

Synthesis of new black pigment ; Carbon black pigment capsulated into the meso-pore of silica as black pigment in cosmetic

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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.

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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.

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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

2-1-1 Materials

Tetraethoxy silane (TEOS, 99.9%, Aldrich), Hydrogenated Lecithin(90%,), polyethylene glycole(3000Mw, 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, 18MO.

2-1-2 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, 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 hours. When reaction finished rinse 3 times with ethanol than filter,

Dry the white settlement at 110 degrees for 24 hours, 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, therefore in this thesis we will explain only about the results of heat treatment at 400 degrees.

2-1-3 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, Bragg'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 $1-8^\circ$ of 2Θ area.

The wavelength of X0ray source is 1.45 A by Cu K line.

The heat treated mesoporous silica particles of morphology is measured by using SEM.

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

Table 1. Synthetic composition of mesoporous silica.

2-2-1 Mascara Materials

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

	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

Table 2. Carbon-silica pigment containing mascara manufacture prescription

2-2-2 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, colorimeter 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)

2-2-3 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°C.

Mix the prepared phase A and C, heating at 80±2°C than add to phase in and diffuse it well.

After diffusing phase A, B, C in homomixer at 2000~2200 for 5 minutes (temperature maintenance) add to phase put D in and homogenizing at 3000~3500 for 7 minutes.

While homogenized in cooling it at 53±2°C add to phase E and phase F and homogenizing for 5 minutes.

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.

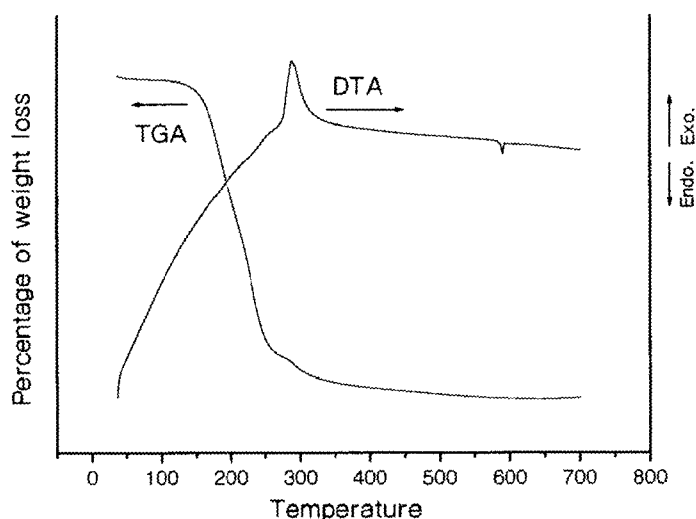


Fig1. TG/DTA curves of Les Sample in atmosphere.

The figure 1 is the result of measurement of TG/DTA of Les Sample in atmosphere. From near 100 degrees, the weight reduces and exothermic reaction appears which are the process of oxidation of samples remaining in the solvent. As the template which is the surface active agent oxidizes near 300 degree, a strong exothermic reaction 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°C 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 2nm.

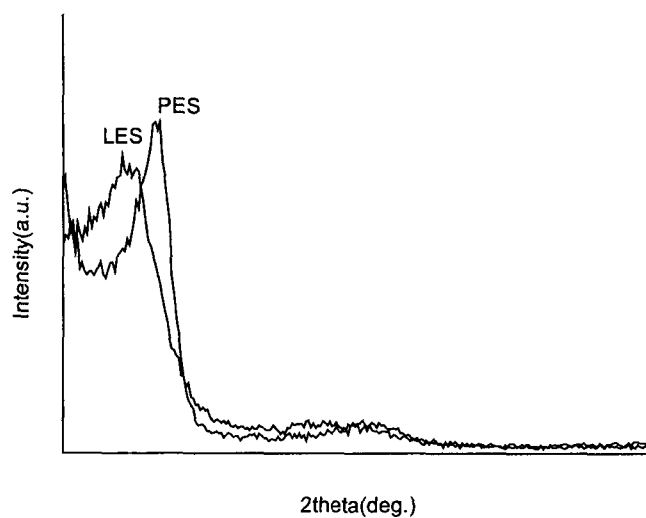


Fig.2 XRD peaks of LES sample and PES sample.

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 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.



Fig. 3 SEM measurement of LPS sample.

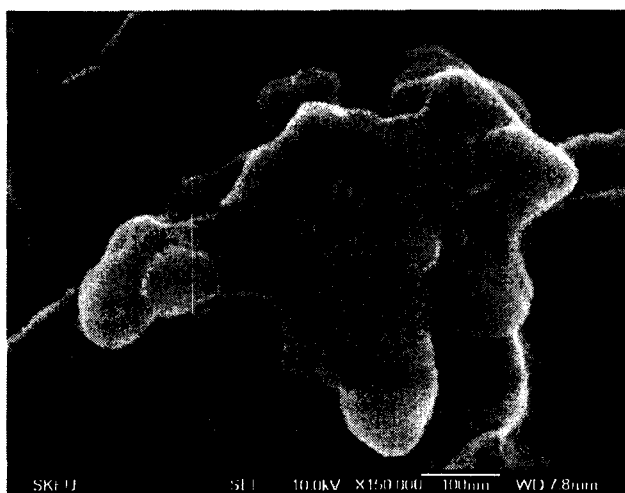


Fig. 4 SEM measurement of PES sample.

Table.4 is blackness of colorimeter 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.

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

Table 4. Compared carbon-silica pigment with Iron Oxide Black Blackness by colorymeter

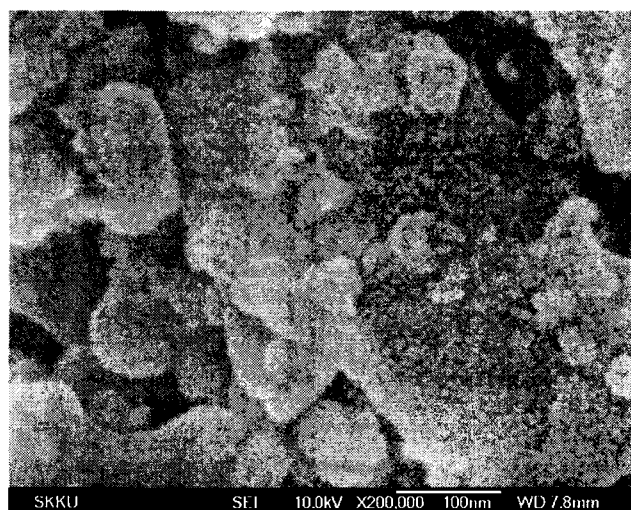


Fig. 5 SEM measurement of LES sample.

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.

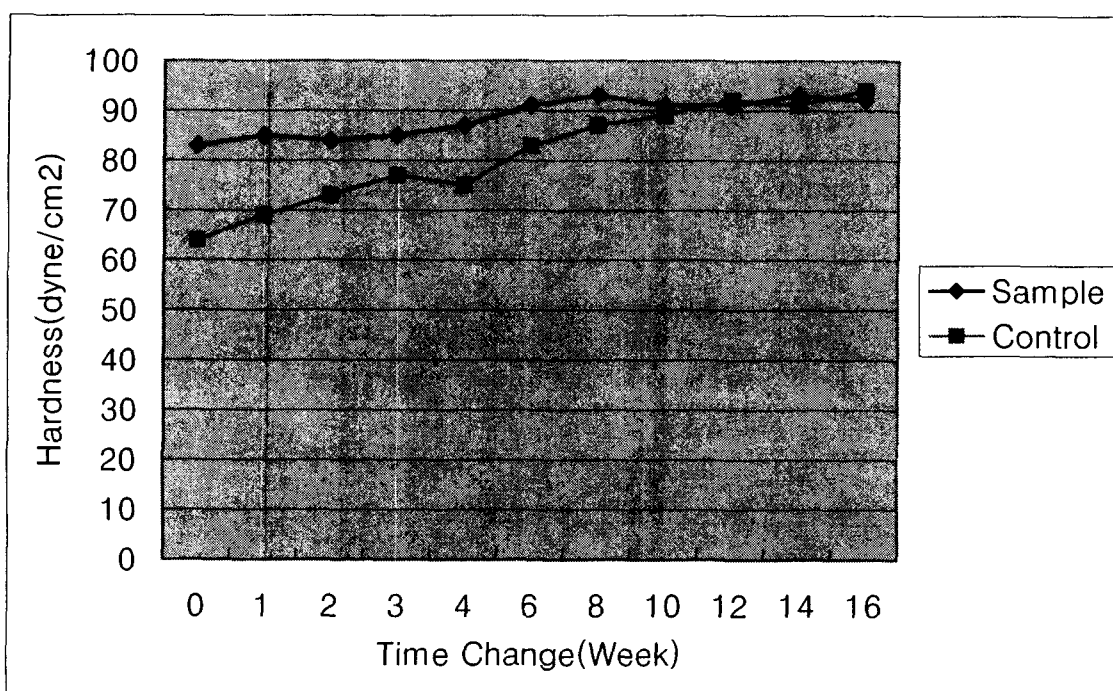


Fig. 6 Hardness of sample (included carbon silica pigment) with control (included iron oxide black) during 4 months, showed bar.

Figure 6 is the comparison 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 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 OW Emulsion or W/O Emulsion, it's adaptation is all possible making it an effective black pigment.

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