Formation of Liquid Crystal Gel with Hydrogenated Lecithin and Its Effectiveness

In-Young Kim* · **Joo-Dong Lee** · **Hee-Chang Ryoo** · **[1]Choon-Koo Zhoh**

Skin Science Institute and R&D Center, ***ENPRANI Co., LTD,*** *Inchon, 400-103, Korea*

[1]Dept. of Chemical & Environmental Eng. ***Soongsil Univ.,*** *Seoul, 156-743, Korea*

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Summary

This study described about method that form liquid crystal gel (LCG) by main ingredient with hydrogenated lechin (HL) in O/W emulsion system. Result of stability test is as following with most suitable LCG's composition. Composition of LCG is as following. To form liquid crystal, an emulsifier used 4.0 wt% of cetostearyl alcohol (CA) by 4.0 wt% of HL as a booster. Moisturizers contained 2 wt% of glycerin and 3.0wt% of 1,3-butylene glycol (1,3-BG). Suitable emollients used 3.0 wt% of cyclomethicone, 3.0 wt% of isononyl isononanoate (ININ), 3.0 wt% of cerpric/carprylic triglycerides (CCTG), 3.0 wt% of macademia nut oil (MNO) in liquid crystal gel formation. On optimum conditions of LCG formation, the pHs were formed all well under acidity or alkalinity conditions. Considering safety of skin, pH was the most suitable 6±1.0 ranges. The stable hardness of LCG formation appeared best in 32 dyne/cm^2. Particle of LCG is forming size of 1~20 μm range, and confirmed that the most excellent LCG is formed in 1~6 μm range. According to result that observe shape of LCG with optical or polarization microscope, LCG could was formed, and confirmed that is forming multi-layer lamellar type structure around the LCG. Moisturizing effect measured clinical test about 20 volunteers. As a result, moisturizing effect of LCG compares to placebo cream was increased 36.6%. This could predicted that polyol group is appeared the actual state because is adsorbed much to round liquid crystal droplets to multi-lamellar layer's hydrophilic group. It could predicted that polyol group is vast quantity present phase that appear mixed because is adsorbed to round liquid crystal to multi-lamellar layer's hydrophilic group. This LCG formation theory may contribute greatly in cosmetics and pharmacy industry development.

1. Introduction

Liquid crystal gel (LCG) tells mixing state of crystallization and liquid. That is, molecular arrangement with crystallization is not regular. Regular state is known as liquid crystal or meso-phase to differ with liquid [1]. By method that improve O/W (oil-in-water) emulsion's stability, already used cetyl alcohol (CA) or stearyl alcohol (SA). 1976, S. Fukushima [2] mixed cetyl/stearyl alcohol (CSA) and secured stability of liquid crystal. So that Japanese T. Suzuki [3] stabilizes O/W emulsion in liquid crystal theory that supply suitable emollients and hydrant in skin to cosmetics applied. To improve emulsification stability, it was known as that cetanol and fatty alcohol of SA etc. concerned in O/W emulsion's formation do action that increased hardness of emulsion system [4]~[7]. Fatty alcohols are already used much in emulsion system. Such fatty alcohol's action relates with

formation of structure of liquid crystal in emulsion. N. Nakanishi [8] compounds composing ingredient of intercellular lipid properly and succeeded though moisturizing effect of skin makes high liquid crystal. Also, the same year, I. Sasaki etc. [9] succeeded to make liposome to use phosphatidyl choline (PC) and the derivatives. This liposome is multi-lamellar type differ with liquid crystal. Recently, Japanese H. Kunieda etc. [10] cleared new liquid crystal structure that qubic phase's micelle forms in octa-ethylglycol dodecyl ether ($C_{12}EO_8$)-water-oil, 3 phase systems. Thus, about liquid crystal, a lot of studies are proceeding in various fields.

Purpose of this study wished to makes O/W emulsion, and applies manufacture method and this that make multi-layer's liquid crystal inside this emulsion and makes essence, cream including various unstable active materials to use hydrogenated lecithin (HL). To make optimum LCG to use HL, experimented about condition of pH and particle size of liquid crystal. And about the most superior prescription formation availability of LCG shape and structure through microscope confirmed. Also, reported result that test moisturizing effect of LCG to use moisturizing effect measuring instrument by clinical test.

2. Experimental

2.1. Reagents

All materials used in this study used medicine or cosmetics grade. To do to form LCG structure of O/W emulsion's multi-lamellar type, used an emulsifier used hydrogenated lecithin (HL, Lucas Meyer) that is contained more than PC's content 95.0%. Emollient oil used raw material of capric/caprylic triglycerides (CCTG, Kokyu alcohol, Japan), squalane (Kishimoto, Japan), cyclomethicone (Dow corning, USA), and octyldodecanol (ODC, Cognis, Germany) etc. cosmetics grade. Wax concerned in formation of liquid crystal used cetostearyl alcohol (CSA, Cognis, Germany). Moisturizers used glycerin (LG Chemical, Korea) and 1, 3-butylene glycol (1,3-BG, Dow Chem. USA).

2.2. Devices

To make LCG used T.K Robomics (Tokushu Kika Kogyo, Japan). To observe shape of general O/W emulsification particle used optical microscope. Also, observed, and magnifies microscope by 400 ~ 1,000 magnifications to examine closely ternary lamellar liquid crystal and observed using polarization microscope to measure change of LCG formation. Also, used Rheometer (Model: CR-150, Suncaps, Japan) to observe stability by passage time about LCG.

Table 1. Composition of Lipid-LCG with Hydrogenated Lecithin in Oil-in-Water

Classification	Ingredients	Content (wt%)	Remarks
(A)	Hydrogenated lecithin (HL)	4.00	
Water phases	1,3-butylene glycol (1,3-BG)	3.00	
	Glycerin	2.00	
	EDTA-2Na	0.02	
	Methyl paraben (MP)	0.2	
	Water	Q.S	
(B)	Carpric/carprylic triglycerides (CCTG)	3.00	
Oil phase	Isononyl isononanoate (ININ)	2.00	
	Macadamia nut oil (MNO)	3.00	
	Cyclomethicone	3.00	
	Cetostearyl alcohol (CSA)	4.00	
	Propyl paraben (PP)	0.10	
	Tocopheryl acetate (TA)	0.10	
(C)	Sodium-hyaluronate	0.20	
Additives	Imidazolidinyl urea (IU)	0.20	
Total		100.00	

2.3. Manufacture method of LCG

It displayed method that makes LCG to Fig.1. Method that make LCG is as following. After, measure exactly (A) phase (water phase) of Table 1 so that total amount becomes 100 g, 75~80 °C heating melt perfectly and keeps separately. Also, (B) Measuring exactly phase (oil phase) 75~80 °C after, melt perfectly heating separately keep. Disperse this adequately projecting (B) phase slowly to (A) phase. This time, mix the first for 3 minutes by 3,000 rpm that is the suitable speed because if make strong or slackens distributed, size of particle is microscopic, or irregularly becomes. This completed emulsification reaction dispersing the second for 3 minutes by 3,000 rpm cooling this to 50 °C. It made cooling 30 °C after made stable LCG through cooling and making a vacuum process and puts (C) phase's admixture in 45 °C. This sample was precocious in 25 °C for about 72 hours when perfect liquid crystal is formed.

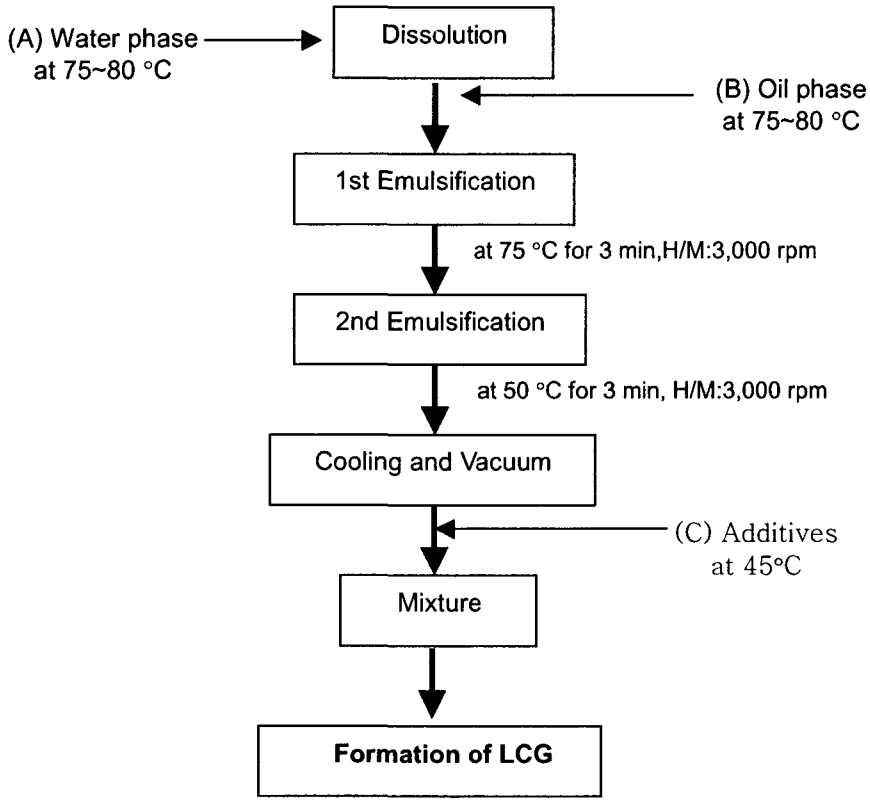

Fig. 1. The manufacturing method of the liquid crystal gel with hydrogenated lecithin in O/W emulsion.

2.4. Moisturizing effect

Device used in skin moisturizing effect measurement about LCG used Corneometer CM-825. Clinical test about skin moisturizing effect experimented according to measuring method that use at cosmetics expert and university hospital dermatology. Clinical test did to woman of 20-40 years old, and tested regardless of skin type. Method of examination chose fixed branch office of both forearms. Moisturizing effect did LCG's cream and general O/W emulsion cream by control and measured by *in-vivo*. Test condition did temperature and humidity within fixed steady temperature and humidity room. Suitable temperature is 25 °C, humidity measured under uniformity condition of 60%. Moisturizing effect test for skin measured durability because 30 minutes test to interval 2 hours, 4 hours, 6 hours after using samples. Effectiveness verification about moisturizing effect of skin verified statistical significant difference to use ANOBA t-test.

3. Results and Discussions

3.1. Structural characteristic of LCG in O/W emulsion

Usually, there are various methods that make O/W emulsion in cosmetics industry. There is seldom much method that form liquid crystal of these [11]~[15]. Usually, methods that use method and cholesterol, cholesteryl mirystate (CM) or ceramide that use CA, SA and BA etc. that is fatty alcohol is a technology that have been developed much recently [16]-[20]. But, these can make LCG but it is hard to make stable LCG. Specially, it is no big advantage in usability and quality side. LCG that is made in this study has other characteristic with general liquid crystal by LCD that use phospholipid. That is, as see in Fig. 2, formed small droplet of oil. It was that HL that has amphoteric property's emulsification forms microscopic multi-layer's lamellar liquid crystal structure because is situated on small droplet's outside. This structure had hydrophilic group of continuous phase, and lipid liquid crystal is forming densely by dispersion phase, and can depend on kind of emulsifiers [21].

Table 2. Optimizing Condition of LCG with Hydrogenated Lecithin in O/W Emulsion

Phase	Ingredients	Content (wt%)				
		F-1	F-2	F-3	F-4	F-5
(A) Water Phases	Hydrogenated lecithin (HL)	1.00	2.00	3.00	4.00	5.00
	1,3-butylene glycol (1,3-BG)	3.00	3.00	3.00	3.00	3.00
	Glycerin	2.00	2.00	2.00	2.00	2.00
	EDTA-2Na	0.02	0.02	0.02	0.02	0.02
	Methyl paraben (MP)	0.20	0.20	0.20	0.20	0.20
	Water	Q.S	Q.S	Q.S	Q.S	Q.S
(B) Oil Phases	Carpric/carprylic triglycerides (CCTG)	3.00	3.00	3.00	3.00	3.00
	Isononyl isononanoate (ININ)	3.00	3.00	3.00	3.00	3.00
	Macadamia nut oil (MNO)	3.00	3.00	3.00	3.00	3.00
	Cyclomethicone	3.00	3.00	3.00	3.00	3.00
	Cetostearyl alcohol (CSA)	4.00	4.00	4.00	4.00	4.00
	Propyl paraben (PP)	0.10	0.10	0.10	0.10	0.10
	Tocopheryl acetate (TA)	0.10	0.10	0.10	0.10	0.10
(C) Additives	Sodium-hyaluronate (SH)	0.20	0.20	0.20	0.20	0.20
	Imidazolidinyl urea	0.20	0.20	0.20	0.20	0.20
Total		100.0	100.0	100.0	100.0	100.0

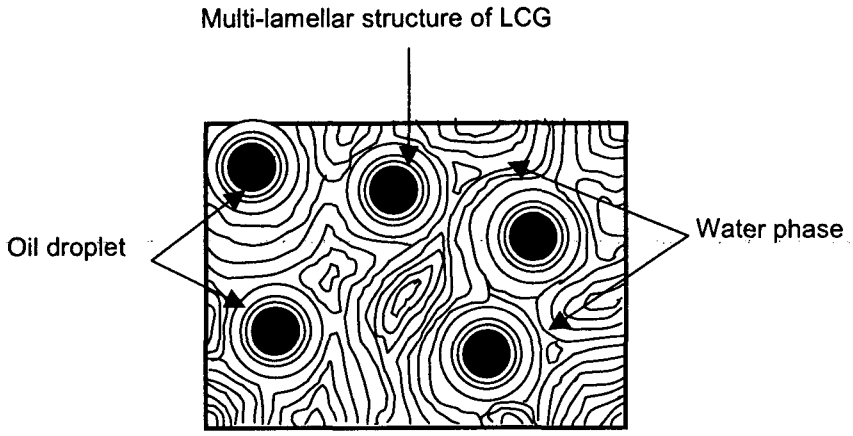

Fig. 2. Diagram of structure for LCG with hydrogenated lecithin.

3.2. Formation mechanism of LCG

3.2.1. Manufacture of LCG

To make LCG, experimented changing furtherance from Formula 1 (F-1) of Table 2 to Formula 5 (F-5) occasion of F-4 was formed best LCG. F-1 ~ F-5 that make by suitable ingredient and suitable usability and excellent quality in formation of LCG in raw material that use directly in cosmetics industry only by raw materials choose. Polyol used to LCG used 3.0 wt% of 1,3-BG and 2.0 wt% of glycerin. Emollient oil used 3.0 wt% of CCTG, 3.0 wt% of ININ, 3.0 wt% of cyclomethicone. Aiso, to make LCG by an emulsifier 1.0 ~ 4.0 wt% of HL were used. Specially, use 4.0 wt% of CA, could do to form stable LCG.

3.2.2. pH conditions

To make the idealist LCG, observed formation of LCG to use that smelt by citric acid and Na-citrate 10.0 wt% to find appropriate pH extent. Experiments about pH change applied F-4 of Table 2 that list in illustration formula, and pH interval experimented increasing by 1.0 in 5.0~10.0 extent. Because of this condition is fit suitable dimension that can be used to cosmetics. Therefore, formation of LCG by pH change could know through polarization microscope that LCG is formed well in acidity, neutrality and alkalinity. In case of make liquid crystal to use HL confirmed that hardly receive effect of pH.

3.2.3. Hardness effect of LCG

To make LCG, according to hardness effect confirmed stability of LCG. Effect of hardness applied F-4 of Table 2. Formation of LCG observed hardness change increasing CA from 1.0 wt% to 6.0 wt%. This result displayed to Fig.3. As see in Fig.3, according as CA increases, hardness increased, and hardness of cream that have suitable structure of liquid crystals were the most suitable hardness 32 dyne/cm^2 in 4.0 wt% of CA. LCG of in case of hardness is high was formed as is stable. But, quality drops in usability, and liquid crystalline shape is formed unstable in case is so low, stability of system was bad.

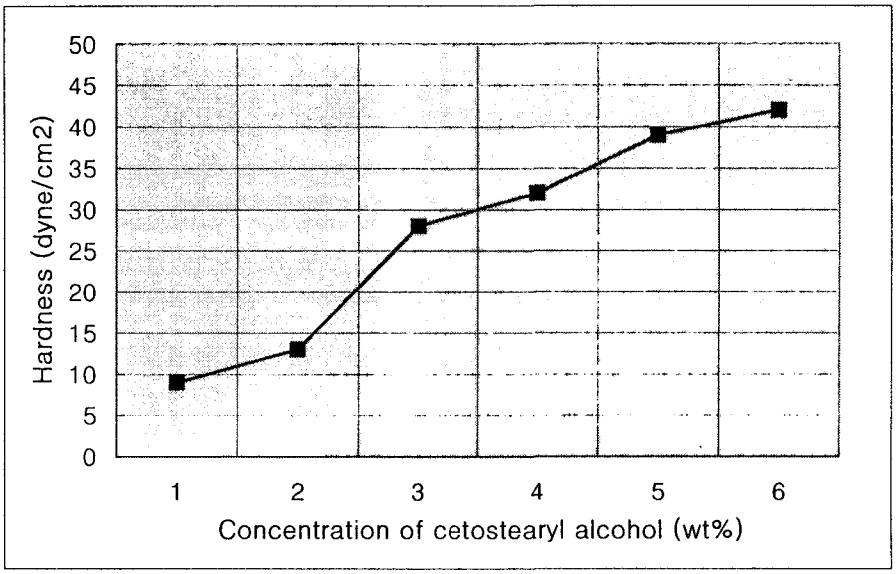

Fig. 3. Hardness of LCG depending on validation of cetostearyl alcohol.

3.3. Shape observation of LCG

LCG displayed the formed picture to Fig.4 using HL of 4.0 wt%. When observed magnifying LCG by 200 magnifications through polarization microscope, if see LCG appearing to Fig. 4(a), great many LCGs were formed very small clear. Fig.4 (b) is the picture that observe LCG by 400 magnifications, confirmed that great many LCG droplet was created. The very particular multi-lamellar layer was formed observing result expanding by again 1,000 magnifications around of liquid crystal, could know that very pellucid LCG is protecting around them (Fig.4(c)). Picture of Fig. 4(d) is prescription that use cholesterol by same content instead of phospholipid, and could know being oily and because was not mixed, that LCG was not formed perfectly. Fig.5 is the picture that observe magnifying optical microscope by 1,000 magnifications and expands outside floor of LCG to confirm whether multi-lamellar layer was formed by some structure. As see in Fig.5, protect surroundings of small droplet of oil and could confirm that lamellar layers of several fold are formed.

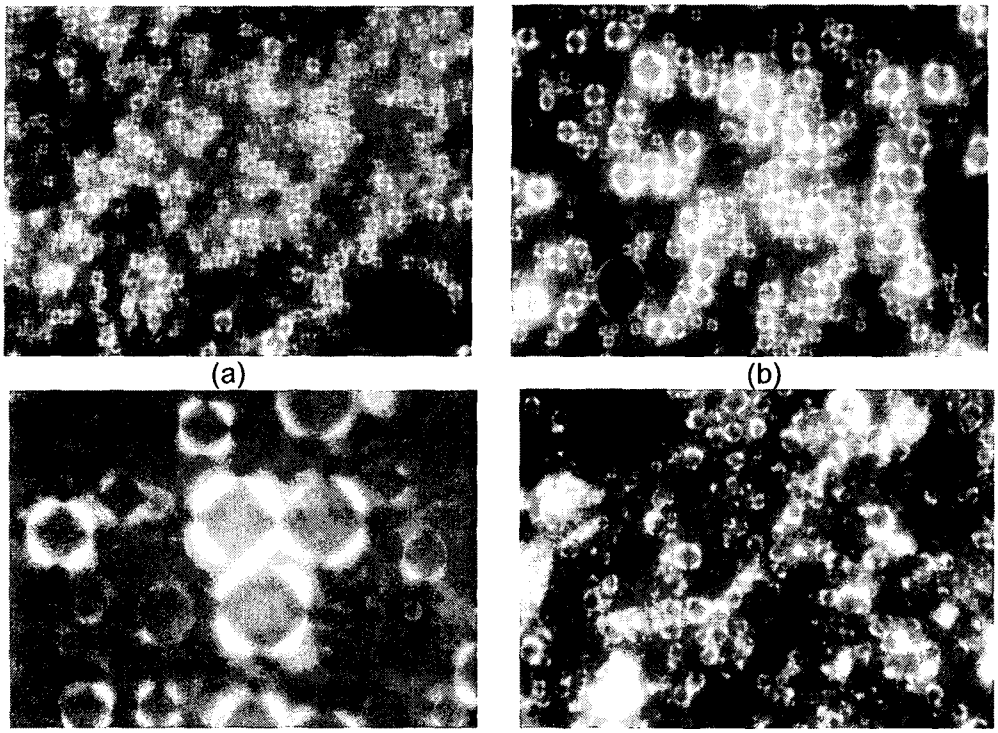

Fig. 4. Photograph of the polarized light for forming liquid crystal gel (a); 200 max, (b); 200 max, (c); 1,000 max with 4% of hydrogenated lecithin, (d); 4% of hydrogenated lecithin with 1% of cholesterol.

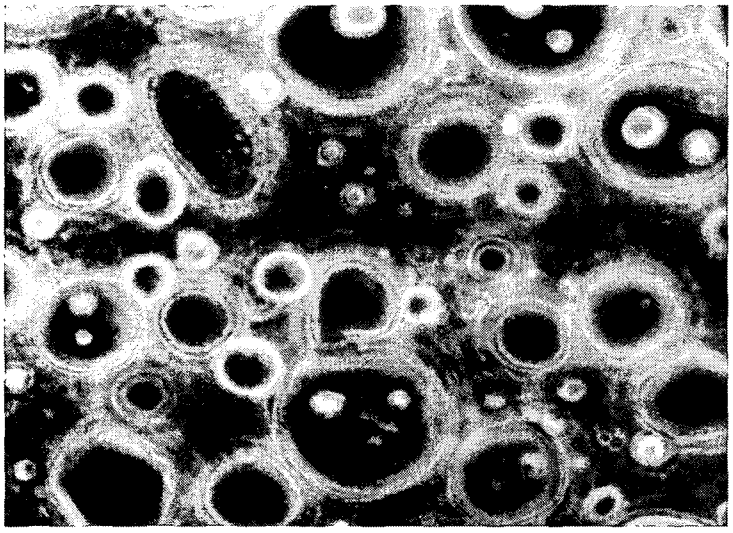

Fig. 5. The photograph of microscope of 1,000 magnifications for the formation of liquid crystal gel using 4.0 wt% of hydrogenated lecithin.

3.4. Particle measurement of LCG

Fig. 6 is size and distribution graph of particle of LCG (Table 2, F-4). Measurement of particle fills water to become 100 mL because measures exactly sample 1g and mixed by 200 rpm for 10 minutes. Using particle measuring instrument and measured particle size in 0.04 ~ 500 mm extent. As see in Fig. 6, particle distribution formed in 8.6 μm extent greatly from 0.04 μm as is small. Average particle's size could know that is 1.80 μm in grading 50 % extent. Size of particle that liquid crystal appears best could appeared best, and know that the best stable LCG is formed in 1~6 μm range by in detail in about 1~8 μm extent.

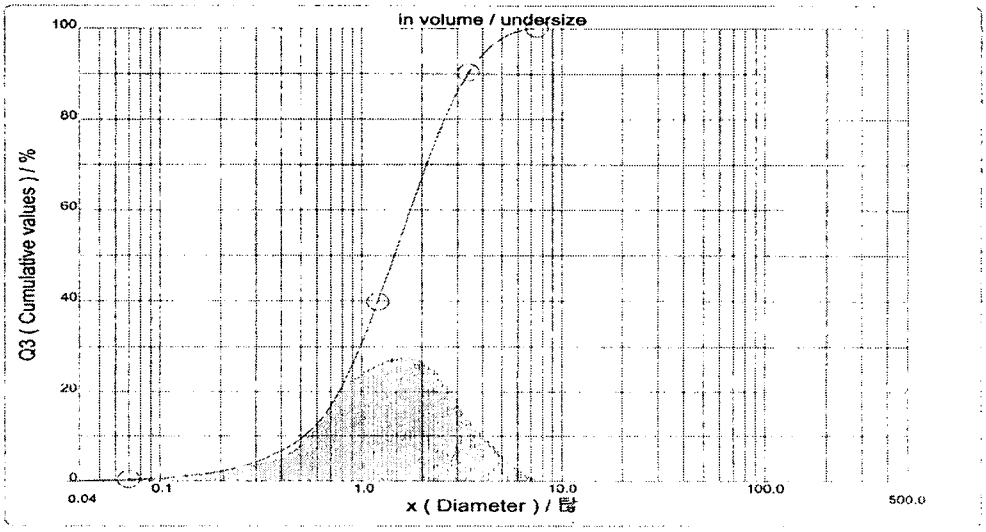

Fig. 6. Distribution of particle size for Lipid-LCG; particle size ranges: 0.1~8.0 μm (mean size :1.80 μm).

3.5. Moisturizing effect

Measurement of moisturizing effect displayed result that measure using Corneometer CM-825 that is moisturizing effect measurement equipment to Fig.7 Skin moisture activity was 62.6 before treated sample. After treated sample, by moisturizing effect of 1 hour and after, general O/W emulsion cream's moisture power by 132.7, 52.8 % increased. Because LCG was increased 54.2 % by 136.8, it was equal level by level similar to comparison sample. Also, because become low according as time passes, after passed 6 hours moisturizing effect by in case of 70.2 in O/W emulsion cream about 10.8% was low. LCG sample was shown moisturizing effect of 36.6 % by 98.7. O/W emulsion cream could see phenomenon that drop rapidly from 1 hour after treated sample. For the reason is expected in phenomenon that general O/W emulsion cream is

dehydrated fast, and stays in the case of LCG and to stratum corneoum slowly moisture action because moisture is kept long hours. This result verified statistics significant difference using ANOBA t-test, moisturizing effect confirmed that significant difference is because p-value is small more than 0.05. By method to raise moisturizing effect, LCG expects that application is possible in various formulation developments.

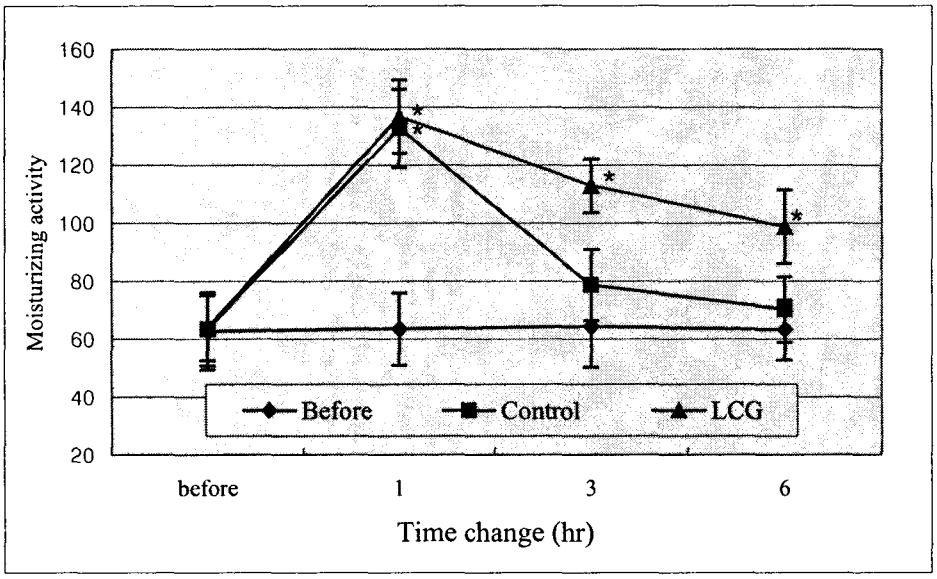

Fig. 7. Moisturizing activity of the on LCG compared with O/W emulsion cream by Corneometer CM-825 (n=20, *p<0.05).

4. Conclusions

This study found optimum to make O/W emulsion's LCG to use hydrogenated lecithin. Also, to make LCG, this study uses a various technology and testified. Stability test result is as following with most suitable composition of LCG. As composition to do to form optimum LCG, did to form LCG to use 4.0 wt% of HL, 4.0 wt% of CA. Moisturizers contained, 2.0 wt% of glycerin and 3.0 wt% of 3-BG. Suitable emollients used 3.0 wt% of cyclomethicone, 3.0 wt% of ININ, 3.0wt% of CCTG, 3.0wt% of MNO in LCG formation. On optimum of LCG formation, the pHs were formed all well under acidity or alkalinity conditions. The optimum range of pH was 6.0±1.0 ranges considering pH of skin. The best stable hardness range of formation of LCG appeared best in 32 dyne/cm^2. The particle size of LCG is forming size of 1~20 μm range, and confirmed that the most excellent LCG is formed in 1~6 μm extent. According to result that observe shape of LCG with optical or polarization microscope, LCG could was formed, and confirmed that is forming multi-layer lamellar type structure around the LCG. Measuring result, moisturizing effect of LCG, compare to placebo cream

and increased 36.6 %. The reason could forecast that polyol group is present phases that appear because is adsorbed much around LCG to multi-lamellar layer's hydrophilic group. This LCG formation theory may contribute greatly in cosmetics industry development.

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