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Preparation of Spherical Poly(methylsilsesquioxanes) Beads and Their Properties

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The spherical poly(methylsilsesquioxane) (PMSQ) beads with the diameter of 2, 5 and 10 micron, respectively were prepared from methyltrimethoxysilane (MTMS) by two steps, acid hydrolysis and base condensation process in aqueous solution. Acetic acid and ammonium hydroxide were used to initiate the acid hydrolysis and base condensation, respectively. The bead size was affected and controlled by the reaction variables, such as the agitation speed, reaction temperature, solvent and concentration of monomer and catalyst. The prepared PMSQ beads were characterized by ^{29}Si CP/MAS NMR and FT-IR. Especially in preparing the spherical PMSQ bead with the diameter of 10 micron, it was found that organic solvent was necessary to obtain the desired size compared with the preparation condition of 2 and 5 micron beads. The prepared PMSQ beads showed good thermal stability and compression recovery ratio. The haze value of PMSQ beads was remarkably higher than that of acrylic beads due to the relatively low refractive index of PMSQ.

Keywords: compression recovery; condensation; haze value; hydrolysis; poly(methylsilsesquioxane)

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1. INTRODUCTION

Polyorganosilsesquioxane (POSQ) is a ladder or cage type siloxane polymer [1] used widely in paint, cosmetics and coating applications by its thermal stability and mechanical strength. Since Brown *et al*. [2] first introduced the structure of POSQ and Stöber *et al*. [3] developed the preparation system of POSQ, many scientists have studied synthetic methods including size control [4–9] and applications of POSQ [10–11]. But almost all studies were related to the preparation of POSQ beads with the diameter of around 2 μm and it was difficult to prepare larger spherical beads with the diameter of over 2 μm. Recently, poly (methylsilsesquioxane) (PMSQ) beads with the diameter of over 2 μm become increasingly needed for the applications to light diffuser film and plate in liquid crystal display because optical properties are strongly related to the size and refractive index of PMSQ beads.

In this paper, the optimum preparation condition for preparing spherical PMSQ beads with the diameters of over 2 μm and with the narrow diameter distribution was intensively studied by controlling the experimental variables such as the agitation speed, concentration of monomer and catalyst, reaction temperature and solvent. The thermal stability, elastic property and optical properties of prepared PMSQ beads were investigated for the applications of light diffuser film and plate.

2. EXPERIMENTAL

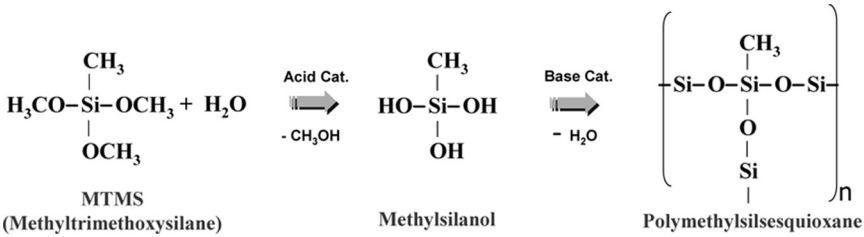
Chemicals

The chemicals used for the preparation of PMSQ beads were ACS grade (Aldrich). Methyltrimethoxysilane (MTMS) as starting monomer, acetic acid (AA) as hydrolysis catalyst, ammonia water (NH_4OH) as condensation catalyst and methoxytrimethylsilane (MOTMS) as end-capping monomer were purchased from Aldrich. Deionized water (DIW) was used as main solvent and additional organic solvent, isopropyl alcohol (IPA) and 1-hexanol were used without further purification.

Preparation of Poly(methylsilsesquioxane) (PMSQ) Beads

For the preparation of PMSQ beads, hydrolysis and condensation reactions shown in Scheme 1 were carried out under dry inert nitrogen gas.

Step 1. Acid hydrolysis of MTMS
DIW and AA were mixed and stirred for 10 min under nitrogen atmosphere in 1L double jacket glass reactor and followed by addition of MTMS.



SCHEME 1 The preparation route of PMSQ beads.

Step 2. Base condensation of methoxysilanol

DIW was added and mixed into the solution of step 1 for 10 min, followed by addition of 28% ammonia water. When turbidity formed, stopped stirring and stayed for 3 hours at room temperature. Methoxytrimethylsilane (MOTMS) was added and stirred for 10 min, then kept overnight. The precipitate was filtered and washed with DIW and dried in vacuum oven for 3 hours at 150°C.

Characterization and Analysis of PMSQ Beads

The structure of prepared PMSQ beads was characterized by ^{29}Si cross polarization-magnetic angle spinning (CP/MAS) NMR (Bruker) and FT-IR (Perkin Elmer, Spectrum 2000) spectroscopy. The size and morphology of resulting beads were determined with a field emission scanning electron microscope (FE-SEM, HITACHI S-4300). The bead size distribution was measured with a particle size analyzer (Beckmann Coulter, LS 13 320).

Thermal Stability and Compression Property of PMSQ Beads

The thermal stability of prepared PMSQ beads was investigated with a TGA (TA Instrument Q50). The compression and elastic property of prepared PMSQ and commercial poly(methyl methacrylate) (PMMA) beads (KOLON, Diasphere® PU-510) were determined by nano indenter (Shimadzu Co., MCT-W500). The recovery ratio was calculated using the following equation [12]

$$\text{Recovery ratio } (\%) = \frac{(D_1 - D_2)}{D_1} \times 100,$$

where D_1 is the indented depth at the force of 1 gf, D_2 is the depth indentation after removing force.

Application and Optical Properties of PMSQ Beads

Light diffuser films were prepared by coating the formulation solution with PMSQ beads and PMMA beads, respectively. Acrylic resin (Aekyoung Co.), methyl ethyl ketone, toluene and PMSQ or PMMA beads were well mixed and dispersed by mill. Prepared composition mixture was coated on 188 μm PET film, the final coating thickness of 25 μm was obtained after drying. The light diffuser plate was prepared by melt-extruding polystyrene mixed with prepared PMSQ and PMMA beads, respectively. The light transmittance (TT) and haze value (Hz) of diffuser film and plate were calculated in the backlight unit (BLU) system composed of lamp, reflection sheet, light diffuser plate and film.

3. RESULTS AND DISCUSSION

The prepared PMSQ was reacted additionally with end capping monomer, MOTMS because the existing free hydroxyl group in PMSQ as shown in Figure 1 diminishes the water resistance. The prepared PMSQ was characterized by ^{29}Si CP/MAS NMR and FT-IR spectra as shown in Figures 2 and 3, respectively. In ^{29}Si CP/MAS NMR spectrum, only two characteristic methyl modified peaks at −57.6 and −66.5 ppm were appeared, which indicated that silanol group originally at −100.3 ppm was completely converted to the networked Si−O−Si bond. FT-IR spectrum shows the peaks at 2890–2950, 1260 and 1000–1100 cm^{-1} corresponding to C−H stretch, Si−CH_3 symmetric deformation and Si−O−Si asymmetric stretch, respectively. Especially no peak at 3440 cm^{-1} from Si−OH was observed, which means that complete condensation reaction has occurred.

In order to find the optimum condition for preparing the spherical PMSQ beads with larger diameter and narrower diameter distribution, the agitation speed, reaction temperature and concentration

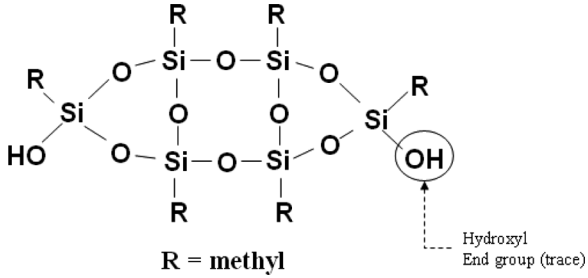


FIGURE 1 Chemical structure of PMSQ.

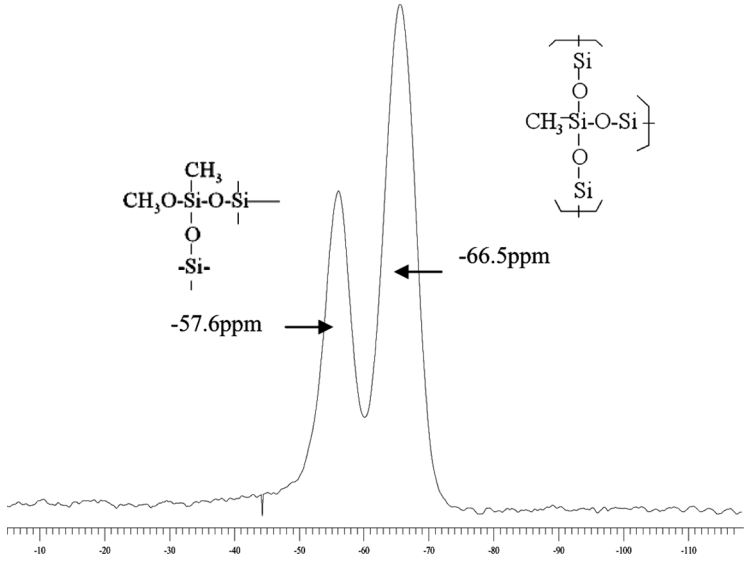


FIGURE 2 ^{29}Si CP/MAS NMR spectrum of PMSQ.

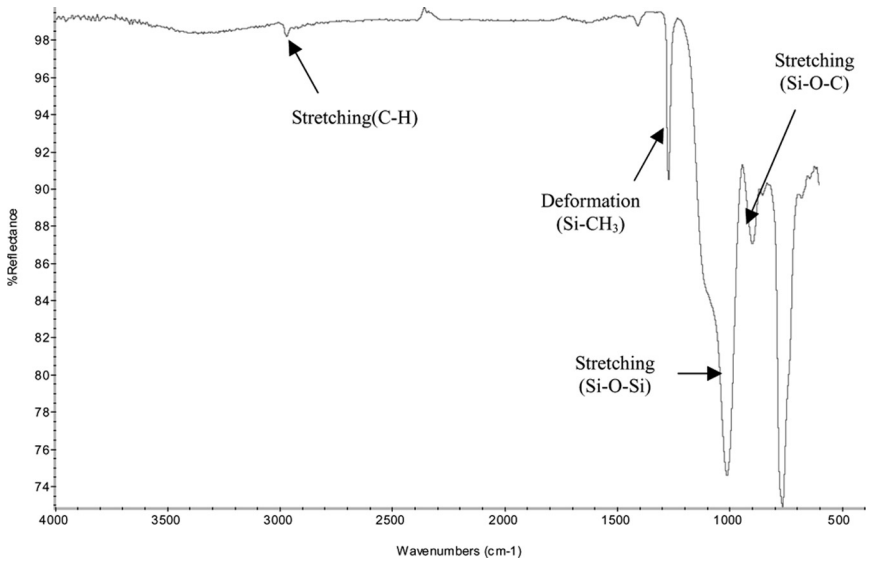


FIGURE 3 FT-IR spectrum of PMSQ.

TABLE 1 Effect of Agitation Speed and Temperature on the Final PMSQ Bead Diameter at the Condition of [AA] = 0.01 mol%, [NH_4OH] = 0.1 mol%, [MTMS] = 1.39 mol%, [MOTMS] = 0.04 mol% and [DIW] = 98.47 mol%

	Process Parameter		Results	
Experiment No.	Agitation speed (rpm)	Temperature (°C)	Average diameter (μm)	C.V. (%)
A-1	100	10	3.4	48.1
A-2	100	20	2.9	49.5
A-3	100	40	1.5	50.2
B-1	50	10	2.8	14.2
B-2	50	20	2.6	20.7
B-3	50	40	1.7	35.2
C-1	20	10	2.5	8.1
C-2	20	20	2.4	8.5
C-3	20	40	1.8	20.1

of monomer and catalyst were varied systematically. As shown in Table 1, high agitation speed at step 2 led to obtain the spherical PMSQ bead with larger diameter but broad diameter distribution with coefficient value (C.V.) of over 40%. This might be due to the following argue, high speed agitation makes more frequent collision between small aggregates and consequently gives larger coagulations. The result of this preparation technique is contrary to that of the seed-growth preparation technique such as the emulsion polymerization. However, the desired beads with narrow diameter distribution were obtained at the temperature below 20°C. The minimum amount of AA as a hydrolysis catalyst was needed only to decrease the reaction time because the PMSQ beads were not formed in this step 1 and AA did not affect critically on the final bead size. When introduced the alkali (NH_4OH) catalyst in hydrolyzed solution, the turbidity was formed and the final bead diameter decreased gradually with the increase of alkali concentration. From the several repeated experiments it was found that the optimum AA and NH_4OH concentration for preparing PMSQ beads were 0.01 mol% and 0.1 mol%, at the pH range of 3.5–3.6 and 9.4–10.5, respectively. The effect of monomer (MTMS) concentration on the diameter of PMSQ beads is shown in Figure 4. The final bead diameter increased drastically with the increase of the monomer concentration in the range of below 2.19% but the bead size gradually decreased in the range of above 2.19%. From the result of Figure 4 it was concluded that the beads with the diameter of below 8 μm can be prepared by varying monomer

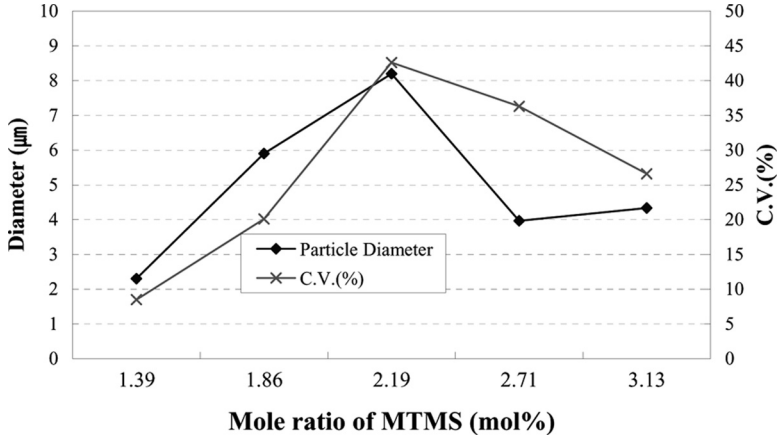


FIGURE 4 Effect of MTMS concentration on the final PMSQ bead diameter and diameter distribution at the condition of [AA] = 0.01 mol%, [NH_4OH] = 0.1 mol%, [MOTMS] = 0.04 mol%, T = 20°C and agitation speed = 20 rpm.

concentration, whereas the beads with the diameter of above 8 μm cannot be obtained easily by controlling the monomer concentration under the condition of agitation speed (20 rpm), temperature (20°C) and concentration of AA (0.01 mol%) and NH_4OH (0.1 mol%) at 20°C. Recently, S.M. Koo *et al*. [13] reported that the spherical beads with the diameter of 1–2 μm could be prepared from the seed-growth technique through hydrolysis and condensation process with the introduction of additional solvent such as alcohol.

In order to obtain the spherical PMSQ beads with the diameter of 10 μm in this preparation technique, 1-propanol and 1-hexanol in addition to DIW were used, respectively. 0.33 mol% of 1-hexanol was useful for preparing 10 μm beads with relatively narrow diameter distribution (C.V. of 35%) under the MTMS concentration of 4.07 mol%.

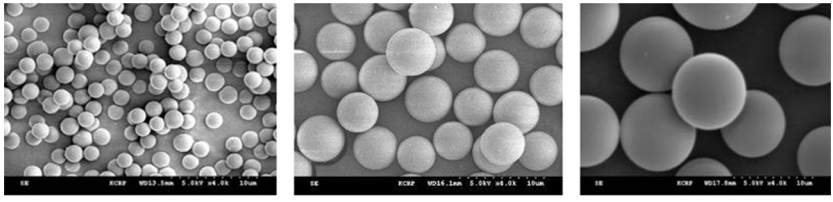


FIGURE 5 SEM images of spherical PMSQ beads with the diameter of (a) 2 μm, (b) 5 μm, and (c) 10 μm.

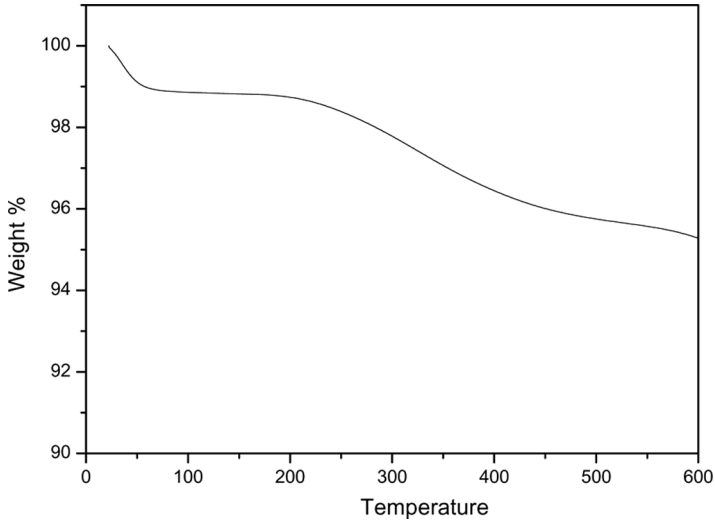


FIGURE 6 TGA curve of PMSQ bead.

When introduced the shorter chain alcohol, 1-propanol, the bead diameter was increased to 10 μm but the diameter distribution was broad (C.V. of over 56%). It was explained that long chain alcohol lowered repulsive polarity and made the colloidal particles more stable. The SEM images of prepared PMSQ beads with the diameter of 2, 5 and 10 μm, respectively are shown in Figure 5.

Thermal stability of PMSQ beads was investigated by thermogravimetric analysis (TGA) in N_2 flow at 20–800°C. As shown in Figure 6, the initial decomposition occurred at about 250–300°C originated from the thermal decomposition of methyl group of PMSQ and total weight loss in the range of 200–600°C was under 4%, which was in accordance with the decomposition of typical polysilsesquioxane. Hardness and elasticity of polymeric beads are important for the evaluation of resistance to external compression and scratch. To evaluate the compression and recovery property, prepared PMSQ and commercial

TABLE 2 Compression and Recovery Ratios of PMSQ and PMMA Beads

		Compression and recovery ratio		
Bead type	Bead size (μm)	D_1 (μm)	D_2 (μm)	Recovery ratio (%)
PMSQ	5.745	2.704	2.252	16.7
PMMA	5.215	2.454	2.246	8.5

TABLE 3 Optical Properties of PMSQ and PMMA Beads

Applications	Substrate	Bead	Bead diameter (μm)	Weight contents (%)	Transmittance (TT, %)	Relative brightness (%)	Haze value (Hz.%)
Diffuser Film	PET	PMSQ (n = 1,42)	5.0	18.0	97.7	−14.9	91.8
	(n = 1.49)	PMMA (n = 1.49)		18.0	85.2	Reference	83.5
Diffuser Plate	PS	PMSQ (n = 1.42)	5.0	1.6	62.0	5.7	70.0
	(n = 1.50)	PMMA (n = 1.49)		1.6	68.0	Reference	59.0

'n' refers to the refractive index which was measured at 589 nm in Abbe refractometer

poly(methyl methacrylate) (PMMA) beads with the diameters of 5 μm were adopted and compared. It can be known from the value of D_1 and recovery ratio in Table 2 that the prepared PMSQ bead is less hard and more elastic than the PMMA bead. It is assumed that these results are due to the ladder or cage type molecular structure of prepared PMSQ beads. In order to evaluate the potential application to light diffusion film and plate, the optical properties of prepared PMSQ and commercial PMMA bead with the diameter of 5 μm, respectively were investigated. The comparative results were shown in Table 3. In general, the haze value could be described by the equation shown as below.

$$\text{Haze value } = \frac{(DF)}{(TT)} \times 100(\%)$$

where (DF: Diffuse Luminous Transmittance, TT: Total Luminous Transmittance)

According to the equation, haze value correlates with DF value which is directly influenced by different refractive indices of two media as the light passes through. Therefore, the higher haze value of the diffusion film and plate with PMSQ was obtained, which is due to greater difference of refractive indices between PMSQ bead and PET film or polystyrene plate than that of refractive indices between PMMA bead and PET film or polystyrene plate.

4. CONCLUSION

The spherical PMSQ beads with the diameter of 2, 5 and 10 μm were successfully prepared by two steps, acid-catalyzed hydrolysis and alkali-catalyzed condensation of MTMS monomer under the appropriate preparation condition. In preparing PMSQ beads with the diameter of 2 and 5 μm, MTMS concentration had an important effect on the desired bead size under the condition of agitation speed (20 rpm), temperature (20°C) and concentration of AA (0.01 mol%) and NH_4OH (0.1 mol%). Organic solvent, 1-hexanol was needed to prepare the 10 μm PMSQ bead with the narrow diameter distribution under the MTMS concentration of 4.07 mol%. The prepared PMSQ beads showed good thermal stability, elasticity and high haze value.

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