Novel soft touch silicone beads from methyltrimethoxysilane and dimethyldimethoxysilane using easy aqueous solution reaction

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Conventionally, commercialized spherical silicone powders, such as silicone resin powder [INCI: POLYMETHYLSILSESQUIOXANE (PMSQ beads)]¹⁾ and silicone rubber powder [INCI: DIMETHICONE/VINYL DIMETHICONE CROSSPOLYMER (DVDC beads)],²⁾ have been formulated into cosmetics for soft and smooth feeling. Due to the low crosslink density, silicone rubber powder shows soft touch and high oil absorption. However, it is too agglomerative to be formulated into powder foundation. In this work, we have developed the novel soft touch spherical silicone beads made from methyltrimethoxysilane (MTMS) and dimethyldimethoxysilane (DMDMS), using a surfactant, cetyltrimethylammonium chloride (CTAC). The preparation procedure of the novel silicone beads requires only homogeneous mixing and includes no other complicated operations. The ²⁹Si NMR and TG measurements indicate that DMDMS is randomly incorporated into the methylsiloxane network. The particle size of the beads can be controlled by the concentration of urea as well as by the stirring speed in the sol-gel reaction. By carefully adjusting these parameters, the size of the beads has been optimized for the use in make-up cosmetics. It was revealed by various evaluation measurements that the novel silicone beads exhibit unique characteristics, such as softness, low oil absorption, high transparency and light diffusion effects.

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1. Introduction

Organic-inorganic hybrid materials, especially silicone compounds, are formulated into numerous kinds of cosmetic products in the form of liquid (oil), gel or powders.³⁾ Spherical silicone powders, such as silicone resin powders (PMSQ beads) and silicone rubber powders (DVDC beads), have been formulated into cosmetics for smooth feelings. Due to the presence of organic groups, these organic-inorganic silicone powders show higher flexibility and compatibility with the skin than inorganic spherical silica powders. The characteristics of these silicone powders are greatly affected by the crosslinking density in the silicone network. Silicone resin powders are characterized by very high crosslinking density. Due to their rigid mechanical response, silicone resin powders show relatively hard touch feelings and high fluidity. On the other hand, due to relatively low crosslinking density, silicone rubber powders show a lot of interesting characteristics such as elasticity, soft touch feelings and high oil absorption. However, it is too agglomerative to be formulated into a pressed powder foundation. The improvement of fluidity of silicone rubber powders, such as silicone rubber powders coated with silicone resin [INCI: VINYL DIMETHICONE/METHICONE SILSESQUIOXANE CROSSPOLYMER (VDMSC beads)]⁴⁾ have been studied. Recently, transparent methylsilsesquioxane (MSQ) aerogels and xerogels prepared from MTMS using surfactant and the urea-assisted acid-base two-step process were reported by Kanamori and co-workers.⁵⁾⁻⁸⁾ The synthesis of these monolithic gels are easy and reproducible in an

aqueous solution. For the improvement of the brittleness of these MSQ gels against tensile and shear stresses, an incorporation of difunctional silane such as DMDMS into the MSQ network was conducted by Hayase and co-workers.⁹⁾ It was revealed that the incorporation of difunctional silane leads to the reduction of the crosslinking density of the siloxane network and brings about flexible marshmallow-like monolithic aerogels and xerogels with a bendable feature. In this work, we have developed a process for the novel soft touch spherical silicone beads from MTMS and DMDMS under rigorous mechanical stirring of the gelling solution. The evaluated properties of the novel silicone beads for make-up cosmetics are reported.

2. Experimental procedure

2.1 Materials

Surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) was obtained from Kao Corp., Japan as a 30 wt % aqueous solution. The silane precursors MTMS and DMDMS were purchased from Shin-Etsu Chemical Co., Ltd. In this work, silicone resin powders (PMSQ beads) and silicone rubber powders coated with silicone resin (VDMSC beads) were evaluated for comparison with the novel spherical silicone beads. Since the silicone rubber powders (DVDC beads) tended to make tight agglomerates, VDMSC beads were evaluated instead of DVDC beads.

2.2 Synthesis procedure

The typical synthesis has been performed as follows; 225.21 g of H₂O, 0.09 g of acetic acid, 106.7 g of 30wt % aqueous solution of CTAC and 0.5 g of urea were mixed in a separable flask. Then, the mixture of 12.24 g (89.9 mmol) of MTMS and 13.20 g (109.8 mmol) of DMDMS was added and stirred at 800 rpm for 30 min at room temperature for hydrolysis. The stirring speed was then

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reduced to 200 rpm and the separable flask was heated up to 85°C in 30 min in a closed condition (in this step the solution became weakly basic due to the hydrolysis of urea), followed by the aging at the same temperature for 20 h. After the reaction, the products were filtered through a 100 mesh screen and washed successively with water, 2-propanol, and *n*-hexane to remove CTAC and other unreacted reagents. Finally, the particles were dried up completely at 105°C. In the case of scale-up experiments, only the stirring speed has been modified while the molar ratios were kept constant.

2.3 Measurements

The ^{29}Si solid-state cross polarization magic angle spinning (CP-MAS) NMR measurements have been performed on Avance III 800 (Bruker Biospin, Inc., Germany) under a static magnetic field of 18.8 T. The contact time for the CP was fixed at 6 ms and the rate of sample spinning was set to 15 kHz. The ^{29}Si chemical shifts were expressed as values relative to tetramethylsilane using the resonance line at -9.66 ppm for hexamethylcyclotrisiloxane crystal as an external reference.^{10),11)} Mechanical property of spherical silicone beads was measured by a microcompression tester (MCT-510, Simadzu Corp., Japan). The relation between the test strength and displacement was measured putting pressure on a particle (around $10\ \mu\text{m}$) at a constant rate. The loading was applied at a rate of $0.8924\ \text{mN/s}$. The stress of a spherical particle $C(x)/\text{MPa}$ was calculated as $C(x) = 2.48P/\pi d^2$ (P : testing load/N, d : diameter of a particle/mm).¹²⁾ Particle size distribution was determined by a laser diffraction/scattering particle size distribution apparatus (Microtrac MT3300EX II, NIKKISO Co., Ltd., Japan) in an ethanol solvent. The morphology of the particles was observed by a scanning electron microscope (SEM; S-3400N, HITACHI Co., Ltd., Japan). Thermogravimetry (TG) measurements were performed on Thermo plus EVO, RIGAKU Co., Ltd., Japan. The rheological properties were measured for silicone beads dispersed in the dimethylpolysiloxane oil with viscosity of 100 cSt at 50 wt %. Frequency dependence of the storage and loss moduli, G' and G'' , of the dispersion of each spherical silicone beads sample was measured at 25°C using a cone-and-plane rheometer (AR-200ex, TA Instruments, U.S.A.). The angle and the diameter of the cone and plate were 1° and 60 mm, respectively. Steady-state shear viscosity of the dispersion of each spherical silicone beads sample was also determined at various shear rates. Oil absorption of each silicone beads sample was determined using an ordinary apparatus (S410D, FRONTEx Co., Ltd., Japan). After the sample powders were poured into a double-blades mixer, dimethylpolysiloxane oil (6 cSt) was titrated into the mixing chamber at a constant rate while measuring the torque continuously. The amount of oil absorbed per 100 g of the sample powder A/mL was calculated as $A = 100B/C$ [B : the amount of silicone oil at 70% of the maximum torque (in mL), C : the weight of the sample powder (in g)].¹³⁾ Transparency test has been performed as follows; First, sample beads were mixed with skin milk prepared by the formulations shown in Table 1 at a predetermined weight ratio (sample beads/skin milk = 2.0/5.0), until the mixture became a homogeneous paste. The paste was then applied to the glass plate evenly using the 1 MIL-applicator. After drying at room temperature, light transmission was measured by Si-photodiode (Hamamatsu Photonics K.K., Japan).

3. Results and discussion

3.1 Verification of the incorporation of difunctional alkoxy silane

Figure 1 shows the solid-state ^{29}Si NMR spectra of the novel

Table 1. Formulations of the skin milk

Ingredients	(%)
GLYCERYL MONOSTEARATE	1.500
SORBITAN MONOSTEARATE	0.400
POLYOXYETHYLENE SORBITAN	0.500
MYRISTYLALCOHOL	1.000
CAPRYLIC/CAPRIC	2.000
SQUALANE	8.000
HYDRO GENATED SOYBEAN	0.100
D-DELTA TOCOPHEROL	0.050
PROPYL PARAHYDROXYBENZOATE	0.100
1,3-BUTYLENEGLYCOL	6.000
GLYCERIN	2.500
METHYLPAHYDROXYBENZOATE	0.200
CARBOXY VINYL POLYMER	0.180
PURIFIED WATER	75.922
DECAGLYCERYL STEARATE	0.500
SODIUM HYDROXIDE	0.048
SODIUM HYALURONATE	1.000
TOTAL	100.000

Fig. 1. ^{29}Si CPMAS NMR spectra of the novel silicone beads (A) and PMSQ beads (B).

silicone beads (A) and PMSQ beads (B). In the spectra of PMSQ beads, only T species were detected (T^3 : -67 ppm, T^2 : -57 ppm) indicating that the network is composed solely of trifunctional components. On the other hand, in the spectra of the novel silicone beads, D species appear around -10 to -22 ppm (D^2 : -21 ppm, D^1 : -12 ppm) in addition to the T species. The D^2 silicon was detected as two peaks; it is highly probable that the peak at -19.5 ppm can be attributed to D^2 silicon associated with a neighboring T unit.¹⁰⁾ Since the ^{29}Si NMR signal at -19.5 ppm is also close to that for cyclic tetrasiloxane (i.e., octamethylcyclotetrasiloxane), it is difficult to exclude the possibility of the presence of D^2 cyclic species formed by self-condensation of D species within the particles. However, since sufficient washing and drying processes were conducted, the amount of D^2 cyclic species entrapped in the gel network would be negligible. The data shown above indicates that, in the present synthesis of the novel silicone beads, DMDMS is randomly incorporated into the PMSQ network.¹⁴⁾ Figure 2 shows the results of thermogravimetry (TG) measurements of the identical silicone beads shown in Fig. 1. In either sample, the mass decrease due to the exothermic decomposition of $\text{Si}-\text{CH}_3$ group was observed from 300 to 500°C,^{15),16)} and there was no indication of the other phases than co-polymerized DMDMS and MTMS. It shows a reasonable agreement with the results shown in Fig. 1: DMDMS is homogeneously incorporated in the PMSQ network. In addition, no effective weight loss was detected from 150 to 200°C in the novel silicone beads, indicating that the surfactant CTAC was completely removed by the washing process from the obtained beads.

Fig. 2. TG curves of the novel silicone beads and PMSQ beads.

3.2 Particle size control

Many kinds of spherical particles have been formulated into cosmetics for smooth feelings and improved light diffusion effects.¹⁷⁾ Since the size of particles strongly influences these properties, it is important to control the size of the spherical particles. As reported by Hayase and co-workers, the amount of urea affects the microstructures of marshmallow-like aerogels and xerogels derived from MTMS and DMDMS.⁸⁾ With an increase of urea, the size of the particles consisting of the monolithic gel becomes smaller, whereas with a decrease of urea, the particles are enlarged. **Figure 3** shows the SEM images and the particle size distributions of the samples prepared with varied amount of urea. The reaction was conducted in the batch scale described above (total amount of alkoxysilanes = 200 mmol). As shown in Figs. 3(A)–3(E) and 3(G) with an increase of concentration of urea, the average particle size of the novel silicone beads decreased. In this reaction scale, the spherical beads were obtained in the range $0.2 \text{ g} \leq w_{\text{urea}} \leq 1.0 \text{ g}$. With the urea amount of $w_{\text{urea}} < 0.2 \text{ g}$, the cured products were obtained not in the form of dispersed particles but solid precipitates at the bottom and on the inner wall of the vessel. With the addition of $w_{\text{urea}} > 1.0 \text{ g}$, only hydrophobic oil was obtained. Figures 3(F) and 3(H) show the effect of stirring speed in the polymerization reaction. Comparison between Figs. 3(B) and 3(D): 200 rpm, $w_{\text{urea}} = 0.5 \text{ g}$ with Figs. 3(F) and 3(H): 100 rpm, $w_{\text{urea}} = 0.5 \text{ g}$, reveals that at the lower stirring speed, the average particle size slightly decreases, which is accompanied by narrowing of the size distribution. **Figure 4** shows the SEM images and particle size distributions of the samples prepared with various amount of urea in an order larger synthesis scale than the case of Fig. 3 (total amount of alkoxysilane = 2000 mmol). The stirring speed in the polymerization reaction was set at 600 rpm. Similarly to the case of a smaller batch (total amount of alkoxysilane = 200 mmol), with an increase of the concentration of urea, the average particle size of the novel silicone beads tends to become smaller. The dependence of average particle size on the concentration of urea becomes stronger in the larger batch. From the dependence of average particle size on the stirring speed, it is reasonably anticipated that the local shear rate, influenced by the size and shapes of the stirring blades and those of reaction vessels, will have a crucial role in determining the resultant particle size and the size distribution. Further detailed experimental confirmation is needed to clarify the effects of synthesis parameters over the batch scales.

3.3 Characteristics of the novel silicone beads

Figure 5 shows the oil absorption results of the three silicone

Fig. 3. SEM image and particle size distribution of the samples prepared with varied amount of urea. (A), (C) $w_{\text{urea}} = 0.2 \text{ g}$, (B), (D) $w_{\text{urea}} = 0.5 \text{ g}$, (E), (G) $w_{\text{urea}} = 1.0 \text{ g}$ (F), (H) sample prepared with $w_{\text{urea}} = 0.5 \text{ g}$ at stirring speed of 100 rpm instead of 200 rpm.

Fig. 4. SEM image and particle size distribution of the samples prepared with varied amount of urea in 10 times scale-up experiments. (A), (D) $w_{\text{urea}} = 2.0 \text{ g}$, (B), (E) $w_{\text{urea}} = 5.0 \text{ g}$, (C), (F) $w_{\text{urea}} = 9.0 \text{ g}$.

beads. Due to the low crosslinking density of the silicone rubber at the core, VDMSC beads indicate larger oil absorption than PMSQ beads. The oil absorption of the novel silicone beads was further smaller than that of PMSQ beads. It is highly probable that this result stems from the difference of the lipophilicity of two kinds of silicone beads. In general, the lipophilic treated powders show lower oil absorption than the untreated powders. Since the sur-

Fig. 5. Mechanical properties and oil absorptions of three kinds of silicone beads.

Fig. 6. Rheological properties of the three kinds of silicone beads dispersed in dimethylpolysiloxane oil (100 cSt) at 50 wt %. (A) Frequency dependence of storage modulus and loss modulus. (B) Shear rate dependence of steady-state viscosity.

faces of untreated particles have relatively weak affinity for oil, untreated powders show low wettability and dispersibility in the oil. For this reason, when mixed with the oil, untreated powders gradually form tight agglomerates and can hold a large amount of oil within the gaps between particles. On the other hand, due to relatively strong affinity for oil, lipophilic treated powders show high wettability and dispersibility in even a small amount of oil. Therefore, lipophilic treated powders cannot hold a large amount of oil. The result of the oil absorption test is assumed that in the formulation of pressed powder foundation, the novel silicone beads require a smaller amount of binder oil compared to the formulations containing other silicone beads. The results of the micro compression test of three kinds of silicone beads are also included in Fig. 5. At the initial low compression, VDMSC beads exhibit very small stress values, showing a soft deformable feature. With further increase in the deformation, it shows a very high modulus under the strain values exceeding 10%. The particle becomes almost incompressible, showing effectively no strain over 20% even under higher stresses. No destruction of the particle was observed. The above mentioned mechanical properties indicate that VDMSC beads show softness based only on easy compression of the silicone rubber cores, and they behave as if they are hard spheres under pressures exceeding a certain threshold. The stress-strain curves of the novel silicone beads are located between those of PMSQ beads and VDMSC beads. By incorporating difunctional silane into the PMSQ network, the crosslinking density is reduced and the novel silicone beads exhibit broader ranges of elastic deformation, being yet harder than the silicone rubber powders. The stress values at 10% strain of the novel silicone beads are the lowest among these three kinds of silicone beads. The rheological properties of these three kinds of silicone beads also suggested that the novel silicone beads show intermediate characteristics between silicone resin powders and silicone rubber powders. As shown in Fig. 6(A), dispersed PMSQ beads behave as solid particles having almost no interaction

Fig. 7. (A) Comparison of the visible light transmittance of the silicone beads spread on a glass plate. (B) Digital photo graphs of the coated layers of three kinds of silicone beads.

among them. On the other hand, VDMSC beads behave as strongly interacting and highly deformable networked particles, showing plateau regions both in storage modulus (G') and loss modulus (G''). The values of G' and G'' of the novel silicone beads exhibit an intersection in the measured frequency range. With increasing frequency, the properties of the novel silicone beads change from elastic to viscous. As shown in Fig. 6(B), the novel silicone beads exhibit an intermediate shear-thinning behavior between those of PMSQ and VDMSC beads. Since the shear-thinning is observed when the shear breaks attractive interactions among dispersed particles to inhibit their cooperative response, dispersions composed of strongly interacting particles tend to show a strong dependence of viscosity on the shear rate. The absolute values of viscosity of the novel silicone beads, as well as its shear rate dependence, are in-between those of PMSQ and VDMSC beads. It again suggests that the novel silicone beads are more susceptible to deformation than PMSQ beads; at the same time the novel silicone beads behave more like independent solid particles than VDMSC beads. The texture evaluation shows that PMSQ beads exhibit high fluidity and dry touch feelings, whereas the novel silicone beads show lower fluidity and considerably moist touch feelings. These differences of touch feelings derived from the incorporation of difunctional silane can be reasonably correlated with the result of microcompression test

(more deformable) and dynamic viscoelasticity measurement (retains high enough viscosity). The novel silicone beads also show high transparency. The novel silicone beads exhibit the highest transparency among these three kinds of spherical silicone beads as shown in Fig. 7(A). Since the novel silicone beads show natural light diffusion effects as shown in Fig. 7(B), the novel beads may be useful for preparing the make-up cosmetics which are characterized by transparency and bare skin feelings.

4. Conclusions

The novel silicone beads have been synthesized easily in aqueous solution from methyltrimethoxysilane and dimethyldimethoxysilane under rigorous mechanical stirring. The size of the beads can be controlled by the concentrations of urea and the stirring speed in the polymerization reaction. The novel silicone beads powder shows unique characteristics, such as softness, low oil absorption, high transparency and light diffusion effects. The novel silicone beads can more favorably be formulated into a pressed powder foundation than the case of silicone rubber powders that are too agglomerative. For these reasons, the novel material presented here will be more useful for make-up cosmetics than the conventional PMSQ or VDMSC beads, and will contribute to provide unique sensual properties such as enhanced moisture and soft touch feelings.

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