Synthesis of Monodisperse Hydrophobic Silicone Particles in the Submicron Size

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Abstract

In the electronics field, monodisperse hydrophobic particles in the submicron size are used as additives for adhesives. The purpose of this study is to develop a process to synthesize monodispersed poly(alkoxysilane) (silicone) particles that have strong hydrophobicity. Dimethyldimethoxysilane (DMDMS), methyltrimethoxysilane (MTMOS), and tetraalkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), were used as monomers for synthesizing the hydrophobic silicone particles. By optimizing the alkoxysilane concentration, the blending ratio of monomers, the amount of catalyst and the reaction temperature, it is possible to synthesize small monodispersed silicone particles.

Key-words: Silicone particle, Monodisperse, Dimethyldimethoxysilane, Methyltrimethoxysilane, Tetraethoxysilane

1. Introduction

Synthesis of monodisperse silica has attracted considerable attention because of their importance in technological applications in the fields of optical devices, catalysts, filler for polymers, and so on. The sol-gel process is an excellent process to synthesize hydrophilic monodisperse silica1-5). Especially the Stöber process of forming silica particles has been utilized in many investigations for preparation of narrowly dispersed silica particles6). However, the sol-gel process has rarely been exploited in more hydrophobic media. On the other hand, silica particles are used as additives for adhesive, which is a part of the electronic materials with high heat resistance and excellent reliability that matches the high requirements of the devices. Since monodispersed silica particles can be easily synthesized, surface treatment is the common way to control the surface hydrophobicity (wettability)7-11). However, scale-up production of polymer-grafted nanoparticles is still to be fully achieved. The production requires complicated procedures, such as centrifugation, filtration, and solvent extraction, which result in the consumption of a lot of spent solvent.

Poly(organosiloxane), i.e., silicone, particles are used for additives to impart lubricating property to paints, plastic, rubber, cosmetics, and paper, improving dispersibility and giving light-scattering function. However, the method to control the particle size can rarely be found in the published literature. For the electronic materials, controlling the particle size is very important. S. H. Jhung and his coworkers have reported that they could control the size of silicone particles made from organotrialkoxysilane as monomer11). In Japanese industry, the synthesis of monodisperse silicone particles was investigated by many researchers as a matter of necessity. Organotrialkoxysilane is used as monomer to synthesize monodispersed silicone particles. But silicone particles made by organotrialkoxysilane still have weak hydrophobicity12-17).

The purpose of this study is to develop a process to synthesize monodisperse silicone particles that have strong hydrophobicity. The methanol wettability was used to check the hydrophobicity of silicone particles. If the methanol wettability is less than 50 %, then the hydrophobicity of silicone particles is considered insufficient because of the residual silanol18).

We synthesized methyltrimethoxysilane (MTMOS)/tetramethoxysilane (TMOS) copolymerized polymers, MTMOS/tetraethoxysilane (TEOS) copolymerized polymers, and MTMOS/TMOS/dimethyldimethoxysilane (DMDMS) copolymerized polymers.

2. Experimental

2.1 Materials and reagents

DMDMS, MTMOS, TEOS and TMOS were obtained from Tokyo Chemical Industry Co., Ltd., Japan. Ammonia solution (28 %) and hydrochloric acid (HCl) from Wako Chemical were used as catalysts without further purification.
2.2 Effect of the amount of TMOS added on particle size
Silicone particles were prepared from hydrolysis of MTMOS and TMOS under an acidic condition and successive polycondensation of the above hydrolyzed product in an aqueous alkaline solution similar to the reported methods. The silicone particles were prepared by the method as shown in Scheme 1.

For example, 0.05 mol of MTMOS, 0 ~ 0.005 mol of TMOS and 47.7 g of 0.5% HCl aqueous solution were added to a 500 ml plastic bottle. The mixture was stirred at 400 rpm using a magnetic stirrer to start hydrolysis of MTMOS and TMOS. After 3 hours, silicone particles were prepared by adding 1.6 g of water containing $1.6 \times 10^{-3}$ mol of NH$_3$ into the above hydrolyzed solution. The primary polycondensation of silanol groups occurs due to the catalytic effect of basic ammonia. The onset of the polycondensation of the sol particles could be visually observed as the instantaneously emerging opacity. The colloidal suspension was continuously stirred for 4 hours at 10 °C. After that, the resulting silicone particles were centrifuged and washed with methanol. After the final centrifuge, precipitated silicone particles were dried for 2 hours at 150 °C.

2.3 Effect of the amount of water added on MTMOS/TMOS silicone particle size
0.05 mol of MTMOS, 0.004 mol of TMOS and 37.1 ~ 200 g of 0.5 wt% HCl aqueous solution were added to a 500 ml plastic bottle. Silicone particles were prepared by a similar procedure as that shown in Scheme 1.

2.4 Effect of tetraalkoxysilane (TMOS and TEOS) on the particle size
0.05 mol of MTMOS, 0.004 mol of TMOS or TEOS and 47.7 g of 0.5 wt% HCl water solution were added to a 500 ml plastic bottle. Silicone particles were prepared by a similar procedure as that shown in Scheme 1.

2.5 Effect of mixing ratio of MTMOS and DMDMS on the particle size
$\alpha$ mol of MTMOS, 0.05 ~ $\alpha$ mol of DMDMS, 0.004 mol of TMOS and 47.7 g of 0.5 wt% HCl aqueous solution were added to a 500 ml plastic bottle. Silicone particles were prepared by a similar procedure as that shown in Scheme 1.

2.6 Effect of the amount of NH$_3$ on the particle size
0.025 mol of MTMOS, 0.025 mol of DMDMS, 0.004 mol of TMOS and 47.7 g of 0.5 wt% HCl aqueous solution were added to a 500 ml plastic bottle. Silicone particles were prepared by a similar procedure as that shown in Scheme 1, varying the amount of NH$_3$.

2.7 Effect of synthesis temperature on the particle size
0.025 mol of MTMOS, 0.025 mol of DMDMS, 0.004 mol of TMOS, and 47.7 g of 0.5 wt% HCl water solution were added to a 500 ml plastic bottle. Silicone particles were prepared by a similar procedure as that shown in Scheme 1, varying the temperature of condensation.

2.8 Characterization of silicone particles
The morphology of silicone particles, particle size and particle size distribution, was observed with a scanning electron microscope (SEM, Hitachi S-4800). 200 pieces of silicone particles were measured to calculate the average diameter of a sample. The coefficient of variation (C.V.) of the diameter of the sample was calculated by Eq. (1).

\[
\text{C.V.} = \frac{A}{B} \times 100 \%
\]

where $A$ is standard deviation of the particle diameter and $B$ is average diameter of the particles.

The water absorption ratio of silicone particles was calculated by Eq. (2). 1000 mg of silicone particles in the container were placed at 50 °C 90 % humidity condition for 500 hours and weighed. Then the container was placed at 130 °C dry condition for 2 hours and weighed.

\[
\text{Water absorption ratio} (\%) = \frac{(C - D)}{C} \times 100 \% - (2)
\]

where $C$ is weight of silicone particles after 90% humidity condition (mg) and $D$ is weight of silicone particles after dry condition (mg).

Hydrophobicity (methanol wettability) of silicone particles was calculated by Eq. (3). 50 ml of distilled water and 0.2 g of silicone particles were placed in a 200 ml beaker. Then 1 ml of methanol was slowly added to the beaker and stirred for 10 seconds. This process was repeated until the whole of the particles were wet enough to precipitate to the water. The

Scheme 1 MTMOS/TMOS silicone particles preparing method.
amount of methanol required was \( E \) (ml) in Eq. (3).

\[
\text{Hydrophobicity} = \left( \frac{E}{E + 50} \right) \times 100 \% \tag{3}
\]

The yield of silicones (based on the MTMOS, DMDMS and TMOS) was calculated from the dried weight of silicones by considering Eq. (4).

\[
\alpha_{\text{MTMO}} + \beta_{\text{DMDMS}} + \gamma_{\text{TMOS}} \rightarrow \alpha_{\text{CH}_3\text{-Si-O}_{1.5}} + \beta_{\text{CH}_3\text{-Si-O}} + \gamma_{\text{SiO}_2} \tag{4}
\]

3. Results and discussion

3.1 Effect of the amount of TMOS on the particle size of MTMOS/TMOS silicone particles

Fig. 1 shows the relationship between the amount of TMOS and the average diameter or the coefficient of variation of MTMOS/TMOS particles. The average diameter of MTMOS/TMOS particle depends on the amount of TMOS used. Small amount of TMOS leads to large particle size and high coefficient of variation. Fig. 2 shows SEM image of MTMOS/TMOS particles made by different amount of TMOS. It became apparent that in this range of TMOS, it is possible to synthesize relatively uniform spherical particles.

3.2 Effect of the amount of HCl aqueous solution on the particle size of MTMOS/TMOS silicone particles

Fig. 3 shows the relationship between the amount of HCl aqueous solution as catalyst and the average diameter or the coefficient of variation of MTMOS/TMOS particles: the ratio of MTMOS and TMOS was fixed to 0.05 mol: 0.004 mol. The average diameter of MTMOS/TMOS particles decreased with the increasing amount of HCl aqueous solution. It is considered that in accordance with lower monomer concentration, the number of the grain nuclei should be increased. The coefficient of variation increased with decreasing monomer concentration. Fig. 4 shows SEM image of MTMOS/TMOS particles made by the different amount of HCl aqueous solution.

3.3 Preparation of MTMOS/TEOS silicone particles

TEOS was used instead of TMOS, MTMOS/TEOS silicone particle was prepared and the effect of tetraalkoxyxilane on the silicone particle size was investigated. Fig. 5 shows the average diameter or the coefficient of MTMOS/TEOS particles.
in comparison with that of MTMOS/TMOS particles. The average diameter of particles made by TMOS was smaller than that made by TEOS. **Fig. 6** shows SEM image of MTMOS/TMOS and MTMOS/TEOS particles. The variant substances were likely to occur during the synthesis of MTMOS/TEOS particles. Because the ethoxy group had poor reactivity, it was considered that not all the TEOS was used for the formation of the silicone particles.

### 3.4 Effect of mixing ratio of MTMOS and DMDMS

**Fig. 7** shows the effect of mixing ratio of MTMOS and DMDMS and the average diameter or the coefficient of variation of the MTMOS/DMDMS/TMOS particles. When the amount of DMDMS was larger than MTMOS, it was not possible to synthesize the monodisperse particles. The particle size was increased with the increasing amount of DMDMS. **Fig. 8** shows the relationship between the mixing ratio of MTMOS and DMDMS and the methanol wettability of silicone particles. The methanol wettability of silicone particles was increased with increasing ratio of DMDMS. **Fig. 9** shows the relationship between the mixing ratio of MTMOS and DMDMS and water absorption ratio of the silicone particles. The water absorption ratio of the silicone particles was decreased with the increasing amount of DMDMS.

### 3.5 Relationship of NH₃ amount and particle size of MTMOS/DMDMS/TMOS

**Fig. 10** shows the relationship between the amount of ammonia as catalyst and the average diameter of MTMOS/DMDMS/TMOS particles. The size of particles was decreased with the increasing amount of ammonia as catalyst. **Fig. 11** shows the relationship between the amount of ammonia and the coefficient of variation of particles. Low amount of ammonia leads to the low coefficient of variation of particles. It is important to adjust the amount of ammonia as the catalyst in order to synthesize small monodispersed...
particles. Fig. 12 shows the MTMOS/DMDMS/TMOS silicone particles made by the different amount of ammonia.

3.6 Relationship of synthesis temperature and particle size of MTMOS/DMDMS/TMOS

Fig. 13 shows the relationship between reaction temperature and the average diameter or the coefficient of variation of MTMOS/DMDMS/TMOS particles. At low temperature, the small monodisperse MTMOS/DMDMS/TMOS silicone particles could be synthesized. Fig. 14 shows SEM image of MTMOS/DMDMS/TMOS particles synthesized at 5 °C. The yield of the particles was 96.5%.

3.7 Optimizing conditions for the synthesis of hydrophobic monodisperse MTMOS/DMDMS/TMOS silicone particles

Based on the above results, by optimizing the amount of tetraalkoxy silanes, the monomer concentration, kinds of monomer, the blending ratios of monomer, the amount of catalyst and reaction temperature, it is possible to synthesize small monodisperse silicone particles. Scheme 2 shows...
the optimized process of synthesizing small monodisperse silicone particles. Table 1 shows the characteristic of monodisperse MTMOS/DMDMS/TMOS silicone particles.

4. Conclusion

- MTMOS/DMDMS/TMOS silicone particles have small water absorption ratio and high methanol wettability (hydrophobicity).
- By optimizing the alkoxysilane concentration, the blending ratio of monomers, the amount of catalyst and the reaction temperature, it is possible to synthesize small monodispersed silicone particles.

References


サブミクロンサイズの単分散疎水性シリコーン粒子の合成

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要　旨

ハイエンドのエレクトロニクス分野において、サブミクロンサイズの単分散ポリアルコキシシラン（シリコーン）粒子は絶縁材料の添加剤として用いられる。本研究の目的は強い疎水性を有する単分散のシリコーン粒子の合成方法を確立することである。ジメチルジメトキシシラン（DMDMS）、メチルトリメトキシシラン（MTMOS）およびテトラアルコキシシランをモノマーとして粒子合成に用いた。モノマー濃度、モノマーの配合比、触媒量および反応温度の最適化により単分散疎水性シリコーン微粒子を合成できることがわかった。

キーワード：シリコーン微粒子、単分散、ジメチルジメトキシシラン、メチルトリメトキシシラン、テトラメトキシシラン