Size Control of Silicone Particles Using Sonochemical Approaches

Sung Hwa Jhung,[†] Ki Cheon Yoo, Young Kyu Hwang, and Jong-San Chang[*]

*Research Center for Nanocatalysts, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusung,
Daejeon 305-600, Korea. [*]E-mail: jschang@krict.re.kr
[†]Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea*

Particle size of silicones can be controlled by changing the reaction conditions such as temperature and concentrations of water and tetramethoxysilane (TMOS). Alternatively, the use of ultrasound radiation is also an elegant technique to decrease the particle size. Small silicone particles can be obtained at low temperature from diluted reagent containing TMOS, especially under the powerful ultrasound radiation. The size control may be explained by the rate of particle growth rather than that of nucleation.

Key Words : Silicone, Ultrasound, Size

Introduction

Silicone, organosilica or polysiloxane fine particles are used as additives for imparting lubricating property to paints, plastic, rubber, cosmetics and paper, improving dispersibility, and giving light-scattering function.[1] Moreover, the silicone particles, if with monodispersed and with specific particle size, can be used for personal care such as cosmetics.[2] For versatile uses, several properties including well-defined particle size and monodispersity are necessary.[3] However, the method to control the particle size is scarcely known in an open literature even though a process to control the particle size of inorganic silica had been known since sixties.[4]

Only a few patents claim that addition of alcohols[5] and dilution of reagents[6] are effective to decrease the particle size distribution and the particle size, respectively. Currently, silicones with specific sizes (2, 4.5, 4-6, 4-7 or 11 μm) are commercially available in the market.[2]

Recently, sonochemistry, a research area in which molecules undergo a reaction under powerful ultrasound radiation, has been widely studied.[7] Various nanomaterials, especially with 1-dimensional structures, have been synthesized by the application of ultrasound[7] because of extremely high cooling rates from high temperature (5000-25000 K), obtained from a collapse of bubbles. Sono-crystallization of zeolite A has demonstrated to offer the possibilities of increasing both the nucleation and crystallization rates of zeolites, thus improving the yield and particle size distribution of the product crystals.[8] However, to the best of our knowledge, no result has so far been reported for the synthesis of silicones with small size using the ultrasound radiation technique.

In this paper, several synthesis conditions are evaluated to decrease the particle size of silicones. Especially, the effect of ultrasound on the synthesis of silicone particles will be discussed.

Experimental

Silicone particles were prepared from hydrolysis of MTMOS (methyltrimethoxysilane, Aldrich, 98%) and TMOS (tetramethoxysilane, Aldrich, >99%) under an acidic condition and successive polycondensation of the hydrolyzed product in an aqueous alkaline solution similar to the reported methods.[1,3] Aqueous HCl solution (0.35%) was added to deionized water at a constant temperature and MTMOS and TMOS (if necessary) were added further to the acidic water under vigorous stirring. Hydrolysis was conducted further for 5 h under continuous stirring at the constant temperature by using a thermostat and a cooling coil, and aqueous silanol solution was obtained accordingly. Adequate amount of ammonia solution (0.37%) was added to the pre-hydrolyzed solution and stirred further for 3 min. The molar composition of the reactant mixture was (1−x)MTMOS: xTMOS: 5×10^{-5} HCl: 7×10^{-3} NH$_4$OH: yH$_2$O where x = 0, 0.05 or 0.1 and y = 37, 50 or 63. The total weight of the reactant mixture was about 22 g per batch. Unless otherwise specified, the value of x, H$_2$O/silanes ratio and the temperature are 0, 50 and 10 °C, respectively.

To change the particle size of silicones, ultrasonification was conducted during this stage of 3 min for some cases using an ultrasonic processor (Sonics and Materials, VC-750, max power 750 W, 20 kHz, titanium standard tip, tip diameter 1/2 inch). The reactant mixture was maintained static for 4 h to complete polycondensation even though the polycondensation is nearly completed in 10 min. The solid product was separated from mother liquor by centrifugation. White solid product was recovered by drying the wet cake, after thorough washing with water, at 150 °C for 12 h.

The morphology of silicones including particle size and particle size distribution was observed with a scanning electron microscope (SEM, JEOL JSM-6700F). The particle size was calculated by using the sizes of twenty particles that were determined by SEM. The yield of silicones (based on the MTMOS and TMOS) was calculated from the dried weight of silicones by considering the equation (1).

$$a \text{ MTMOS} + b \text{ TMOS} \rightarrow a \text{ CH}_3\text{-Si-O}_{1.5} + b \text{ SiO}_2 \qquad (1)$$
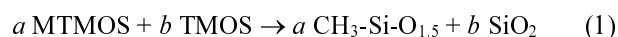
The content of organic component was calculated, after calcination of the silicones at 900 °C under the air flow, based on equation (2).
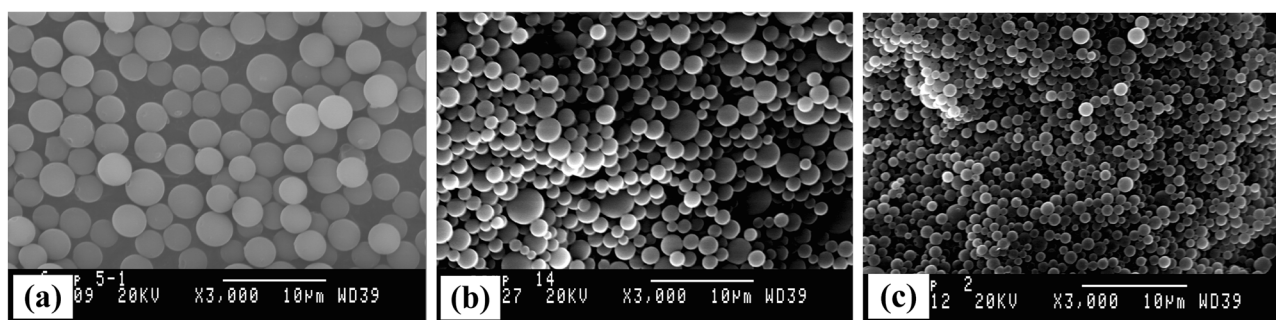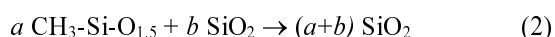
Figure 1. Change of size of silicones with the power of ultrasonification: (a) power was 0%; (b) power was 50% and (c) power was 100%.

Table 1. Reaction conditions and results depending on the power of ultrasound and TMOS/(TMOS+MTMOS) ratio[a]
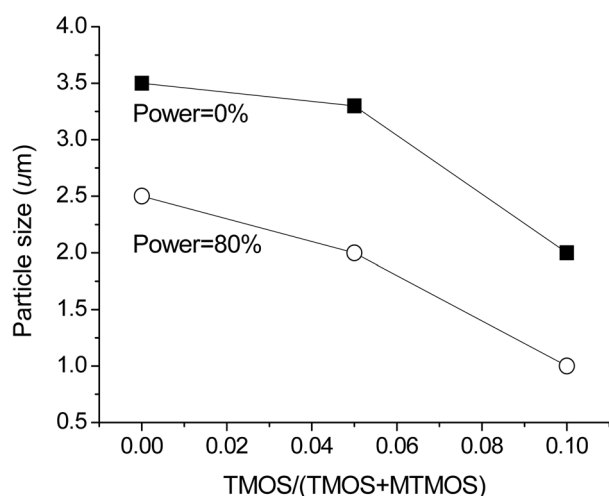
Sample	TMOS	MTMOS	Sonification power (%)	Particle size (μm)	Silicone yield (%)[b]	Silica yield after calcination (%)[c]
A	0.0	1.00	0	3.5 ± 0.3	97.2	99.8
B	0.0	1.00	50	2.0 ± 0.7	96.3	99.4
C	0.0	1.00	100	1.2 ± 0.3	97.5	99.9
D	0.05	0.95	0	3.3 ± 0.4	96.1	99.7
E	0.10	0.90	0	2.0 ± 0.3	95.1	99.3
F	0.05	0.95	80	2.0 ± 0.3	96.6	99.9
G	0.10	0.90	80	0.9 ± 0.1	95.0	99.0

[a]Temperature: 10 °C; H_2O/(TMOS+MTMOS) = 50. [b]Yield of silicone based on equation (1) and the weight of used silanes (TMOS and MTMOS). [c]Yield of silica after calcination at 900 °C, based on the weight and composition of silicones and equation (2).

$$a \ CH_3\text{-}Si\text{-}O_{1.5} + b \ SiO_2 \rightarrow (a+b) \ SiO_2 \qquad (2)$$
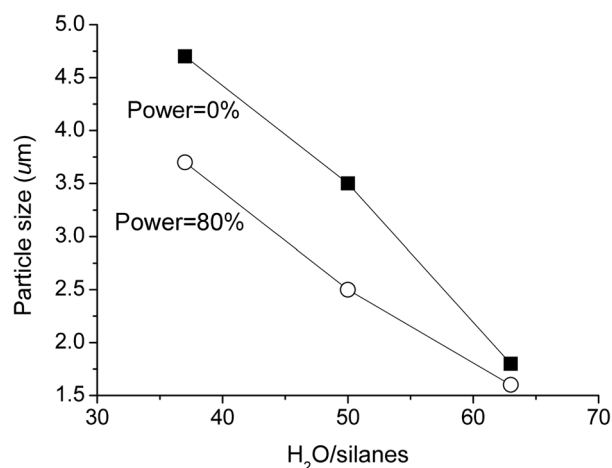
Results

Figure 1 shows the typical morphology of silicones with the power of ultrasonification. As the power increases, the particle size decreases monotonously (also refer to Table 1), suggesting the efficiency of ultrasound in decreasing the particle size. Figure 2 illustrates the effect of TMOS concentration and ultrasound on the particle size of silicones. Small particles can be obtained in the presence of high concen-

tration of TMOS especially under the ultrasound radiation. As the water content increases, the particle size concomitantly also decreases sharply irrespective of the ultrasound treatment (Figure 3). Figure 4 shows the typical morphology with water content under the ultrasound, and the particle size is very monodisperse. It can also be shown that the temperature has remarkable influence on the particle size (Figure 5).

Table 1 illustrates the effect of reaction conditions such as ultrasound radiation and TMOS addition not only on the particle size but also on reaction and calcination yields. As shown in Table 1, the silicone yields are nearly constant of

Figure 2. Effect of TMOS concentration and ultrasonification on the size of silicones. The reaction temperature and H_2O/silanes were 10 °C and 50, respectively.

Figure 3. Effect of water content and ultrasonification on the size of silicones. The reaction temperature and TMOS/(TMOS+MTMOS) ratio were 10 °C and 0, respectively.
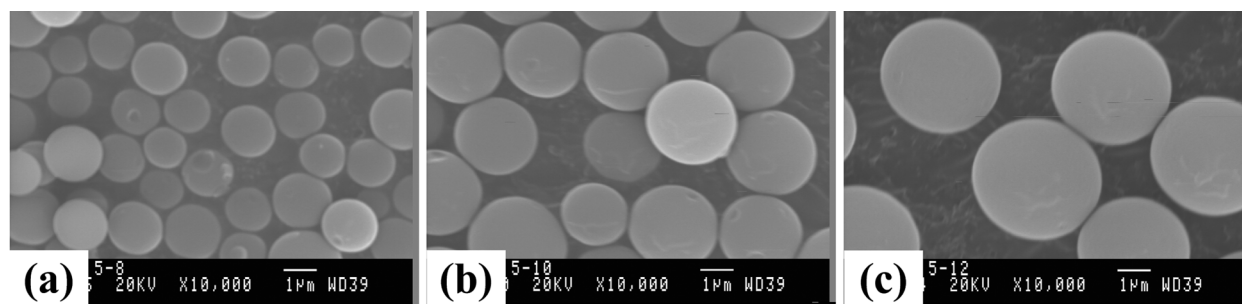
Figure 4. Typical morphology of silicones changed with the water content of reaction mixture: (a) H_2O/silanes was 63; (b) H_2O/silanes was 50 and (c) H_2O/silanes was 37. The reaction temperature, TMOS/(TMOS+MTMOS) ratio and sonification power were 10 °C, 0 and 80%, respectively.
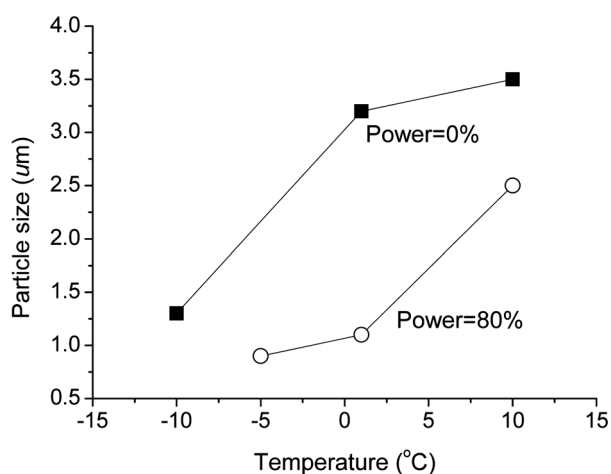
Figure 5. Effect of reaction temperature and ultrasonification on the size of silicones. The TMOS/(TMOS+MTMOS) ratio and H_2O/silanes ratio were 0 and 50, respectively.

above 95%, confirming the quantitative conversion of silanes (MTMOS and TMOS) into silicones, irrespective of the reaction conditions. Moreover, the yield of silica after high temperature calcination of silicones is nearly 100%, thus reconfirming the quantitative conversions of silanes into silicones irrespective of the reactant composition of MTMOS and TMOS.

Discussion

The shape and size of a material have been controlled by various methods,[9,10] mainly by optimizing the nucleation rate and crystal or particle growth rate. The particle size is small when the nucleation rate is larger than crystal growth rate.[9] The high nucleation rate is attained by the increased supersaturation because the nucleation rate, compared with the growth rate, rises more sharply (or exponentially) with supersaturation.[9] For instance, small materials are obtained at low temperature after aging (below the synthesis temperature) due to high nucleation rate compared with the rate of particle growth. Stirring a reaction mixture is also helpful to decrease the particle size. On the other hand, large particles can be obtained by using a nucleation suppressor and clear solution, etc.[10] However, the morphology has been generally changed by modifying the chemical composition of reactant

mixtures (for example, addition of auxiliary compounds, using different precursors and changing pH).[11]

Very recently, we have shown that a particle size can be decreased noticeably by the application of microwaves in the synthesis of a porous or perovskite-type material.[12,13] One reason is the appreciable increase of nucleation rate, compared with crystal growth rate. Moreover, the nuclei size is very small and very homogeneous under the microwave irradiation. The crystal size can be decreased further by increasing the ramping rate from room temperature to a reaction temperature.[14]

It has been reported that nanomaterials can be obtained under the powerful ultrasound radiation[7] because extremely high cooling rate ($>10^{11}$ K/s, from 5000-25000 K to reaction temperature or usually room temperature) hinders organization or crystallization of a product. Even though the nucleation rate and particle growth rate are not compared quantitatively in this study, it can be understood that the growth rate is relatively low (compared with nucleation) under the ultrasound, similar to the microwave irradiation,[12,13] as confirmed by the decreased size of the silicones under the ultrasound radiation (Figure 1 and Table 1).

The size of silicones can be decreased by dilution the reactants (with extra water) or by decreasing the reaction temperature (Figures 3 and 5), probably due to the decreased growth rate. However, the polycondensation reaction might be very facile because the reaction is quantitative, and is practically completed within 10 min. Further, the reaction is not hindered at all by decreasing the reaction temperature up to −10 °C and increasing the water content. However, nucleation rate might be even higher than growth rate under the reaction conditions. Hence, it may be suggested that the decreased size of silicones might be due to the decreased growth rate as explained in the synthesis of nanomaterials due to the hindrance of organization or crystallization from extremely high cooling rates. The decreased silicone size with increasing TMOS might be due to low growth rate caused by the inhomogeneity between MTMOS and TMOS.

Conclusions

The size of silicones can be controlled by changing the

reaction conditions. The size can be decreased up to 1 μm or less by increasing water content, decreasing the reaction temperature and adding TMOS, and ultrasound radiation is very helpful to decrease the size. The decrease of the size might be due to the low rate of particle growth compared with the rate of nucleation.

References

1. US Patent 6495649, assigned to GE Toshiba Silicones Co., 2002.
2. http://www.gesilicones.com/siliconesweb/as1/en/techdocs/ Tospearl%20Micro%20MB.indd.pdf
3. Vogel, R.; Surawski, P. P. T.; Littleton, B. N.; Miller, C. R.; Lawrie, G. A.; Battersby, B. J.; Trau, M. *J. Colloid Interface Sci.* **2007**, *310*, 144.
4. Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.
5. (a) Japanese Open Patents, JP-2003-183396-A, assigned to GE Toshiba Silicones Co., 2003. (b) Japanese Open Patents, JP-2003-183395-A, assigned to GE Toshiba Silicones Co., 2003. (c) Japanese Open Patents, JP-2003-2973-A, assigned to GE Toshiba Silicones Co., 2003.
6. Japanese Open Patents, JP-2000-186148-A, assigned to GE Toshiba Silicones Co., 2000.
7. Gedanken, A. *Ultrason. Sonochem.* **2004**, *11*, 47.
8. Andaç, Ö.; Tather, M.; Sirkecioğlu, A.; Ece, I.; Erdem-Şenatalar, A. *Microporous Mesoporous Mater.* **2005**, *79*, 225.
9. (a) Renzo, F. D. *Catal. Today* **1998**, *41*, 37. (b) Lethbridge, Z. A. D.; Williams, J. J.; Walton, R. I. ; Evans, K. E.; Smith, C. W. *Microporous Mesoporous Mater.* **2005**, *79*, 339. (c) Drews, T. O.; Tsapatsis, M. *Current Opinion Colloid Interface Sci.* **2005**, *10*, 233.
10. (a) Qiu, S.; Yu, J.; Zhu, G.; Terasaki, O.; Nozue, Y.; Pang, W.; Xu, R. *Microporous Mesoporous Mater.* **1998**, *21*, 245. (b) Lethbridge, Z. A. D.; Williams, J. J.; Walton, R. I.; Evans, K. E.; Smith, C. W. *Microporous Mesoporous Mater.* **1998**, *79*, 339.
11. Jhung, S. H.; Chang, J.-S.; Hwang, Y. K.; Park, S.-E. *J. Mater. Chem.* **2004**, *14*, 280.
12. (a) Jhung, S. H.; Jin, T.; Hwang, Y. K.; Chang, J.-S. *Chem.-Eur. J.* **2007**, *14*, 4410. (b) Jhung, S. H.; Lee, J.-H.; Yoon, J. W.; Serre, C.; Férey, G.; Chang, J.-S. *Adv. Mater.* **2007**, *19*, 121. (c) Choi, J. Y.; Kim, J.; Jhung, S. H.; Kim, H.-K.; Chang, J.-S.; Chae, H. K. *Bull. Kor. Chem. Soc.* **2006**, *27*, 1523. (d) Jhung, S. H.; Lee, J.-H.; Chang, J.-S. *Bull. Kor. Chem. Soc.* **2005**, *26*, 880.
13. Jhung, S. H.; Lee, J.-H.; Yoon, J. W.; Hwang, Y. K.; Hwang, J.-S.; Park, S.-E.; Chang, J.-S. *Mater. Lett.* **2004**, *58*, 3161.
14. Jhung, S. H.; Lee, J.-H.; Chang, J.-S. *Microporous Mesoporous Mater.* **2007**, *in press (DOI: 10.1016/j.micromeso.2007.09.039)*.