

# Organic-Inorganic Hybrid UV Blocking Powders Based on Polysilsesquioxane

Young Baek Kim\* and Kyung-Sup Yoon\*\*

\*Department of Nanotechnology, PaiChai University, Daejeon  
South Korea, ybkim@mail.pcu.ac.kr

\*\*R&D Center, Saimdang Cosmetics, Yeongdong, Chungbuk  
South Korea, ksyoonjh@hanmail.net

## ABSTRACT

Trimethoxysilylpropyl-*p*-methoxycinnamamide (TMSPMCA) and triethoxysilylpropyl-*p*-methoxycinnamamide (TESPMCA) were synthesized and polymerized into spherical shapes by hydrolysis and condensation reactions under basic conditions. Diameters of spheres were controlled from sub-micrometer to a few micrometers by adjusting reaction conditions. Sun protection factors (SPF) of petrolatum that contained 5 and 10 wt% these spheres were 6.5 and 17, respectively. None of these mixtures turned white as applied to skin even when they were not scrubbed. These spheres had good compatibility with other organic materials and had both characteristics of organic and inorganic UV blocking materials; high boosting effects (>100%) when mixed with organic UV blocking agents and showed significant absorbance of UV-A as well as UV-B. The properties of these spheres proved that they were promising materials as UV blocking agents that were truly made of a hybridized organic-inorganic material.

**Keywords:** polysilsesquioxane, spheres, UV blocking agent, hybrid

## 1 INTRODUCTION

UV blocking agents are typically classified into organic and inorganic types. Organic UV blocking agents usually have chromophores that absorb UV light while inorganic UV blocking agents are powders that cut off UV lights mostly by physical manners such as reflecting and scattering.

Organic UV blocking agents have low molecular weights and good solubility in organic solvents. These types of UV blocking agents come into direct contact with skin when they are applied and have possibility of being absorbed through skin.[1] As a result, organic UV blocking agents often causes troubles to users with highly sensitive skin and there are some potential risks for every user.

Inorganic UV blocking agents do not have problems related to contact and absorption. These types of UV blocking agents are insoluble powders that have high refractive indices. The most typical inorganic UV blocking agents are titanium dioxide and zinc oxide. Inorganic UV blocking agents have relatively lower SPF values than

organic ones if they are used in the same contents. These materials have low compatibility with other ingredients in cosmetics that can induce easy aggregation of inorganic UV blocking agents and the aggregated powders turn white due to their high refractive indices. This whitening problem has been avoided by using particles with diameters in nanometer ranges. Nanoparticles of titanium dioxide and zinc oxide are now commercially available and widely used as powdery inorganic UV blocking agents. However, it should be noted that particles with too small diameters may cause troubles when inhaled and dusts with sub-micrometer diameters are already attracting a great attention regarding their hazardous effects on human health.

One of the ideal UV blocking agents, therefore, would be high molecular weight powders with significant diameters that are compatible with other ingredients in cosmetics and absorb both UV-A and UV-B efficiently. To our best knowledge, materials with all of such properties have not been developed yet.

One of the most appropriate candidates for such ideal UV blocking agents would be truly hybridized materials of organic and inorganic molecules. There are only a few known materials that are truly hybridized organic and inorganic molecules. Among them silsesquioxanes,  $(\text{RSiO}_{1.5})_n$ , are the most easily available.[2] Silsesquioxanes can be prepared in different forms depending on the nature of R groups and reaction conditions.

In this presentation, we are describing the very first example of insoluble polysilsesquioxane spheres that contain UV absorbing chromophores as R groups, SESQUV. SESQUV almost fulfilled the properties required for an ideal UV blocking agent described above.

## 2 EXPERIMENTALS

Trimethoxysilylpropyl-*p*-methoxycinnamamide (TMSPMCA) and triethoxysilylpropyl-*p*-methoxycinnamamide (TESPMCA) were prepared through reactions between equivalent amounts of 3-aminopropyltrimethoxysilane (APTMS), 3-aminopropyltriethoxysilane (APTES) and *p*-methoxycinnamic acid (PMCA) using dicyclohexylcarbodiimide (DCC) and toluene as coupling agent and solvent, respectively. Yields were approximately 70 %.

Spheres used in this study were prepared by hydrolysis and consequent condensation of TMSPMCA and TESPMA in aqueous solutions of sodium hydroxide at 50 °C. The concentration of sodium hydroxide varied from 0.5 to 3 wt% depending on the aiming sizes of spheres. TMSPMCA and TESPMA were added slowly to the aqueous sodium hydroxide solution and the pH was adjusted to 7.0 at appropriate moment that was determined by the appearance of spheres observed by an optical microscopy. Hardened spheres were obtained by heating the mixture at 70 °C for 6 hours and spheres were recovered by centrifugation followed by washing with excessive amounts of water and ethanol.

Resulting spheres were dried at 90 °C in the air until the weights remained constant.

Boosting effects of SESQUV on SPF values when mixed with organic UV screening agents were examined by determining SPF values of different mixtures prepared by adding different amounts of SESQUV and ethylhexyl methoxycinnamate (OMC) to a cream that contained 0.5 wt% of butyl methoxydibenzoylmethane (BMDDBM).

The boosting effect was calculated by the following equation.

$$\text{Boosting effect (\%)} = \frac{\text{SPF}_S - \text{SPF}_{\text{OMC}} - \text{SPF}_{\text{BMDDBM}}}{\text{SPF}_{\text{OMC}} + \text{SPF}_{\text{BMDDBM}}} \times 100$$

where  $\text{SPF}_S = \text{SPF}$  of the sample,  $\text{SPF}_{\text{OMC}} = \text{SPF}$  of petrolatum containing OMC and BMDDBM,  $\text{SPF}_{\text{BMDDBM}} = \text{SPF}$  of petrolatum containing BMDDBM.

### 3 RESULTS AND DISCUSSION

Figure 1 shows SEM images of spheres obtained from TESPMA in this study (SESQUV).

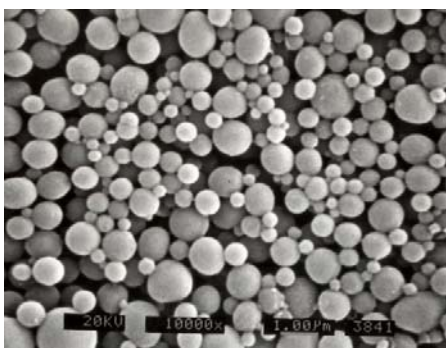


Figure 1. SEM image of poly(*p*-methoxycinnaminyl)propylsilsesquioxane (PMCAPSQ) particles (SESQUV)

Although individual particles of SESQUV were spherical, the size distribution of the spheres was relatively large. TMSPMCA gave spheres with narrower size distributions than TESPMA. TMSPMCA apparently dispersed in water better than TESPMA showing that triethoxy compound was more hydrophobic than trimethoxy compound.

The narrower size distribution of SESQUV spheres prepared from TMSPMCA was ascribed to the higher water compatibility of TMSPMCA than TESPMA. In our previous paper, we have described the difference between emulsion polymerization and suspension polymerization of organotrialkoxysilanes (OTAS).[3] In general, OTAS that contain larger organic and alkoxy groups are less compatible with water and undergo slower hydrolysis and condensation reactions. Even the hydrolyzed molecules are not hydrophilic enough to dissipate into aqueous medium and they stay at the water-OTAS interface where they were produced. These hydrolyzed molecules at the interface start to condense to form solid shells around liquid molecules. The entrapped liquid molecules eventually harden to give solid spheres with wider size distribution. In such situation, reactions of precursors proceed just like that in suspension polymerization.

The only reported spherical silsesquioxane that had bulky organic groups is phenylsilsesquioxane that was prepared by hydrolysis and condensation of phenyltrialkoxysilane (PTAS). However, spheres prepared from PTAS were reported to be soluble in organic solvents such as alcohols and acetone indicating that they spheres of oligomers instead of crosslinked polysilsesquioxane.[4]

None of spheres prepared in our method were soluble in organic solvents including alcohols, ether, methyl acetate, acetone and hexane. The crude spheres prepared in this study lost less than 1% of their weight when they were agitated in ethanol or methanol for approximately 24 hours. Also, SEM images of SESQUV spheres recovered after treating with alcohols did not show any deformation or after heating up to 200 °C.

It is notable that both TMSPMCA and TESPMA formed crosslinked spherical products although *p*-methoxycinnamoyl group was even bulkier than phenyl group. These results may be explained that propyl group between *p*-methoxycinnamoyl group and silicon relieved the steric hindrance.

Solid phase UV/Vis spectra of SESQUV particles showed that these spheres absorbed both UV-A and UV-B lights. The ratios between the SPF values for UV-A to UV-B were respectively 0.4, 0.8 and 0.12 for SESQUV, titanium dioxide, and ethylhexyl methoxycinnamate. The fact that the ratio of SPF of UV-A to SPF of UV-B for SESQUV lied between those of organic (ethylhexyl methoxycinnamate) and inorganic UV blocking compounds (titanium dioxide) suggested that SESQUV had both characteristics of organic and inorganic UV blocking agents.

SPF values for petrolatum containing 5 and 10 wt% of SESQUV were respectively 6.5 and 17. These SPF values were significantly higher than mixtures containing other powdery inorganic UV blocking materials in the same concentration and also exceed those containing some organic UV blocking agents in the same concentrations. These SPF values were high enough for SESQUV to be used as the only UV absorbing agent in cosmetic products.

The major advantage of SEQUV over titanium dioxide was revealed when they were applied to different surfaces as mixtures with other organic ingredients. Figure 2 shows hands and slide glasses to which the same amounts of petrolatum containing 10 wt% of SEQUV and 10 wt% of titanium dioxide were applied. The white area appeared on the hand might not be clearly visible in Figure 2 due to the background color of the hand. However, the whitening effect is clearly seen from the samples applied on slide glasses in Figure 2. Petrolatum containing 10 wt% of SEQUV formed a virtually transparent layer compared to that containing 10 wt% of titanium dioxide. These results showed that SEQUV spheres had appropriate refractive index not to cause whitening effect and were highly compatible with organic materials.

Boosting effect of SPF values by adding SEQUV to petrolatum that contained other organic UV blocking agents was remarkably high. Figure 3 shows the boosting effect at different concentrations of these ingredients calculated as described in EXPERIMENTALS.

The high boosting effect caused by SEQUV allowed us to obtain SPF values higher than 30 from mixtures that contained less than 10 wt% of UV blocking agents in total. Mixtures with SPF values higher than 50 were easily obtained when the total contents of UV blocking agents were higher than 10 wt%. For example, the SPF value of a mixture of SEQUV (5%), ethylhexyl methoxydycinnamate (3%), butyl methoxydibenzoylmethane (3%) in petrolatum was in the range of 70.

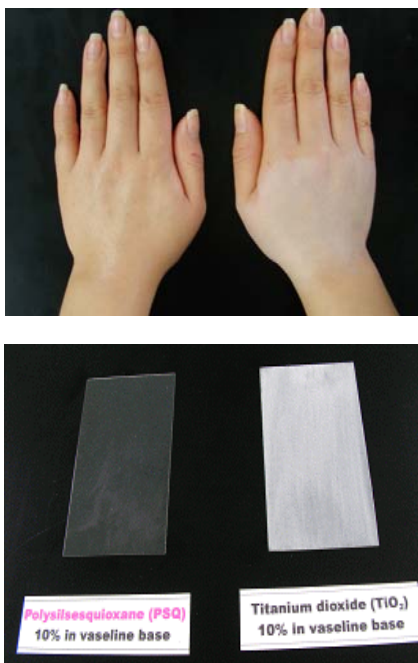


Figure 2. (upper) the hand to which petrolatum containing 10wt% of SEQUV was applied (left), the hand to which petrolatum containing 10wt% of titanium dioxide was applied (right), (lower) same as above applied to slide glasses.

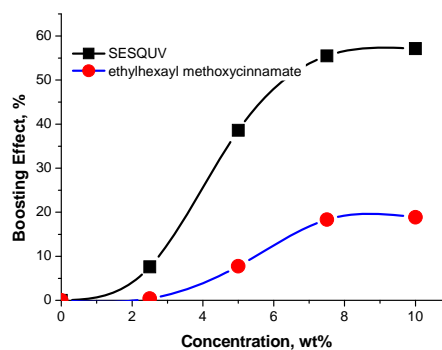


Figure 3. Boosting effect of UV cut-off caused by SEQUV in the presence of ethylhexyl methoxycinnamate

The SPF value of SEQUV increased as the diameter of SEQUV decreased. This was ascribed to the fact that the same amount of SEQUV spheres could cover wider area when the diameter was smaller.

## SUMMARY AND CONCLUSION

We have shown that organotrialkoxysilanes that contain UV absorbing chromophore in the organo group could be polymerized into spheres made of crosslinked polysilsesquioxane (SEQUV) even when the organic group was bulky.

SEQUV had significant SPF values, 6.5 and 17 respectively when they were mixed with petrolatum in concentrations of 5 and 10 wt%. SEQUV showed both characteristics of inorganic and organic UV blocking agents; blocks both UV-A and UV-B, and shows high boosting effects.

SPF values higher than 50 were easily obtained from mixtures whose contents of total UV blocking agents were slightly higher than 10 wt% including SEQUV in concentrations of 5 wt% or so.

These results showed that SEQUV were promising materials as UV blocking agents that might be used in many different types of cosmetic products.

## REFERENCES

- [1] V. Sarveiya, S. Risk, and H. A. Benson, *J. Chromatogr. B Analyt. Technol. Biomed. Life Sci.*, 2004, 803, 225.
- [2] I. Noda, M. Isikawa, M. Yamawaki, and Y. Sasaki, *Inorg. Chim. Acta.*, 263, 149, 1997.
- [3] Y. B. Kim, Y.-A. Kim, and K.-S. Yoon, *Macromol. Rapid Commun.*, 27, 1247, 2006.
- [4] J. Y. Choi, C. H. Kim, and D. K. Kim, *J. Amer. Cer. Soc.*, 81, 1184, 1998.