Study for Organic(Bio)-Inorganic Nano-Hybrid OMC

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Abstract

OMC is essentialiy necessary compound in sun goods as organic UV protecting products. But the skin-trouble problem is raising because of skin penetration of OMC. In this study, non-capsulated pure OMC was compared with Organic-Inorganic-Nano-hybrid OMC for skin penetration force and SPF degree. Organic- Inorganic Nano-Hybrid OMC is OMC trapped in the pore of the mesoporous silica synthesized by the sol-gel method after OMC is nanoemulsified in the system of the hydrogenated Lecithin/ Ethanol/caprylic/capric triglyceride/OMC/water. OMC- nano- emulsion was obtained by a microfluidizing process at 1000bar and then micelle size in the nanoemulsion solution is 100-200nm range. Mesoporous silica nano-hybrid OMC was prepared by the process ; surfactant was added in dissolved OMC-Nanoemulsion, then the rod Micelle was formed. OMC-nanoemulsion was capsulated in this rod Micelle and then silica precursor was added in the OMC-nanoemulsion solution. Through the hydrolysis reaction of the silica precursor, mesoporous silica concluding OMC-Nanocapsulation was obtained. The nano-hybrid surface of this OMC-Nanoemulsion-Inorganic system was treated with polyalkyl-silane compound. OMC-Mesoporous silica Nano-hybrids coated with polyalkyl-silane compound show the higher sun protecting factor (SPF Analyzer : INDEX 10-15) than pure OMC and could reduce a skin penetration of OMC. The physico-chemical properties of these nano-hybrids measured on the SPF index, partical size, strcture, specific surface area, pore size, morphology, UV absorption, rate of the OMC dissolution using SPF Analyzer, Laser light scattering system, XRD, BET, SEM, chroma Meter, HPLC, Image analyzer, microfluidizer, UV/VIS. spectrometer.

Key Words: OMC, OMC-nanoemulsion, Organic(BIO)-Inorganic Nano-Hybrid OMC

1. Introduction

Preparations of mesoporous materials using various templates and their applicability have been intensively investigated for many years. In synthesizing the organic/inorganic hybrid materials, surfactants have been used

as conventional templates.[1-7] Especially non-ionic surfactants are very effective templates on synthesizing the monolithic mesoporous materials and modifying the wall of meso-, nano-pore.[8-10] There are many reports on the synthesis of mesoporous materials using non-ionic surfactant such as PEO(Poly Ethylene Oxide) copolymers, amphiphiles, Lecithin and the like. Those preparations using Lecithin are relatively rare because of more hydrophobic character of amphiphilc surfactants, although Lecithin has been using very much in biochemical field.

Mesoporous materials can encapsulate and immobilize the functional molecules in the pores. We studied on synthesizing mesoporous silica with pores in which sensitive compounds having weak physicochemical properties on heating or UV irradiation and low solubility in solvent are trapped. In this work, OMC(Octyl Methoxy Cinnamate), UV filter in cosmetic, was using as sensitive compound. Prior to trapping OMC in pore of mesoporous silica, OMC was nano-emulsified in O/W system using Lecithin. Thereafter Nano-emulsified OMC was trapped in pore by sol-gel method through the hydrolysis of silicon-alkoxide compound. Main focus of this work is to prepare OMC-trapped mesoporous silica and to trace the stability and solubility of nano-emulsified OMC in the pores of mesoporous silica.

Using XRD, we were able to confirm that synthesized mesoporous silica appeared uniform in pore size and had very large specific surface area. In addition, the OMC trapped in pore were stable over a long period of time from the measuring results of UV/Visible spectroscopy. From this research, our results could be useful in developing new critical materials utilizing nano-emulsified OMC- trapped mesoporous silica.

2. Experiment

2-1 Materials

Tetraethoxy silane (TEOS, 99.9%, Aldrich), Hydrogenated Lecithin(90%,), Octyl Methoxy cinnamate(OMC, 99.9%,), and Cetyltrimethyl ammonium chloride (CTAC, 99%, Aldrich) were used as received, not purified.

2-2 Preparation of nano-emulsified OMC solution

OMC nano-emulsion was synthesized with lecithin/ ethanol /OMC/ water system. First, after dissolving lecithin/ ethanol /OMC/ water in 40℃, nano-emulsified three times with high pressure microfluidizer under 1000BAR and makes OMC nano-emulsion.

2-3 Preparation of mesoporous silica trapped OMC in pore

In this study, mesoporous silica samples were synthesized in ethanol and water solvent, because the characters of synthesized samples depend on the polarity of solvent.[11] The composition of OMC, TEOS, and Lecithin are listed by the ratio of mass in Table 1. The synthesizing process in water and ethanol solvent is same. Because lecithin is dissolved hardly in water, so CTAC was used with lecithin as template. And only lecithin was used in the case of ethanol solvent. In the case of water solvent, organic/inorganic hybrid silica cannot synthesize

uniformly because hydrolysis rate of silicon-alkoxide is so fast under the basic condition. So in the case of water solvent, samples were synthesized using amine surfactant with high Lewis basity under acidic condition. CTAC was added to 500mL of water and stirred for 30 minutes in order to uniform the composition of the solution. The nano-emulsified OMC solution was added to this solution and stirred around 30 minutes. Thereafter TEOS and hydrochloric acid was added in this solution, and reacted at 60 ℃ for 12 hours. After reacting, filtered and dried at 75 ℃. In case of ethanol, lecithin was added to 500mL of ethanol and heated for dissolving at 60 ℃. Nano-emulsified OMC solution was added to this solution and stirred for 30 minutes to uniform the composition of the solution. TEOS and ammonia was added to this solution and reacted for 12 hours at 60 ℃. After reacting, filtered and dried at 80 ℃.

2-4 Characterization

The trapped situation of OMC in pore of the organic/inorganic hybrid silica was confirmed employing Thermal Gravimetry/Differential Thermal Analysis (TG/DTA, Thermal Instrument, SDT 2960 TA 4000) in 25-700℃ temperature range under heating rate of 1℃/minute in air. Bragg's equation $2d\sin\Theta=n\lambda$is used to get the size and shape of the pore in mesoporous silica.

The pore structure of synthesized samples were measured using X-ray diffractometer (XRD, Rigaku, D/MAX 2200 ultima) under the condition of 1° low angle , scanning rate of 1°/minute, and 2Θangle of 1-8° for measuring. X-ray source is Cu Kα line and wave length is 1.45Å.

In order to measure UV/Visible absorption of OMC, synthesized mesoporous silica powders (0.01g) were dispersed in 100mL of water with supersonication and the absorption were measured in the wavelength range of 200nm-700nm using UV/Visible spectrometer (HP, MP8453). To measure the solubility of OMC trapped in the pores with variation of dispersed time; 10, 20, 50, 100 min., 1g of each samples was dissolved in the 100mL acetonitril solvent.

3 Results and Discussion

Sol-gel reaction of silane compound is composed of hydrolysis reaction process, polymerization process, and growth process of particles. Mesoporous materials have been synthesized with surfactant template performing the rod micelle shape in the concentration over critical micelle concentration. By interaction between the polar head group of the surfactant and sol-gel polymers, organic/inorganic hybrid material with hexagonal close-packing structure of rod micelles is made.[12-14] The pore structure of organic/inorganic hybrid materials depends on not only interaction of polar head group and sol-gel polymer but also interaction and length of non-polar group in surfactants.[15] The size and structure of pores depend on the kinds of solvent and surfactants, and concentration of surfactants.

Figure 1 is the XRD results of the synthesized samples with OMC trapped pores and non-trapped pores in

ethanol solvent. The diffraction of X-ray between pore walls is explained by Bragg's equation. As pores have large diameter, X-ray is diffracted at the more small 2Θangle. The pores of sample added nano-emulsified OMC are bigger than the pores of synthesized mesoporous silica sample without OMC in ethanol solvent. Also XRD peak of sample without OMC shows the sharp singular peak. This result is that pore is distributed with ordered structure. Contrary in case of the sample added emulsified OMC, the pores increase in the size and have not the monolithic structure.

Figure 2 is XRD measuring reasults of mesoporous silica sample with variation of added amount of nano-emulsified OMC, which samples were synthesized in the ethanol solvent. According to addition of nano-emulsified OMC, the sizes of the pores did not change, but the intensities of peak only were increased.

Figure 3 is result of XRD measurement of the samples synthesized using surfactants CTAC in water solvent with changing of the addition amount of nano-emulsified OMC. Also in case of water solvent, the size of pores does not show depending on the addition amount of nano-emulsified OMC. However, the pores of samples synthesized in ethanol solvent are bigger than the pores of sample synthesized in water. This result is that diameter of rod micells is increased with lecithin, which is cohered partly because the solubility of lecithin is not good in ethanol. While CTAC that solubility is good in water makes very uniform rod micelle.

Figure4 and 5 are TG/DTA measuring results of synthesized EX and EC samples in ethanol solvent respectively. In case of EC sample, the weight is decreased rapidly from 100 ℃unlike EX sample because nano-emulsified OMC becomes oxidation in trapped rod micelle and the weight is decreased. By oxidation of Lecithin interacting between the polar head group of Lecithin and silica in air, exothermic reaction shows near 300℃. And the mesopores of mesoporous silica decay around 600℃. This decay temperature of the mesopores differs from the structure and size of the pores. In general, as size of pore is big, it decays in lower temperature. The endothermic reaction at 600℃ is evidence that synthesized silica in this study have the meso-sized pores. As shown in Figure 6 and 7,WX and WC samples synthesized in the water solvent are same results in case of ethanol. We can confirm that nano-emulsified OMC is trapped in CTAC and Lecithin rod micelle.

Figure 8 and 9 are the UV/Visible absorption of organic/inorganic hybrid silica synthesized in ethanol solvent without OMC and in ethanol/ nano-emulsified OMC solution respectively. With increment of the added amount of nano-emulsified OMC, the absorption is increased in the UV wavelength range. Nano-emulsified OMC trapped in rod micelle of silica is encapsulated and immobilized by complicated physical force like interaction between the molecules and capillary phenomenon.

To understand these effects, it is interest in comparing with solubility of OMC in acetonitril solvent, which was trapped in the rod micelle of organic/inorganic hybrid silica. Figure10 is the UV absorption results of OMC dissolved in acetonitril solvent after EA, EB, EC, ED samples were dispersed for 20 minutes. As prediction, the UV absorption was increased with increasing of added amount of OMC.

Figure11 is the UV absorption results of OMC dissolved in acetonitril solvent after WA, WB, WC, WD samples were dispersed for 20 minutes. In the case of water solvent, the result also was same in ethanol solvent. This result is evidence that nano-emulsified OMC is trapped stably in rod micelle.

Figure 12 is the solubility of OMC trapped in WC sample with variation of dissolution time in acetonitril solvent. As the dispersion time is increased, the solubility is increased. Figure 13 is the solubility of OMC trapped in EC sample with variation of dissolution time in acetonitril solvent. As the dispersion time is increased, the solubility is increased, too. However, the solubility of OMC trapped in samples synthesized in water solvent is better than that in ethanol solvent. We confirm that samples synthesized in water solvent were more stable than those in ethanol solvent and the method using water as solvent is more effective than ethanol from these results.

From this research, our results could be useful in developing new advanced materials utilizing trapping method another critical molecules as well as OMC in mesopores of mesoporous materials.

The SPF value of both the emulsion with 7% of OMC mixed generally and the solution with 10% of Organic-Inorganic Nano-Hybrid OMC is in Fig.14.,Fig.15. Sun spray prescription in Table 2.The conventional sun spray containing 7% of OMC is compared with that containing 10% of Organic-Inorganic Nano-Hybrid OMC, the SPF of Organic-Inorganic Nano-Hybrid OMC in vitro is higher by 10 or more than that. The reason is that SiO2, lecithin, etc. exist in the Organic-Inorganic Nano-Hybrid OMC causing a boosting action with the organic filter.

. Penetration effect

The ethanolic solution and the two OMC-preparations were non-occlusively and ex vivo applied onto human skin obtained after cosmetic surgery. The experiment was carried out in Franz-type diffusion cells. One made sure that the acceptor compartment was filled with phosphate buffer below the skin to avoid over-hydration. Three hours after application, the skin surface was cleaned and skin cylinders were punched. After cryo-fixation, pieces with a thickness of 10 were cut. The penetration of the marker-molecules were examined by confocal laser scanning microscopy.(Fig.16.).

Organic-Inorganic Nano-Hybrid OMC is very inferior in effects of skin penetration.

4 Conclusion

This study was very useful in synthesizing organic/inorganic hybrid silica, which Nano-emulsified OMC was trapped stably in rod micelle. The mesopores of silica have more monolithic ordered structure in case of using ethanol/Lecithin method, but the trapping ability of nano-emulsified OMC is better in case of using water/CTAC method.

Table 1. Synthetic composition of organic/inorganic silica samples.

sample	solvent (mL)	Lecithin (g)	CTAC (g)	Nanoemulsified OMC (g)	NH4OH (mL)	HCl (mL)	TEOS (g)
EX	50	0.75		0	0.2		11.2
EA	50	0.75		1.4	0.2		11.2
EB	50	0.75		1.7	0.2		11.2
EC	50	0.75		2.0	0.2		11.2
ED	50	0.75		2.4	0.2		11.2
WX	50		2.8	0		10	11.2
WA	50		2.8	1.4		10	11.2
WB	50		2.8	1.7		10	11.2
WC	50		2.8	2.0		10	11.2
WD	50		2.8	2.3		10	11.2

Table 2. Sun spray formulation

	Ingredient	
A	EDTA-2Na	0.01
	Methyl paraben	0.20
	Glycerine	4.00
	Cetyl phosphate	0.20
	Water	make to 100
B	C12-15 alkyl benzoate	4.00
	Stearic acid	0.10
	4-methylbenzylidene camphor	3.00
	cyclomethicone	4.00
	Lecithin	1.00
	BHT	0.03
	OMC(Nanohybrid OMC)	7.00(10.00)

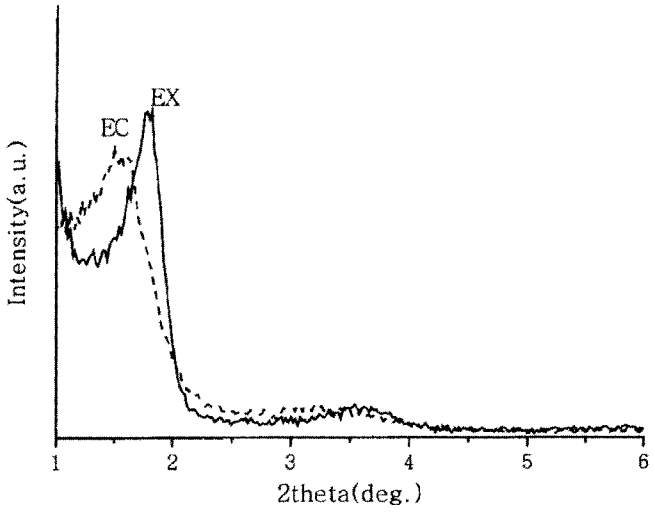


Fig.1 XRD peaks of EX sample and EC sample.

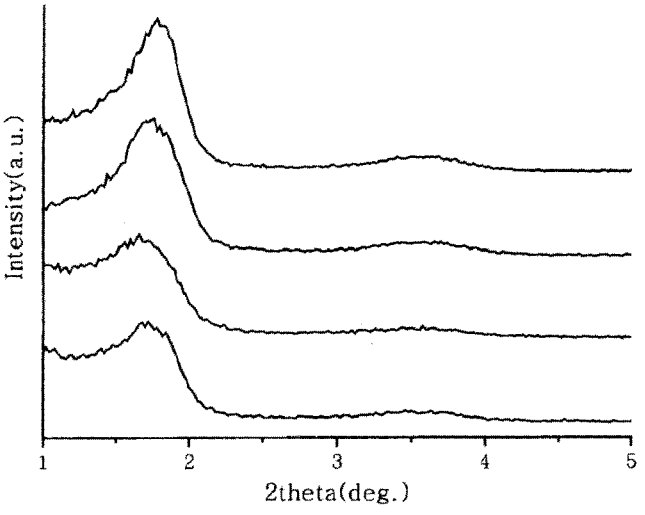


Fig.2 XRD peaks of EA, EB, EC and ED samples.

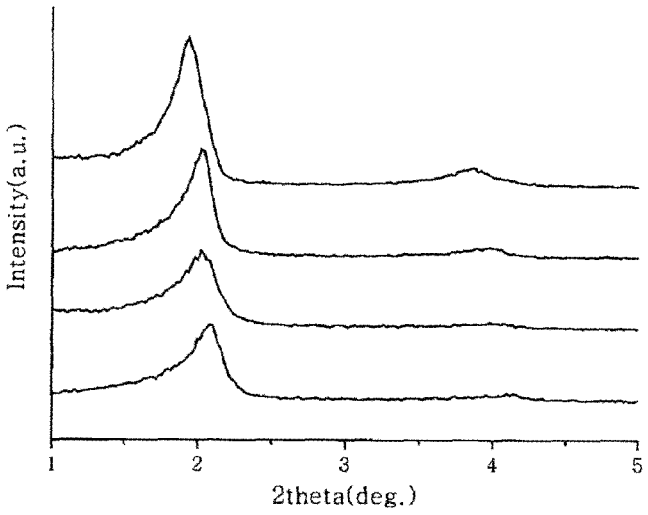
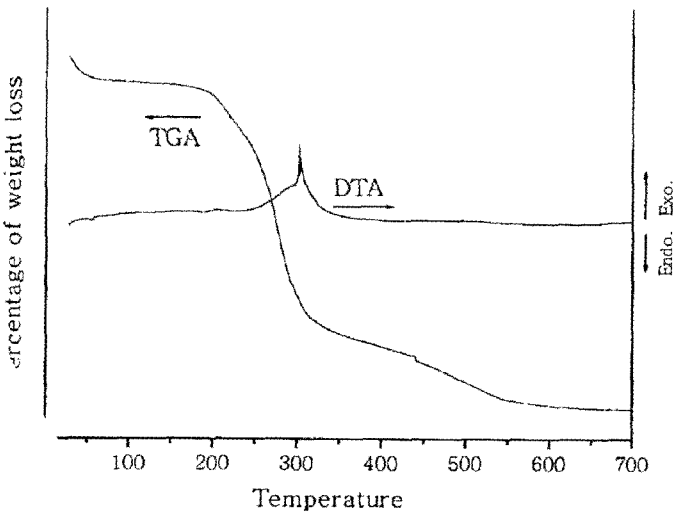


Fig.3 XRD peaks of WA, WB, WC and WD samples.



'A curves of EX sample.

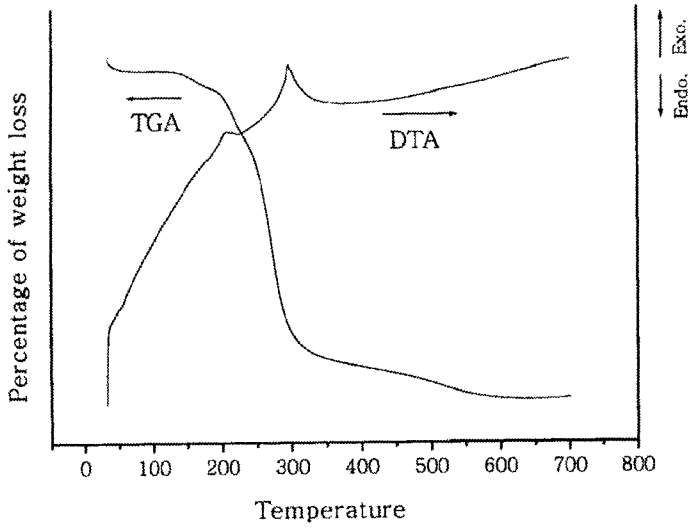


Fig.5 TG/DTA curves of EC sample.

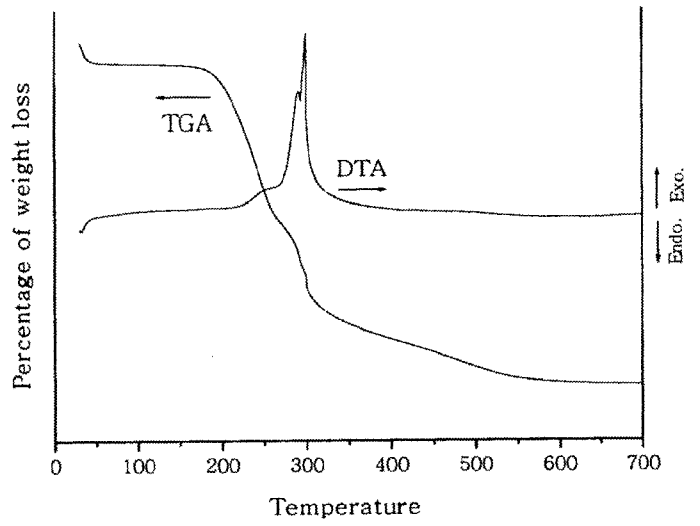


Fig.6 TG/DTA curves of WX sample.

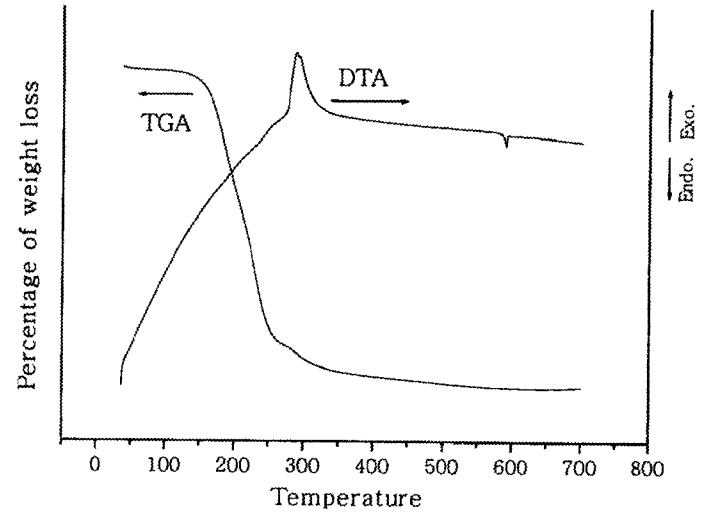


Fig7. TG/DTA curves of WC sample.

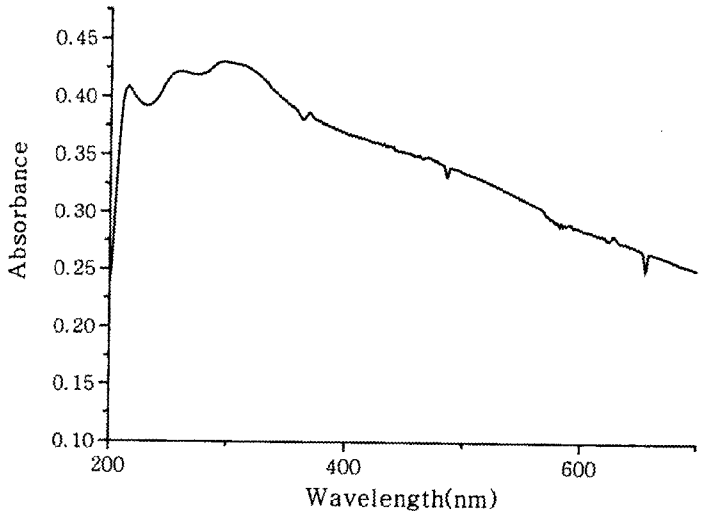


Fig.8 UV/Visible absorption spectrum of Lecithin templated mesoporous silica.

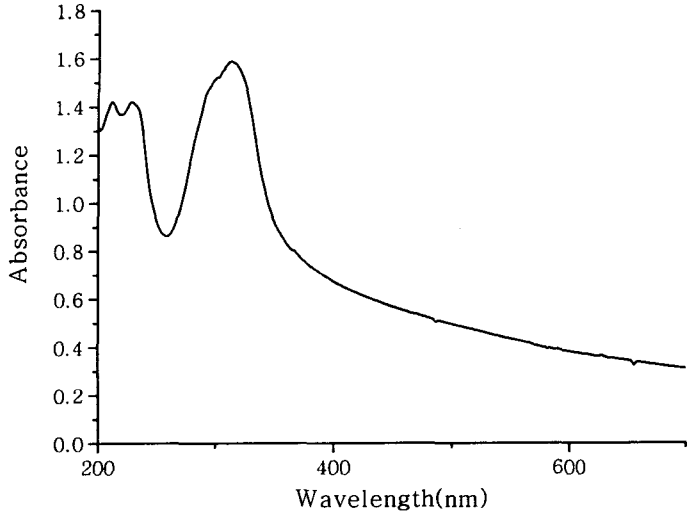


Fig.9 UV/Visible absorption spectrum of OMC trapped mesoporous silica.

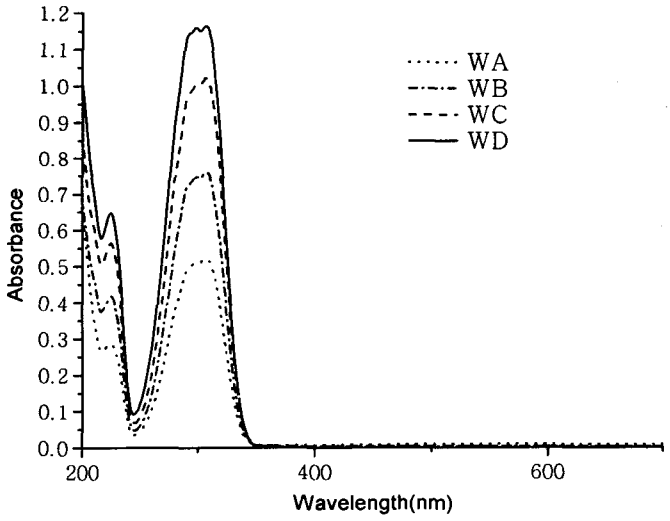


Fig.10 UV/Visible absorption spectrum of WA, WB, WC and WD samples.; absorption with variation of *the OMC concentration.*

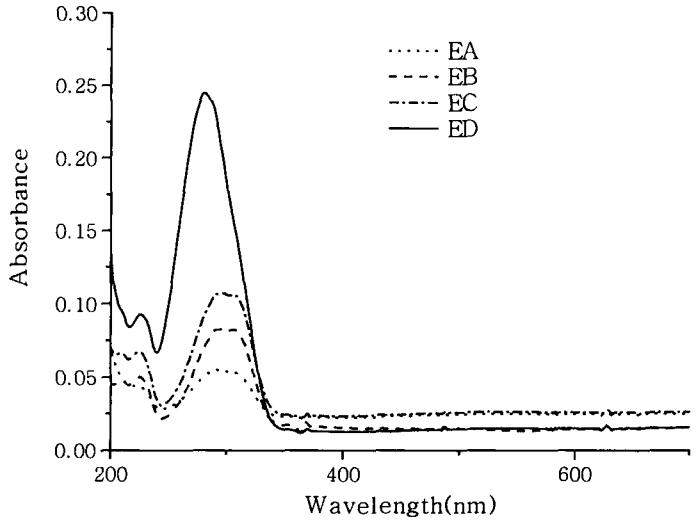


Fig.11 UV/Visible absorption spectra of EA, EB, EC and ED samples; absorption with variation of the OMC concentration.

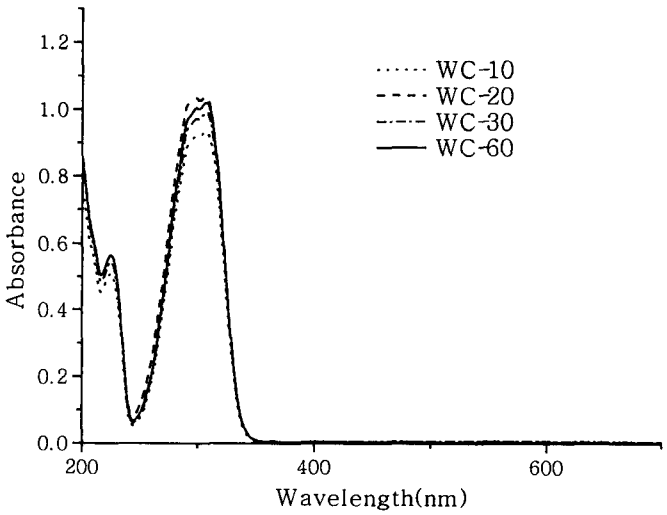


Fig.12 UV/Visible absorption spectra of dissolved OMC in acetonitrile solvent with variation of dissolution time on the WC samples.

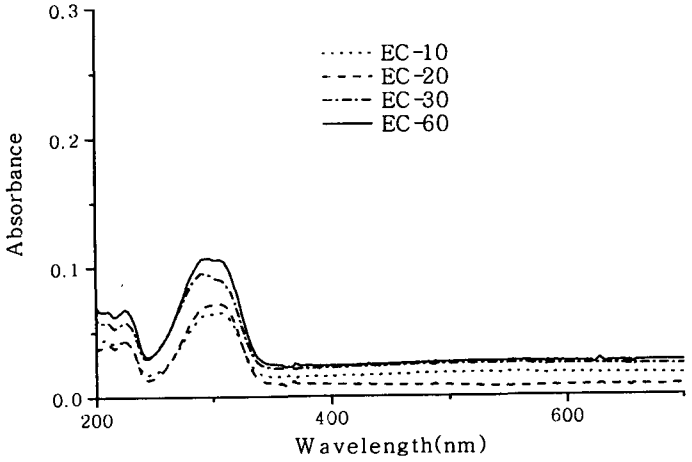
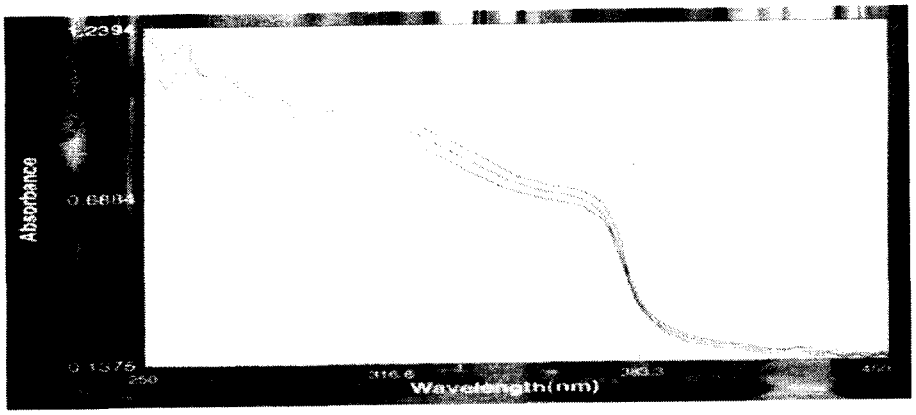
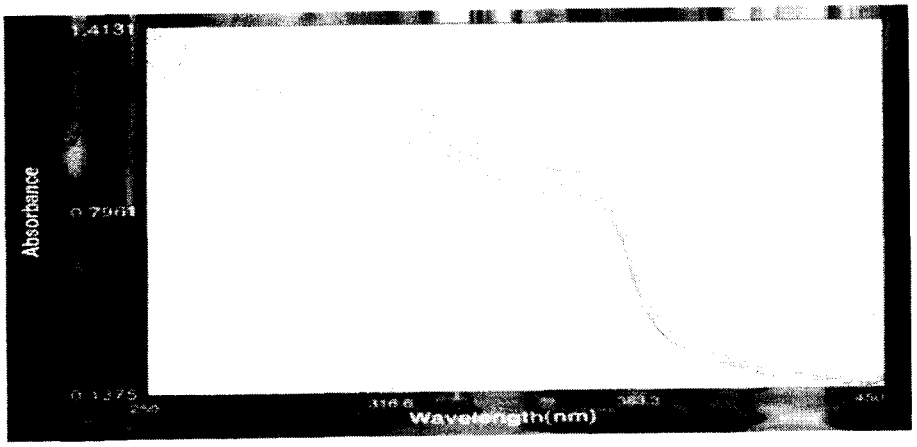


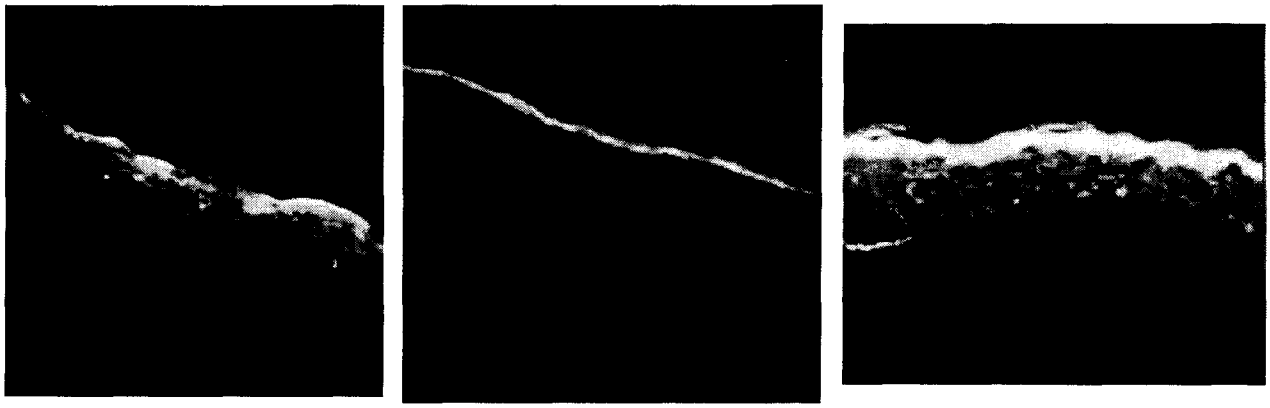
Fig.13 UV/Visible absorption spectra of dissolved OMC acetonitrile solvent with variation of dissolution time on the EC samples



· **Fig.14 The SPF value of the emulsion with 7% of general OMC.**



· **Fig.15 The SPF value of the emulsion with 10% of Nano-Hybrid OMC.**



(a) General OMC emulsion (b) Nano-Hybrid OMC emulsion (c)Ethanol

Fig 16. Penetration of OMC

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