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SHORT COMMUNICATION

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Preparation and characterization of micron-sized polystyrene/polysiloxane core/shell particles

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Abstract A procedure has been developed to coat micron-sized polystyrene (PS) spheres with a smooth layer of polysiloxane by a sol–gel process of methyl trimethoxylsilane (MTMS) without using silane coupling agents. The thickness of the shells can be easily varied with different polystyrene seeds and methyl trimethoxysilane feed ratio. When we used PS particles with diameters of 2.09 μm prepared by conventional dispersion polymerization as seeds, the thickness of the polysiloxane shells can be varied from 0.11 to 0.21 μm. The particle size, size distribution, thermal decomposition, and solvent resistance were investigated by scanning electron microscope (SEM), transmission electron microscope (TEM), size analyzer, and TG, respectively.

Keywords Polystyrene · Polysiloxane · Core/shell particles

Introduction

Coating of polymer particles with a layer of different materials is used as a method to modify their surface chemical, reactive, optical, or catalytic properties. Several preparing techniques have been developed to obtain micron-sized core/shell composite particles. Dynamic swelling method was used to prepare micron-sized polystyrene (PS)/poly(ethyl methacrylate) [1], PS/poly(butyl methacrylate) [2] composite particles. PS/poly(methyl methacrylate) (PMMA) composite particles were prepared by emulsion polymerization with micron-sized polystyrene as seeds that were prepared by dispersion polymerization [3]. Seeded dispersion polymerization has been employed to produce micron-sized PS/PMMA [4], PMMA/PS [5], and PS/poly(*n*-butyl acrylate) (PBA) [6] composite particles.

Most of the works have focused on the micron-sized core/shell composite particles prepared from styrene and acrylic monomer. Nevertheless, there have been few studies available on the micro-sized core/shell composites of vinyl monomers and siloxane. In applications, polysiloxane has many specific properties such as good water repellency, weather resistance, lubricity, and excellent thermal stability. Therefore, the combination of vinyl polymer with polysiloxane can exhibit unusual, even unique properties. There are some studies that investigated the composite latex particles with polysiloxane shell using seeded emulsion polymerization [7–11]. However, most of the composite latex particles are obtained in the form of a thin film or coating. There has been no study on the preparation of composites of vinyl monomers and siloxane in the particulate form, even more so in the form of spherical particles with uniform sizes.

In this study, micron-sized polystyrene/polysiloxane composite particles, consisting of PS core and polysiloxane shell, were first prepared. The polysiloxane network acts as a cross-linking moiety to give enhanced mechanical and thermal properties of PS seed. Furthermore, because the refractive index of polysiloxane shell prepared from methyl trimethoxylsilane (MTMS) is different from that of PS seed, particles with the same PS core but different thickness of the shell can have different light scattering properties. Polystyrene seed particles were prepared by conventional dispersion polymerization [12–15]. The synthesis of the polysiloxane shell was carried out using a sol–gel process of methyl trimethoxylsilane without using silane coupling agents. The sol–gel process provided a convenient route

with mild operating conditions, such as low temperature, and many previous studies have investigated the sol–gel chemistry of MTMS [16–22]. However, the incorporation of polysiloxane onto micron-sized polymer particles to provide core/shell particles has never been investigated. The morphology and the phase structure of the particles were then characterized using scanning electron microscope (SEM) and transmission electron microscope (TEM), and some properties of the core/shell particles were also investigated.

Experimental

Materials

Styrene (St; Shanghai Lingfeng Chemical), methyl trimethoxysilane (MTMS; Hangzhou Guibao Chemical), polyvinylpyrrolidone (PVP K30; Fluka Chemical), ethanol (Shanghai Lingfeng Chemical), hydrochloric acid (HCl; Shanghai Lingfeng Chemical) and ammonium hydroxide (NH_4OH; Yixin Sunan Chemical Material Plant) were all reagent grades and used as received. 2,2′-azoisobutyronitrile (AIBN, the Fourth Shanghai Reagent Plant) was recrystallized from methanol.

Synthesis of polystyrene seed particles

The polystyrene seed particles were prepared by dispersion polymerization. St, AIBN, PVP, ethanol, and deionized water were all weighed into a 250-ml four-neck glass reactor equipped with a mechanical stirrer, a refluxing condenser, and a nitrogen inlet system. In the initial stage, all ingredients were homogeneously dissolved in the ethanol/water mixture. After sealing in a nitrogen atmosphere, the reactor was submerged into a preheated thermostated water bath at 70 °C and the polymerization was carried out for 24 h. The resulting latex was filtrated and the filter cake was repeatedly washed by ethanol, followed by drying under a vacuum at 50 °C. All the ingredients used for sample PS3 and PS6 are summarized in Table 1.

Table 1 Recipe for preparing PS seed particles by dispersion polymerization

Sample	Ethanol (g)	Water (g)	St (g)	PVP K30 (g)	AIBN (g)
PS3	36	4	10	1	0.1
PS6	21	2.3	10	1	0.3

Table 2 The particle size and size distribution of PS seed particles and core/shell particles

Samples	m_{shell}/m_{core}	d_{core}[a] (μm)	CV (%)	$d_{core-shell}$ (μm)		
				Predicted[b]	measured[a]	CV (%)
PS3		2.09	27.3			
SS3-1	18/82			2.21	2.30	28.2
SS3-2	26/74			2.27	2.39	31.5
SS3-3	35/65			2.35	2.65	28.8
SS3-4	42/58			2.43	2.51	38.2
PS6		5.72	28.6			
SS6	15/85			5.97	5.85	31.3

[a]The number average diameters of the particles measured by a size analyzer
[b]The diameters of the core/shell particles calculated from above equation

Preparation of core–shell particles

Polystyrene/polysiloxane core/shell particles were prepared by a sol–gel process. MTMS (1 g) were hydrolyzed in water (5 g) with HCl as catalyst, and the aqueous silanol mixed with polystyrene seeds (2 g) by 10 min sonication. Then, an ammonia solution was added into the mixture to control the pH value of the solution to 9.0 to catalyze the condensation reactions of silanol. The reaction was continued for 5 h and polysiloxane shells were generated on the PS seed particles. The particles with different core/shell weight ratio can easily be prepared by adjusting the feed ratio of the PS seed and MTMS. The resulting latex was filtrated and the filter was repeatedly washed with ethanol. This was followed by drying at 105 °C and the PS/polysiloxane composite particles were attained.

Characterization

The number average diameter (d_n) and size distribution coefficient (CV) of the particles were measured by a size analyzer (Mastersizer 2000, Malrven).The morphology of the particles was observed with a scanning electron microscope (SEM) (JSM-6360LV, JEOL). Dried core/shell particles were dispersed in epoxy resin matrix, cured at room temperature for 24 h, and at 40 °C for 1 h, and were

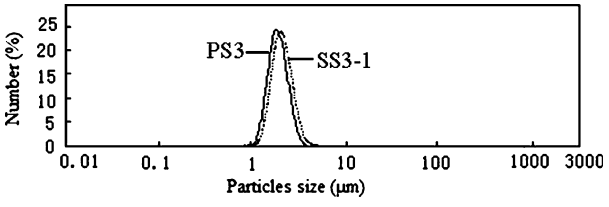

Fig. 1 The particle size and size distribution of particles PS3 and SS3-1

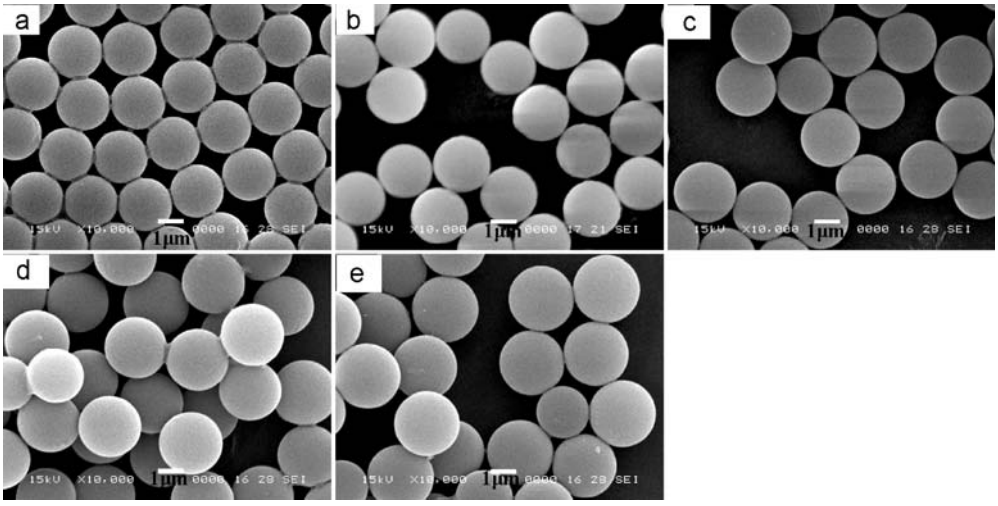

Fig. 2 SEM of PS seed particles and core/shell particles. **a** PS3, **b** SS3-1, **c** SS3-2, **d** SS3-3, **e** SS3-4

microtomed. The ultrathin cross-sections were observed using the transmission electron microscope (TEM) (JEOL-1200EX, JEOL). The solvent resistance of the core/shell particles was evaluated by monitoring the solubility of particles in different solvents with an optical microscope (BX51, Olympus). Measurements of thermal decomposition of the particles were made using a TG (Pyris-1, Perkin-Elmer). The sample was heated at a rate of 20 °C/min to 850 °C in air atmosphere. Proton nuclear magnetic resonance (^{1}H NMR) (AVANCE 500 MHz, Bruker) was used to analyze the PS seed particles. The dried PS particles were dissolved by using $CDCl_3$ as a solvent. Tetramethylsilane (TMS) was used as internal standard.

Results and discussion

Polymer particle size and size distribution

If we suppose the polysiloxane grow in the corresponding PS seed particles, and the density of the polysiloxane is assumed to be equal to the density of the poly(methyl trimethoxysilane) microspheres (1.32 g/cm^3), and that of the PS core is presumed to be close to the density of PS (i.e., 1.05 g/cm^3), the theoretical diameter of the core/shell particles can be calculated as follows,

$$d_{\text{core-shell}} = d_{\text{core}} \times \left(1 + \frac{1.05}{1.32} \times \frac{m_{\text{shell}}}{m_{\text{core}}}\right)^{1/3}$$

In the equation, d_{core} is the diameter of the PS seed particles, $d_{\text{core-shell}}$ is the diameter of the core/shell particles, m_{core} is the mass of the PS seed particles, m_{shell} is the mass of the polysiloxane shell after the sol–gel process. The particle size and size distribution of the seed particles and core/shell particles with different core/shell mass ratio are shown in Table 2. In this table, SS3-1, SS3-2, SS3-3, and SS3-4 are the core/shell particles with PS3 as the seed particles, and SS6 are the core/shell particles with PS6 as the seed particles. The results reported in Table 2 show that the measured diameter of the core/shell particles almost agreed with the calculated one. This indicates that the sol–gel process of MTMS proceeded in the corresponding PS seed particles. We noticed that the measured diameter of SS3-3 is larger than the calculated diameter; maybe it was caused by the conglutination between some particles.

The particle size distribution curves of PS3 and SS3-1 particles are shown in Fig. 1. After the sol–gel process, the particle size increased and the size distribution still

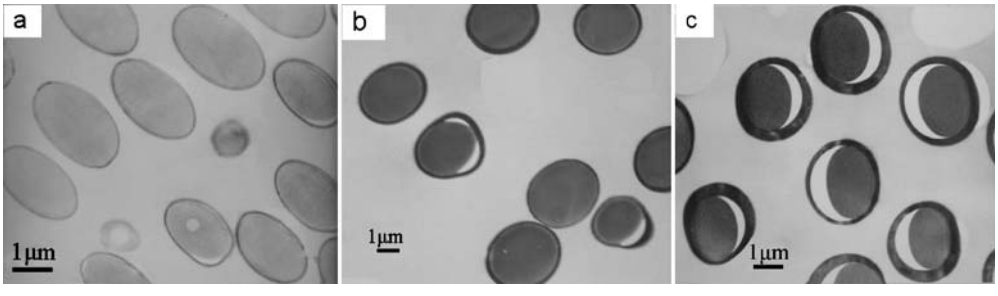

Fig. 3 TEM of the ultrathin cross-section of core/shell particles. **a** SS3-1, **b** SS3-2, **c** SS3-4

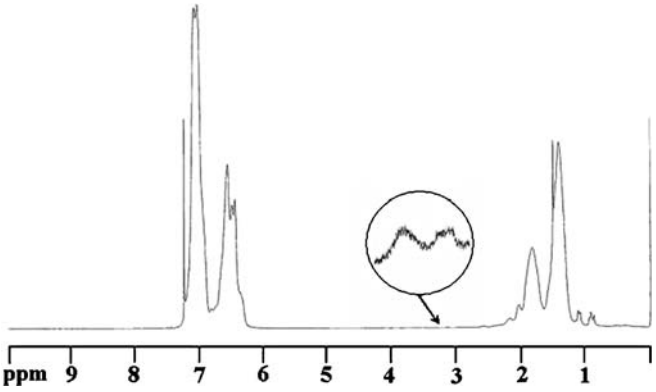

Fig. 4 The ^{1}H NMR spectrum of PS seed particles

appeared as a single peak. Again, the result indicated that the polysiloxane was incorporated into the PS seed particles.

Particles morphology

SEM photographs of PS seed particles and PS/polysiloxane core/shell particles are shown in Fig. 2. All the particles were spherical in shape even at a high MTMS concentration and the particle size increased with the increase of the MTMS feed ratio. It is evident that the polysiloxane shell on the PS seed particles is very smooth and uniform. This suggests that deposition of polysiloxane onto the PS particle surfaces occurs in the form of oligomers or very small particles.

Figure 3 shows TEM photographs of the ultrathin cross-section of the PS/polysiloxane particles. In Fig. 3, the composite particles SS3-1, SS3-2, and SS3-4 have heterogeneous contrasts. The boundaries of the PS core and polysiloxane shell are clearly observed, and the thickness of the polysiloxane increases with more methyl trimethoxysilane feed. The thickness of the polysiloxane shell is easily varied by changing the ratio of MTMS to PS. We can see some clear voids between the core and the shell. The formation of the void may be caused by the different shrinkage of the PS core and the cross-linked polysiloxane shell during the dryness process. So, the void

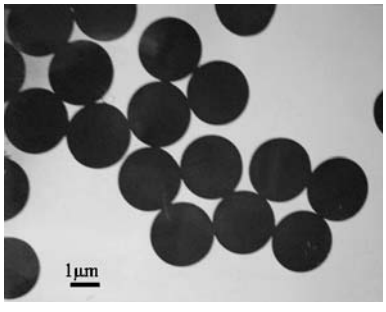

Fig. 5 TEM of SS3-1 particles after extraction with chloroform

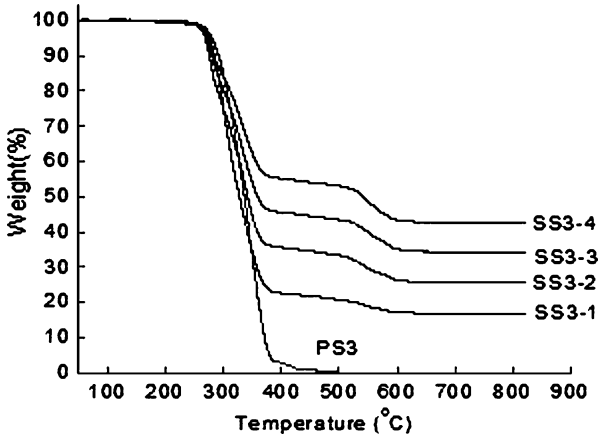

Fig. 6 TG analysis of PS seed particles and core/shell particles

portion of the particles increased with the increase of the relative amount of polymethylsiloxane.

Generally speaking, we need to introduce the silane coupling agent into the PS seed to form the covalent bond between the PS core and the polysiloxane shell just as some works reported [23, 24]. But surprisingly in our system, PS/polysiloxane particles can be successfully prepared with nonmodified PS particles as seeds and the void between the PS core and the polysiloxane shell (Fig. 3) also indicated that there is few chemical affinity between the core and the shell. Why the core/shell particles are formed and not two generations of different particles (polystyrene seeds and homo-polymethylsiloxane particles)? A reasonable assumption may be that the residual stabilizer polyvinylpyrrolidone (PVP) in the PS seed particles can form hydrogen bond with the hydroxyl groups of silanols in the polycondesation process. It is generally believed that the effect of stabilizer PVP in a dispersion polymerization results from some strong interactions, either chemical or physical, between the PVP molecules and the polymers that are being prepared. The in situ formation of PVP-graft-polymer chains during the polymerization is a widely accepted mechanism. El-aasser et al. has reported that the characteristic IR absorbance of PVP could still be observed in PMMA particles that had been repeatedly washed with water [25]. The ^{1}H NMR spectrum of the dried PS seed particles is shown in Fig. 4. The characteristic peaks of the protons in the –N–CH_2– group in PVP (δ=3.2 ppm) in spectrum show that there is still a small amount of PVP in the PS seed even after repeated washing and drying process. So it is presumed that the success of the seeded growth process in our system may be due to the hydrogen bond between PVP and the silanols and the polycondensation of silanols would be, thus, promoted by a high local silanols concentration on the surface of the PS seeds. However, further work should be done to clarify the mechanism of the formation of the special PS/polysiloxane core/shell particles.

Solvent resistance

To observe the solvent resistance of the core/shell particles, SS3-1 particles were dispersed in many solvents, such as toluene, acetone, chloroform, tetrahydrofuran (THF), and *N*,*N*-dimethylformamide, for 24 h at room temperature and the resistance of SS3-1 for these solvents was monitored. Generally, linear PS particles are easily dissolved in organic solvents such as toluene, chloroform, and THF, etc. However, cross-linked polysiloxane shells were hardly dissolved in organic solvents. Because the condensation of the trimethoxysilyl groups generated siloxane networks around the PS seed particles, the core/shell particles can keep their original spherical shapes in these organic solvents.

TEM photo in Fig. 5 was taken after SS3-1 particles were extracted with chloroform for 48 h with Soxhlet extractor under refluence. TEM photo certifies that the core/shell particles SS3-1 still were spherical and smooth in shape after extraction. The mass loses of SS3-1 after extraction for 48 h is 27.4%. The result shows that linear PS molecules (M_w=28,045, M_n=10,701) can penetrate the polysiloxane shell gradually.

Thermal stability of the particles

Figure 6 shows the results of thermogravimetric analysis of PS3 seed particles and core/shell particles with different core/shell mass ratio. As one can see, all the core/shell particles exhibited higher thermal decomposition temperature compared to the PS homopolymer. By comparison with a sample of PS3 particles, the large loss of weight at around 350 °C was found to be due to the removal of polystyrene. The smaller loss at about 500 °C is probably due to the removal of residual methyl from the polysiloxane.

Conclusions

Stable core–shell particles consisting of a polystyrene core and a polysiloxane shell were prepared in this paper by the condensation of silanol in the presence of polystyrene seed particles with diameters varying from 2.09 to 5.72 μm. The shell is very smooth and uniform and can be varied in thickness with different feed ratio of the seed particles and methyl trimethoxysilane. When we used PS particles with diameters of 2.09 μm as seeds, the thickness of the polysiloxane shells can be varied from 0.11 to 0.21 μm. The core/shell particles have nearly the same size distribution as the PS seed particles. The core/shell particles have good solvent resistance and good thermal stability.

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