and flocculants. It is nearly odorless powder and white to yellowish white with bland taste. In cold or hot water, it could form highly viscous thixotropic sol.[12] Arabic gum was used as a stabilizer against syneresis because of its anionic properties from glucuronic acid like xanthan gum. Arabic gum made from removing the bark of trees such as Acacia Senegal is a highly branched heteropolysaccharide. Its backbone consists of β-galactopyranose units to which L-ramnopiranosas residues of L-arabinofuranoses, and glucuronic acid are connected. Therefore, it has various molecular weight between 250000 and 1000000 g/mol. It is a compact molecule in natural state, and it has its high solubility (50%) and the low viscosity in hydrocolloid system.[13-17]

In order to control retrogradation of starch, food additives such as guar gum and arabic gum could change the water activity in starch-water systems. Starch retrogradation is controlled by many factors including additives, water content, storage temperature and storage time in the system. Natural gum additives can greatly control the extent and rate of starch retrogradation by interfering with the reassociation of starch chains or by competition for water with starch.[18] Studies of moisture bonds form during bread storage could be insighted the mechanism of staling slowing effect. On the other hand, it could be explained as a result of a lower content of unbound moisture and lower content of water at the beginning of the storage period.[19] In the presence of arabic gum, swelling power of starch controlled, and other additive such as sucrose could inhibit water absorption by limiting the water availability of starch.[20] With these kinds of gums, we investigated the degradation control of starch, and it is expected that this study is the only one with the effects of amphiphilic starch and its stabilization for liposome emulsion for natural cosmetics.

Experimental

Materials. Starch used in this study was native starch from National Starch and Chemical GmbH of Germany. The guar gum and the arabic gum supplied by Earth Supplied Products, LLC of USA were used. The lecithin was supplied by SAS LUCAS MEYER COSMETICS of France. The starch has various molecular weights between 50000 and 200000 g/mol. The guar gum has mean molecular weight about 200000 g/mol. The arabic gum has various molecular weights between 250000 and 1000000 g/mol. The lecithin, that trade name is organic lecithin, contains about 12% phosphatidylcholin.

Preparation of Liposome Emulsions. Several types of starch/gum composition with the different starch gelatinization were prepared by manufacturing emulsion with lecithin using homo mixer with the chamber size of 400 cm^3. The lecithin content was fixed at 0.4% because more lecithin could make destabilization of liposome emulsion at low temperature. Lecithin is slightly too lipophilic in water-oil systems to spontaneously form the zero mean curvature amphiphile layers and has a strong tendency to form lamellar phases,[21,22] therefore it needed for stabilization of liposome emulsion to add other emulsion stabilizers. Homo mixer speed was 4500 rpm and the mixing time was 15 min for all the cases. In order to make the liposome emulsion, we preheated the water phase with the starch and the other hydrophilic ingredients for the first gelatinization at 75 °C, and then separately heated the oil phase with the lecithin and the other hydrophobic ingredients. Next, we mixed the oil phase into the water phase, and made the emulsion with homo mixer. For the second gelatinization, we mixed the emulsion and pre-dispersed gum phase with guar gum, arabic gum and water. We cooled by 28 °C the emulsion and could make stable liposome emulsion. For confidential data, we couldn't describe the contents of other components and more detailed manufacturing process. Simple formulations are summarized in Table 1. We also checked the aging viscosity for long term stability at 25 °C and freeze thaw cycling between −15 and 40 °C as formulations. The viscosity is measured by Brookfield Viscometer (LVT, BROOKFIELD ENGENEERING LABORATORIES, USA) at 1, 15, and 30 days after preparation. For the measurements, rotor No. 4 was used at 30 rpm for 1 min at 25 °C. The result of long term stability test is shown in Table 2.

Particle Size Analysis of Liposome Emulsion Base with Starch. The average particle size and the size distribution of

Table 1. Formulations and Gelatinization of the Starch/Gum Liposome Emulsion Base

Sample	Starch/Gum (wt%)	Temp. of Gelatinization (°C)	Crystallinity
A	5/0.7	75	low
B	5/0.7	25	medium
C	5/0	75	high
D	5/0	25	high

Table 2. Aging Viscosity and Long Term Stability of the Starch/Gum Liposome Emulsion

Starch /Gum (wt%)	Temp.of Storage (°C)	Viscosity (cps)			Stability
		1 day	15 day	30 day	
5/0.7	25	5000	5300	5200	Completely emulsified
	-15~40	5000	5400	5300	Completely emulsified
5/0	25	4000	4500	4800	Partially emulsified
	-15~40	4500	4700	3800	Partially emulsified

emulsion were determined by the dynamic light scattering using the Mastersizer (Mastersizer 2000, Malvern Instrument, and Worcestershire, UK). The particle size of the emulsion was described by the mean diameter and the size distribution was described by the volume per diameter and the size distribution graph.

Crystallinity Using X-ray Diffraction (XRD). The XRD patterns of the samples were obtained using a X-ray diffractometer (Miniflex, Rigaku Co., Ltd., Japan) performed at 30 KV and 15 mA with nickel-filtered CuKα (wavelength 0.15406 nm) radiation. The XRD patterns were recorded within a diffraction angle range of 5°-30° (2θ) with a scanning rate of 5° per minute and sampling the interval of 0.01°

Thermal Properties Using Differential Scanning Calorimetry (DSC). DSC analysis was conducted using a DSC Q10 model (TA Instruments, USA). Approximately 4.2 mg of a sample (dry weight basis) was weighed in a silver pan. A sealed pan with distilled water was used as a reference. Scans were run at a heating rate of 5,10 and 20 °C/min from 0 to 130 °C.

Visualization of the Emulsion System Using the Cryo-Field Emission Scanning Electron Microscopy (Cryo-FE-SEM). Emulsions were filled into the brass rivets and the plunges were frozen in liquid nitrogen. The samples were then stored with liquid nitrogen and transferred into the cryo-stage (Quorum Technologies, PP3000T, Czech) of the microscope (Tescan, Mira 3 LMU PEG FE-SEM, Czech). The sample was fractured on the cryo-stage with a knife and then coated with platinum. The sample was viewed at a temperature of -140 °C and a voltage of 1-10 kV.

Results and Discussion

The Basic Properties of Starch/Gum Liposome Emulsion. Starch/gum emulsions were prepared by gelatination, and the effect of gum content on the basic properties of the emulsion was investigated. Figure 1 shows the particle size analysis of starch/gum blends. In order to check the stability of emulsion particles, we measured the size of particles. As shown in Figure 1, the liposome had a mean diameter of 45±5 micron, which remained dimensionally stable when stored at 4 °C for 30 days. They formed with the emulsion particles of giant unilamellar vesicles,[23,24] compared to general particle size of 0.5~1 μm. The peak at 50 μm indicates the size of stabilized emulsions. These results indicate that the gum has been compositionally blended in starch/gum liposome emulsion. In order to demonstrate the improved drop stability, we measured both particle size analysis of control formulation and starch/gum liposome emulsion base. The arrow without peak indicates that particle size is uniformed and the starch/gum liposome emulsion base with 10 times dose starch is more stable than the control.

Crystallinity Using X-ray Diffraction (XRD). For stabilization of emulsion system with gelatinized starch, we have to

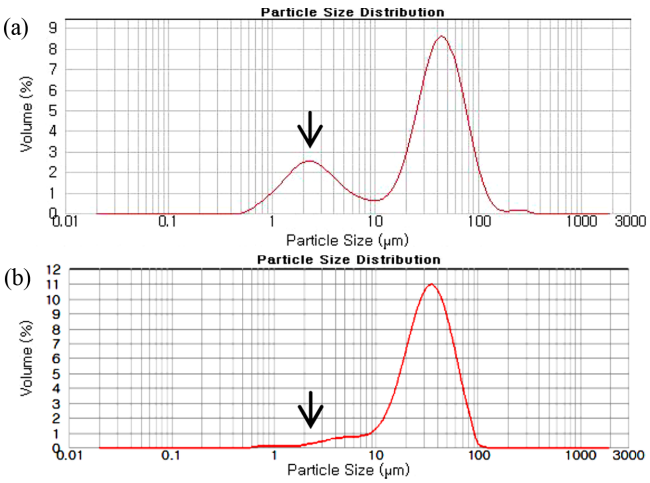

Figure 1. Particle size analysis of starch/gum liposome emulsions with different compositions of starch: (a) control; (b) 10 times dose of starch.

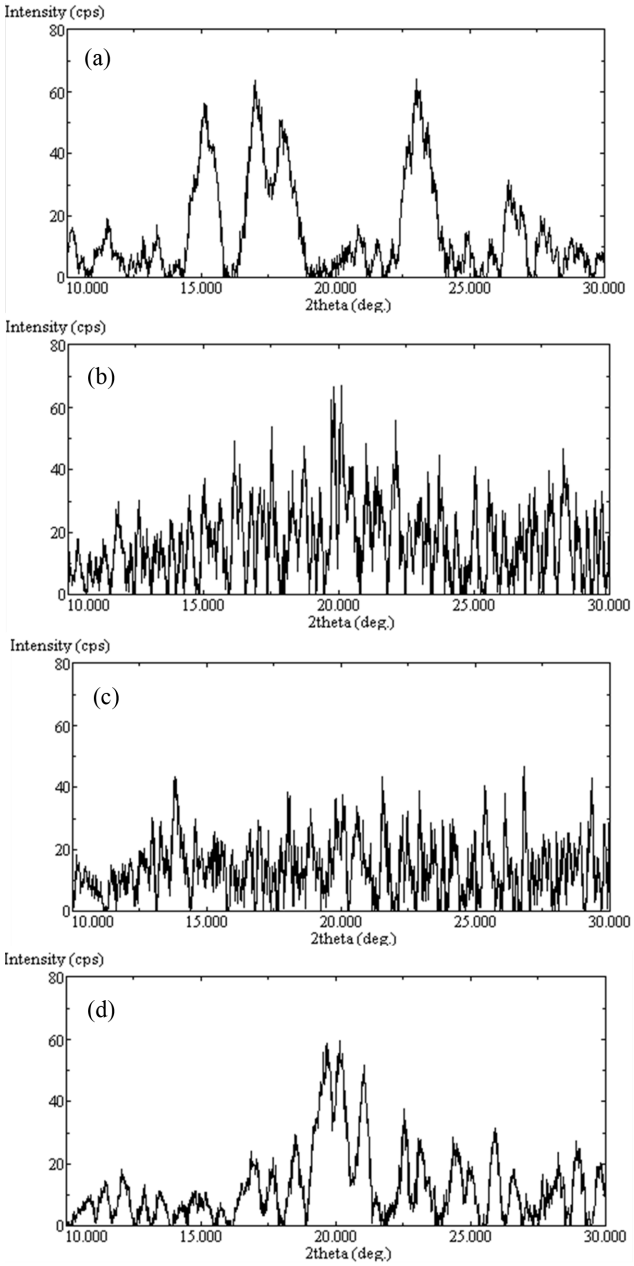

Figure 2. X-ray diffraction patterns of samples: (a) tapioca starch (TS); (b) guar gum; (c) arabic gum; (d) starch/gum liposome emulsion.

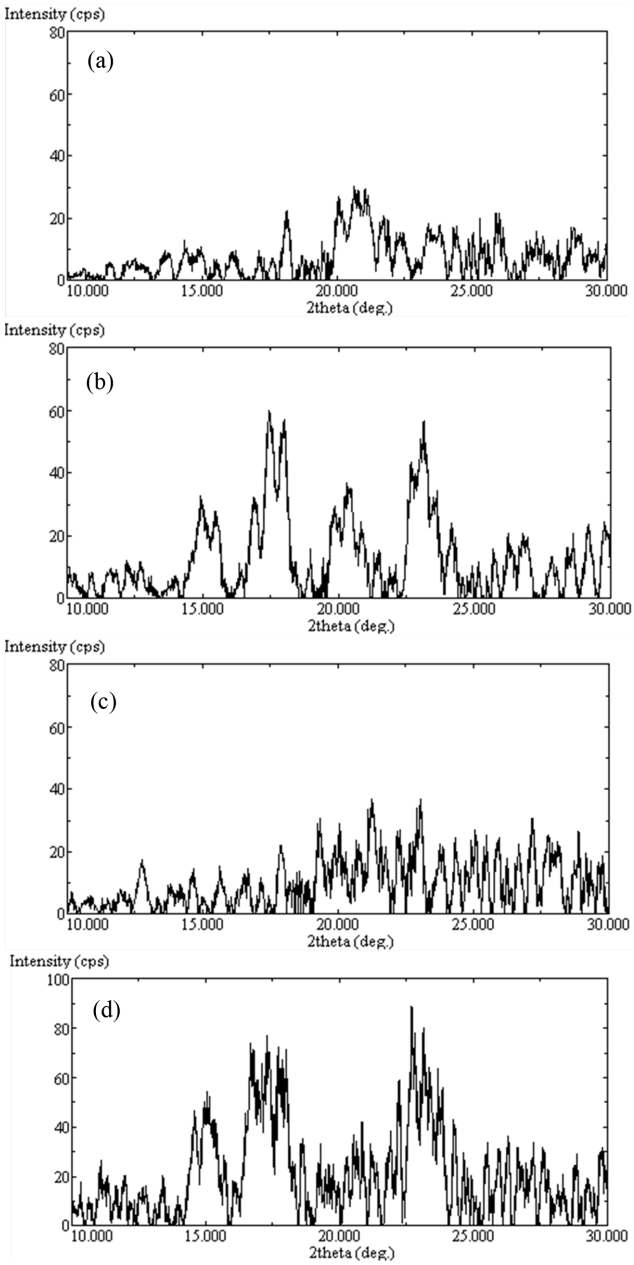

Figure 3. X-ray diffraction patterns of liposome emulsion bases: (a) gelatinized TS with gum blend; (b) non-gelatinized TS with gum blend; (c) gelatinized TS without gum blend; (d) non-gelatinized without gum blend.

control the retrogradation. We compared crystallinity of TS, guar gum, arabic gum powder, and starch/gum liposome emulsion. The XRD patterns for samples are shown in Figure 2. The peak for emulsion was broader than those of TS and gums, therefore we could check usefulness of XRD data for crystallinity of emulsion. The XRD patterns for starch/gum emulsions are shown in Figure 3. The gum blends were guar gum and arabic gum, and they were added to natural TS gelatinized (a) or not-gelatinized (b) sample. Gelatinized (a) one with gum blend could decrease starch crystallinity compared to the gelatinized (c) one without gum blend. Similarly, not-gelatinized (b) one with gum blend could decrease starch crystallinity compared to the not-gelatinized (d) one without gum blend. As a result, it was possible to control the starch retrogradation at emulsion and to make more stable natural grade

cosmetic products by gum blend formulation.

Thermal Properties Using Differential Scanning Calorimetry (DSC). Figure 4 shows DSC thermograms of the starch/gum emulsions with different compositions of starch. The degradation temperatures of the starch/gum emulsions decrease with starch content. On the other hand, the differences of degradation temperature between the samples increase with gum content. This indicats that the content of gum affects the starch crystallinity in starch/gum emulsion. In order to check the stabilization with starch contents, we evaluated DSC. The phase transition enthalpy decreases as the starch amount increases. It also showed similar results when the speed of temperature was increased from 5 to 20 °C, it proved that the result is not the phenomenon by degradation of starch itself. The transition temperatures of the starch/gum emulsions decrease with starch content. On the other hand, the differences of transition temperature between the samples increase with starch content. When the starch was loaded with 10 times higher wt% in the emulsion, the transition temperature decreased significantly. It indicated that the content of starch affects transition temperature and increases the flexibility of emulsion. It also suggests that the stability of starch/gum emulsions could be controlled. Thermal properties of the starch/gum compositions are summarized in Table 1.

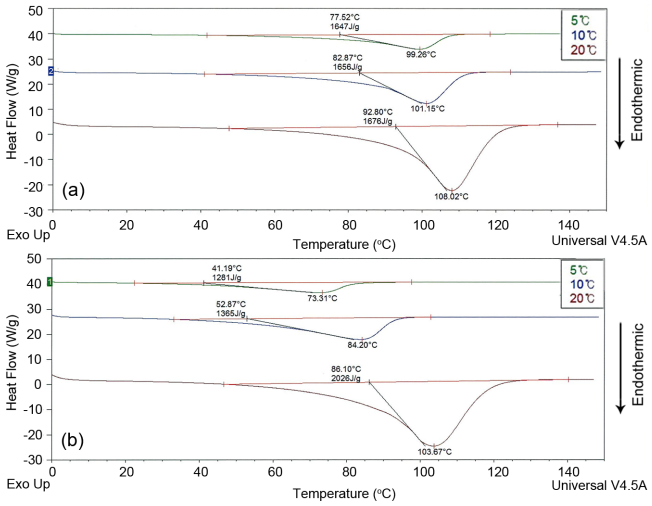

Figure 4. DSC thermograms of starch/gum liposome emulsions with different compositions of starch: (a) control; (b) 10 times dose of starch.

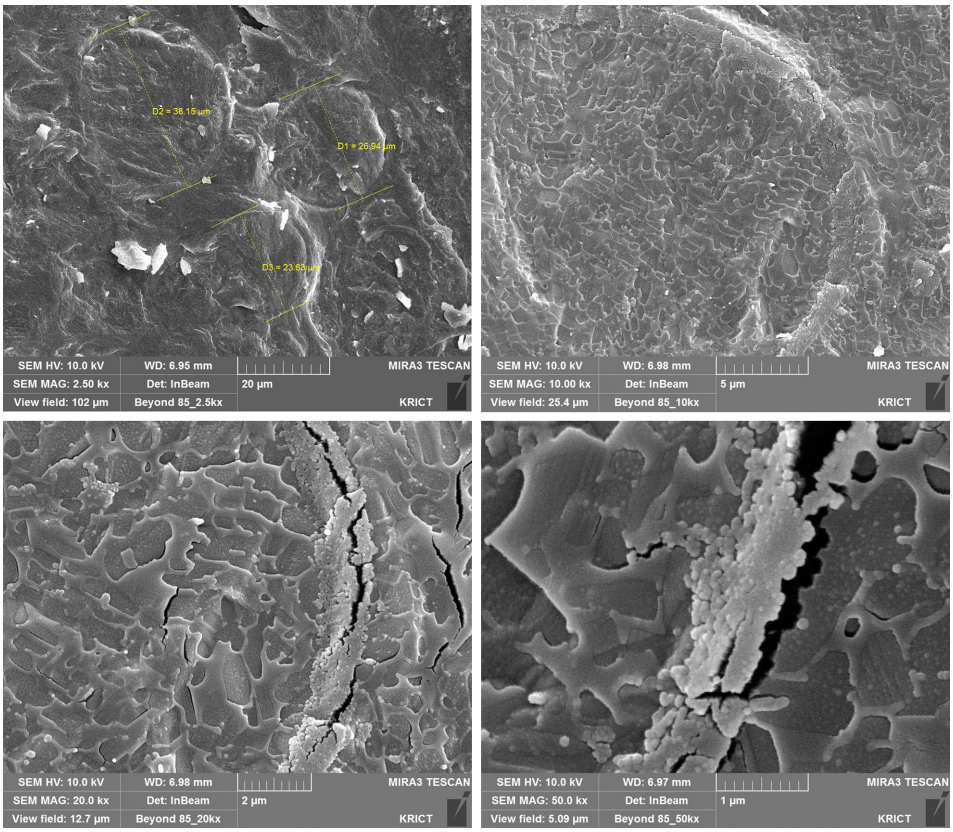

Figure 5. Cryo-FE-SEM photomicrographs of starch/gum liposome emulsion base.

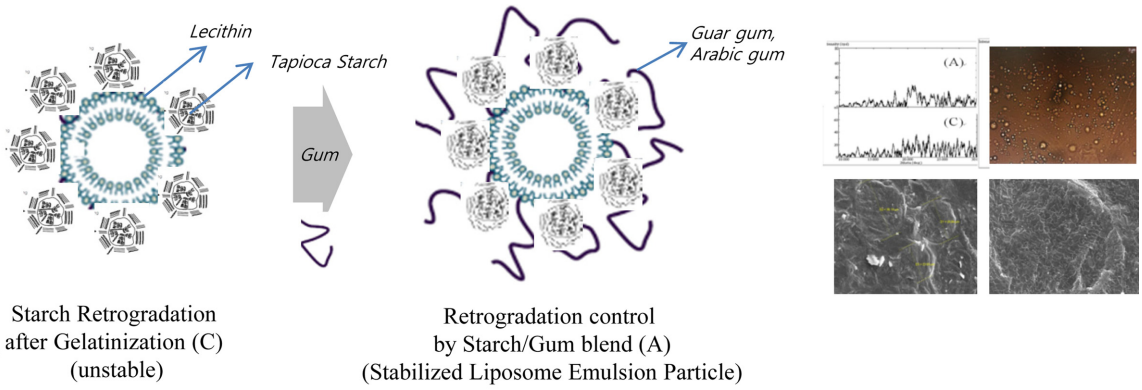

Figure 6. Schematic illustration of liposome emulsion fabricated in this study.

The starch was effective to form the stable emulsion particles. Since gelatinated tapioca starch was generally crystallized by its retrogradation, it needed to add with other gums when used as cosmetic or industrial materials. In order to stabilize the emulsion, crystallinity should be controlled. By this study, it showed that the emulsion with higher contents of starch and lower contents of gums had lower T_g. Therefore, as the contents of gums increased, the crystallinity of emulsion decreased. In the result, the starch could be emulsion stabilizer, but as the contents of starch increase, emulsion could be destabilized. But with the addition of gums, the crystallinity of emulsion could be decreased.

Visualization of Emulsion System Using Cryo-field Emission Scanning Electron Microscopy (Cryo-FE-SEM). Cryo-FE-SEM was used to observe the morphology of stable emulsions. The external morphologies and size of stable emulsions were characterized. Figure 5 shows Cryo-FE-SEM images of the original stabilized sample as each magnifications of 2.5X, 10X, 20X, and 50X. In Figure 5, most particles appear spherical with the surface having a slightly roughened appearance pattern. It indicates that starch granules are contained at its surface. In the result of Cryo-FE-SEM, we could validate the effect of starch for manufacturing of stable emulsion. This study shows that amphiphilic starch system is good for stabilization of emulsion in the field of cosmetic products. Moreover, the technology can be applied to the field of pharmaceutical formulation, in which stabilization of effective ingredients is needed.

Conclusions

We prepared a novel emulsion for cosmetics with starch crystallinity study. Figure 6 shows the schematic illustration of liposome emulsion. The emulsion was manufactured by partial gelatinization to control crystallinity.

The size of emulsion droplet is 45 μm average and the emulsion has giant unilamellar vesicle liposome. The gum blend related to starch crystallinity was reported in the previous studies. Most of the studies were found to be related to the starch that was directly involved in the rigidity control of food such as bread and cakes. In contrast to food case, we had to consider the sensory feeling in the cosmetic field. It was difficult to make good sensory feeling with other natural ingredients. However, we could make sensory and stable emulsion through the starch crystallinity control with tapioca starch and gum blend. On the other hand, we studied to produce such tens of micrometer sized particles for cosmetic formulations, and it could be made good sensory feeling even though it is formulated with many natural ingredients. Therefore, this study is the first report for the stabilization of natural cosmetics with starch and gum blend, which is not directly related to rigidity control for food, and further studies of these starch crystallinity in aspects of natural functional cosmetics are much needed. Also, DSC result demonstrated that starch could be effective emulsion stabilizer depending on the contents with gums.

Acknowledgment: Authors are grateful to LG Household & Healthcare Ltd for their endless effort to provide financial support to undertake this work. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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