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새로운 Black Color의 합성; 화장품에서 블랙 색소로서 Meso-pore Silca에 캡슐레이션된 Carbon-black Silica

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Synthesis of New Black Pigment; Carbon Black Pigment Capsulated into the Meso-pore of Silica as Black Pigment in Cosmetic

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요 약: 카본 블랙은 매우 낮은 밀도로 화장품에는 사용되지 않고 있지만 독성이 없고 안정한 물리적 특성과 검은색의 특성으로 이용 가치가 있다고 사료되는 바이다. 본 연구에서는 TEOS, a) PEO/ lecithin, b) PEO/polyethylene glycol, c) lecithin/polyethylene을 ethanol/water 수용액상에서 계면활성제를 탄화시켜 sol-gel반응에 의해 meso-porous silica샘플을 얻었고 N2 조건하 500℃에서 열처리된 organic-inorganic hybrid silica를 합성하였다. Pore안에 카본 블랙을 함유하는 meso-porous silica는 친수성, 소수성 용매에서 모두 좋은 분산성을 보여준다. 이 샘플은 BET에 의해 specific surface area (750 m^2/g)과 pore size (4~6 nm)이고, XRD측정으로 pore structure (cylindrical type)를, 샘플의 SEM촬영으로 morphology (0.1~0.5 μm 입자 크기를 갖는 spherical powder)를 갖는다는 것을 알아냈다.

이렇게 합성한 카본-실리카 블랙 컬러를 마스카라에 적용하면 일반적으로 마스카라에 사용되던 블랙 컬러 사용시 보다 좀더 검은색을 보여주는 것은 물론이고 우수한 분산성도 갖는다. 무엇보다 이 파우더의 밀도 조절이 가능하여 마스카라 뿐 만 아니라 모든 화장품에의 사용이 가능하다.

Abstract: Carbon black have not been used as pigment material in cosmetic because of very low density and dispersity, but carbon black have applicable character as black pigment because of non-toxic, stable physico-chemical property, and black colority. In this study, mesoporous silica samples were synthesized by sol-gel reaction using surfactants-template method; TEOS (tetraethoxysilane) - a) PEO/lecithin, b) PEO/polyethylene glycol, c) lecithin/polyethylene glycol in ethanol/water solution. Synthesized organic-inorganic hybrid - silica were heat-treated in N2 condition at 500℃. Mesoporous silica with black carbon in pore have the effective density and show the good dispersity in both hydrophilic and hydrophobic solvent. Properties of the samples were measured; specific surface area (750 m^2/g) and pore size (4~6 nm) using BET, pore structure (cylindrical type) using XRD, morphology (spherical powder with 0.1~0.5 μm partical size) of the samples using SEM. Carbon-silica black color applied to mascara, it shows a dark black colority and good dispersity as compared with the general black color titania pigment. Moreover, it is possible to control the density of black color pigment because it is possible to control pore volume and particle size of mesoporous silica properly. It show the good volume effects in mascara. That is why possible to apply all kinds of cosmetic products.

Keywords: *new matrials, organic/inorganic hybrid silica, carbon-silica pigment, mesoporous silica, SEM*

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1. Introduction

Recently the trend of new materials development is extensively and very actively progressing in the study of physical and chemical characteristics developing a totally new material along with the study field of recently discovered material modifying physically and chemically characteristics.

Among these fields of studies, one method to improve adaptation of inorganic material is the study of mesoporous materials. The most general way to synthesize mesoporous materials is to mold the very systematical mesopore into a corpuscle by using templates. These mesoporous materials are studied in a broad field such as catalyst, bio-sensor, optics, nano-composite materials (ceramic), polymer composite materials etc.

Among chemical compounds using mesoporous templates, surface active agent is used most generally, but surface active agent not only at a solvent is dispersed thermodynamically in a equal formation but also variety of template features differ at the active agent species. Surface active agents are divided by polar head group in to cation, anion, non-ionic, and amphiphiles etc[1-8].

If higher density than CMC (critical micelle concentration) of surface active agents is added into the solvent, rod micelles form inside the micelle[9]. Mesoporous silica uses surface active agents as a template and is manufactured with sol-gel method resolving silicon-alkoxide with water. Sol-gel reaction, as known as, divides into an early hydrolysis process, gel process by polymerization of sol that is hydrolyzed, and corpuscle's growth process. At that point, polarity intermediate forming rod micelle reacts with surface active agents' polar head group and forms organic/inorganic hybrid material. So in result, it decides the size and structure of the rod micelle and the pore[10-14]. The size of the rod micelle is depended on the molecule shape and length of surface active agent's non-polar group. Also, the structure of the pore is differed by the interaction of polar head group and silica polymer, interaction between surface active agent's non-polar group, and characteristics the solvent. These interactions by surface active agent are showed by variety and concentration cylindrical form of hexagonal close packing structure or cubic form's structure[15,16].

At this research, we synthesized organic/inorganic hybrid silica by using surface active agent as template at lecithin, PEO from water and ethanol mixed solution. Even though, a large amount of lecithin is used at the field of biochemistry and cosmetics, it has barely been synthesized using organic/inorganic hybrid material. Even though, carbon black is stable non-toxically, physically and chemically since the density is small and dispersion is bad it is hardly used as cosmetics.

At this experiment, surface active agent uses template synthesizes organic/inorganic hybrid silica and we used this template by heat treatment by heat treatment in deoxidization and synthesized black pigment making black carbon that was carbonized by pore trapped.

These kinds of black pigments (called carbon-silica pigment from the following) can control the density by silica and carbon's relative quantity and can also control dispersion at hydrophilic solvent or hydrophobic solvent, so it can be used as very effective cosmetics. So at this research, we are trying to experiment the negligence of property of matter which put great effect on the use and safety of mascara. Also, for a effective use as an black pigment, we are trying to measure the difference of color of synthesized carbon-silica pigment.

2. Experiment

2.1. Materials

Tetraethoxy silane (TEOS, 99.9%, Aldrich), hydrogenated lecithin (90%), polyethylene glycole (3,000 Mw, 99.9%, Fluca), polyethylene oxide (PEO, 99%, Aldrich), ethanol (99%, Aldrich) were used as received, not more purified. High purity water was used as third-distilled, 18 MΩ.

2.2. Preparation of Silica with Mesopore Trapped Carbon

The composition of the solution used for synthesizing the sample is listed on Table 1.

At this research, manufactured samples by altering lecithin, PEO, PEG's density variably had shown excellent results with the composition on Table 1, therefore this thesis will be explaining samples synthesized with these composition.

Add an appropriate amount of lecithin, PEO, poly ethylene glycol in 50 mL of alcohol, apply heat and dissolve. After cooling this dissolvent at room temperature,

Table 1. Synthetic Composition of Mesoporous Silica

Sample	Ethanol (mL)	Lecithin (g)	PEO (g)	Polyethylene glycole (mL)	Water (mL)	Amonia(mL)	TEOS (mL)
LPS	50	0.75	0.25	0	10	0.2	11.2
PES	50	0	0.75	0.25	10	0.2	11.2
LES	50	0.75	0	0.25	10	0.2	11.2

add water and TEOS and for the dissolvent to be even reaction with diapering enough. Finally, if you add ammonia water, heat it 50 degrees, the sol-gel reaction lasts for 12 h. When reaction finished rinse 3 times with ethanol than filter.

Dry the white settlement at 110 degrees for 24 h, than crush the dry sample by milling. There are two ways that dry samples are used. One is heat treatment in nitrogen gas atmosphere and another is heat treatment in a closed up melting pot. Of heat treatment temperature such as 300, 350, 400, 450 degrees while synthesizing black mesoporous silica but the 400 degrees heat treatment sample has showed the best results, there fore in this thesis we will explain only about the results of heat treatment at 400 degrees.

2.3. Characterization

To confirm the synthesized organic/inorganic hybrid silicon's effective temperature during heat treatment we measured TG/DTA at temperature area of room temperature 700 degrees with 1 degree heating rate per minute among atmosphere.

You can confirm the pupil's shape and size formed by mesoporous silica by using the already widely known, Brag's equation '$2d\sin\theta=n\lambda$'. As the pore's diameter size is large, 2θ's angle show smaller diffraction peak. At the this research, we ensured the synthesized sample using 1° low angle, scanning rate of 0.1° per minute, and XRD of $1\text{-}8^{\circ}$ of 2θ area.

The wavelength of X-ray source is 1.45 A by Cu K line. The heat treated mesoporous silica particles of morphology is measured by using SEM.

2.4. Mascara Materials

The basic formation and containment of mascara containing synthesized black pigments are organized on Table 2.

Table 2. Carbon-silica Pigment Containing Mascara Manufacture Prescription

Ingredient		Content (%)
A	Di-Water	To 100
	Triethanolamine	1.0
	1.3 B.G	5.0
	Polyoxyethylene sorbitan monostearate	1.0
B	Carbon-silica pigment	7.0
C	Di-water	10.0
	Hydroxyethylcellulous	1.0
D	Methyl paraben	0.1
	Propyl paraben	0.1
	Carnauba Wax	3.0
	Stearic acid	3.0
	Cetyl alcohol	2.0
	Hydrogenated Stearyl Olive Esters	5.0
	Sorbitan stearate	1.0
	Microcrystalline wax	2.0
	Polyglyceryl-3 Bees wax	2.0
E	Acrylate copolymer emulsion	20.0
F	Di-Water	0.5
	Imidazolidinyl Urea	0.1

2.5. Machinery

The necessary equipment to produce mascara as in oil paint equipment T. K Robomics (Tokushu Kika Kogyo, Co., Japan) was used and as in dispersion agi mixer (Hanyang, Korea) was used.

To predict mascara's visual transition, Sun rheometer (Sun Scientific Co. Ltd., Japan) was used. To measure blackness, colorymeter used Eye 3100 (Mecbeth Co,Ltd., U.S.A). TG/DTA (Thermal Instrument, SDT 2960 TA 4000) XRD (Rigaku, D/MAX 2200 ultima) SEM (Jeol, JSM-6700F).

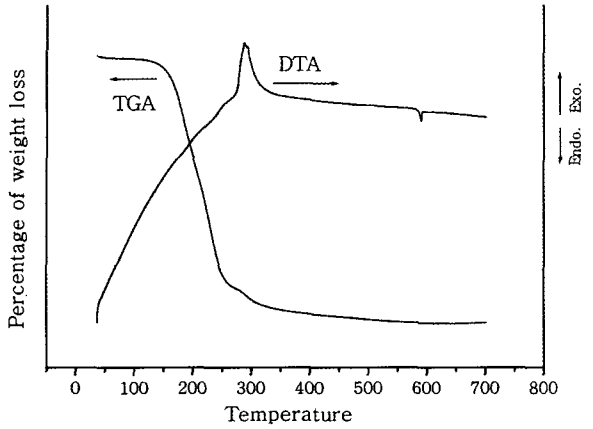

Figure 1. TG/DTA curves of LES sample in atmosphere.

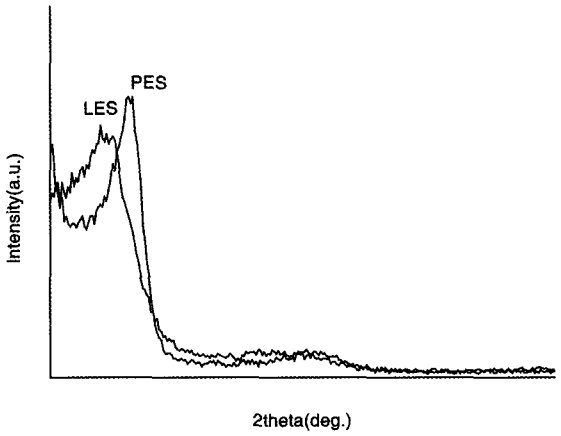

Figure 2. XRD peaks of LES sample and PES sample.

2.6. Manufacture

Mascara manufacture process using Carbon-silica pigment is made by using ingredients on Table 2.

First, diffuse phase C transparent by using Agi Mixer as transparent liquid state. Next, weigh phase A and heating at 70℃. Mix the prepared phase A and C, heating at 80±2℃ than add to phase in and diffuse it well. After diffusing phase A, B, C in homomixer at 2,000~2,200 for 5 min (temperature maintenance) add to phase put D in and homogenizing at 3,000~3,500 for 7 min. While homogenized in cooling it at 53±2℃ add to phase E and phase F and homogenizing for 5 min. Cool it till 30 degrees and complete manufacture. Control was manufactured in a identical method. At control, we used Iron Oxide black manufactured at Japan Titan Industry.

3. Results and Discussion

The synthesized organic/inorganic hybrid silica which used surface active agent as template differs the size and structure of a pupil by the interaction between polar head group and silica's sol-gel polymer and the interaction between non-polar groups. So as in result, by the surface of active agent's sort, the carbonized temperature changes.

To confirm this result, we measured the heat treatment temperature of synthesized organic/inorganic hybrid silica by using TG/DTA. The Figure 1 is the result of measurement of TG/ DTA of Les Sample in atmosphere. From near 100 degrees, the weight reduces andexothermicreaction appears which are the process of oxidation of samples remaining in the solvent. As the template which is the surface active agentoxidizes near 300 degree, a strong exothermicreaction appears.

These exothermic reaction ends near 400 degrees and at near 600 degrees, endothermic reaction appears which originates the decay of pore's meso size during structure phase transition. Also, though it doesn't show here, surprisingly when the template is used as PEO, similar results appear.

Especially, there are some changes by the amount of Lecithin and PEO added, but the amount of addition of PEG. In accordance with this study, mainly comment LES and PES. From the result of this research, we were able to obtain black silica sample from 400℃ carbonization. Like the circumstance, PES sample which uses PEO as template predicts it has smaller pore that LES sample because of the larger 2θ angle diffraction peak. And we can identify the reason peak's half width a show larger is because the formation of the pore is less even than the LES sample. From the measurement results of XRD, if you use Bragg's equation to calculate the pore's size, the PES sample is about 1 nm and LES sample shows 2 nm.

The measurement result of BET 750 m/g of Les's specific surface area and PES's surface area is 600 m/g making the LES surface area larger. And it was measured tat the LES or PES sample's pore size was similar about 1~2 nm. Figure 3, 4, and 5 are the SEM measurement results of each LPS, PES, LES sample's morphologies. For instance, samples using PEO as templates have large size particles and show in a flake shape. In LPS, micro-particle is shown compensation

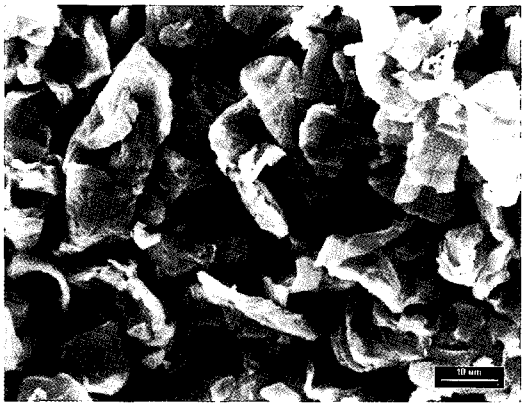

Figure 3. SEM measurement of LPS sample.

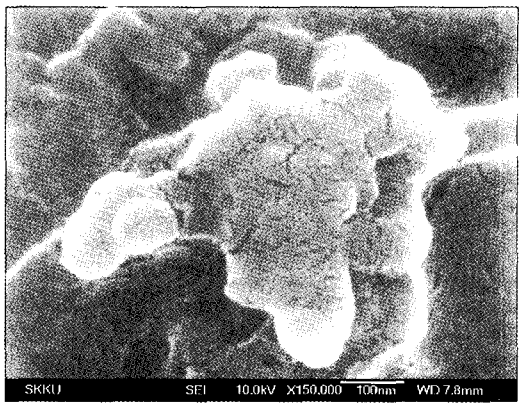

Figure 4. SEM measurement of PES sample.

structure in growth form and as template carbonizes, the carbonized carbon grows forming a crack between particles.

These results are identical to LES samples. But in LES samples, these cracks are formed very evenly and micro particle is formed in large particles as carbonized carbon on grain boundary. From these results, we can predict, the process of templates being carbonized, diffusion phase of carbonized carbon, formation of black silica particle through carbon black's growth process mechanism. From now on, we believe that while these template surface active agent is more variably transformed these mesoporous material synthesizing research would be progressed synthesizing new materials with more superior practical ability and skill. Table 4 is blackness of colorymeter synthesized carbon-silica pigments.

Up to now, blackness rather than iron oxide black which was mainly used as black pigment mascara was more superior. This is one of the important features on black pigment and when applied at mascara, it is a element giving great effect to expression of clear eyes. The result after synthesizing mesoporous silica by carbon that mesopore is trapped, hydrophilic and hydrophobic solvent greatly improved to all at diffusion.

Also, among cosmetics when mascara one of the products that uses black pigments the most, is applied density control is eased and dispersion is superior so it puts great effect on mascara's stability and safety. Not only the property of matter adjustment is easy but also blackness adjustment is possible so that when the regularly used black pigment is compared, it shows superior property of matter. Figure 6 is the comparison

Table 4. Compared Carbon-silica Pigment with Iron Oxide Black Blackness by Colorymeter

Sample	Trial	L
Carbom-silica pigment	1	14.231
	2	14.102
	3	14.352
Iron Oxide Black	1	17.448
	2	17.552
	3	17.956

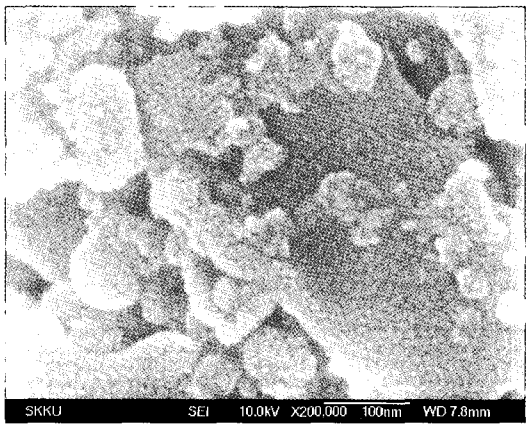

Figure 5. SEM measurement of LES sample.

graph about the hardness of product property of matter. The results are the checks of hardness difference for 4 months. The first month was checked once a week and after that, once in every 2 weeks. The first hardness compared with control was rather big but as time flowed, this research shows that the carbon-silica pigment solidity changes become smaller. The pigment itself, showed excellent diffusion making the solidity

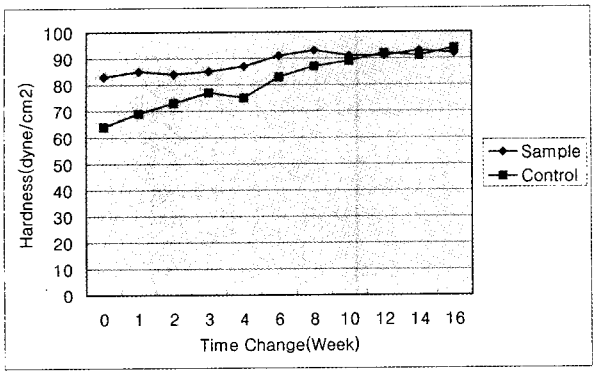

Figure 6. Hardness of sample (included carbon silica pigment) with control (included iron oxide black) during 4 months, showed bar.

large at first but at hardness changing iron oxide black shows smaller change proving excellent effect on mascara's safety.

4. Conclusion

As a result of synthesizing carbon mesopore trapped mesoporous silica, hydrophilic and hydrophobic solvent all diffusion largely elevated.

From this research's result, rather than template using as PEO using Lecithin is more effective way to synthesize black color mesoporous silica. Through template's carbonized process, carbonized carbon's diffusion phase, carbon black's growth phase reaction mechanism, it is predicted surface active agent template is carbonized forming black color mesoporous silica. Through these reaction mechanisms, black color mesoporous silica forms particles by cohering silica micro corpuscles, between silica corpuscles carbonized carbon shows compensation structure forming grain boundary.

These carbon-silica pigment is possible at density control of powder and excellent blackness when applied at mascara, enough efficacy can be shown even only when general black pigment's 50% is used so that the product itself not only can easily control property of matter but is also able at controlling diffusion of hydrophilic solvent and hydrophobic solvent and to O/W Emulsion or W/O Emulsion, it's adaptation is all possible making it an effective black pigment.

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