Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 46 (2005) 7598–7604
polymer
www.elsevier.com/locate/polymer

Polystyrene/melamine-formaldehyde hollow microsphere composite by self-assembling of latex particles at emulsion droplet interface

Xiaodong He, Xuewu W. Ge*, Mozhen Wang, Zhicheng Zhang

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Received 27 March 2005; received in revised form 31 May 2005; accepted 11 June 2005
Available online 6 July 2005

Abstract

Submicron scale particle aggregates with defined shape were prepared by self-assembling of sulphonated polystyrene latex particles at the interface of emulsion droplets. Several parameters were considered during the preparation, including the sulphonation time of the polystyrene latex particles, the composition of the oil phase, and the zeta potential of the sulphonated latex particle. To further improve the mechanical stability of the particle aggregates, a hard composite layer was formed by addition of melamine-formaldehyde (MF) prepolymer into the emulsion. The prepolymer was crosslinked onto the particles surface of sulphonated PS particle aggregates. The crosslinking reaction was catalysed by the acidity of sulfogroup. After evaporating off solvent, PS/MF hollow microsphere composites were obtained as mechanically stable dry material. The hollow microsphere composite was characterized by TGA, FTIR, optical microscopy, scanning and transmission electron microscopy.

Keywords: Hollow microsphere composite; Latex particles self-assembly; Emulsion droplet interface

1. Introduction

The development of fabrication methods for advanced colloid materials is an important area in science and technology. The synthesis of hollow spheres in the nanometer to millimeter range has attracted much interest in recent years due to a wide variety of applications ranging from light weight composites encapsulation for controlled release systems and drug delivery to catalytic applications by incorporation of catalyst materials inside the hollow spheres or the capsule wall [1–3].

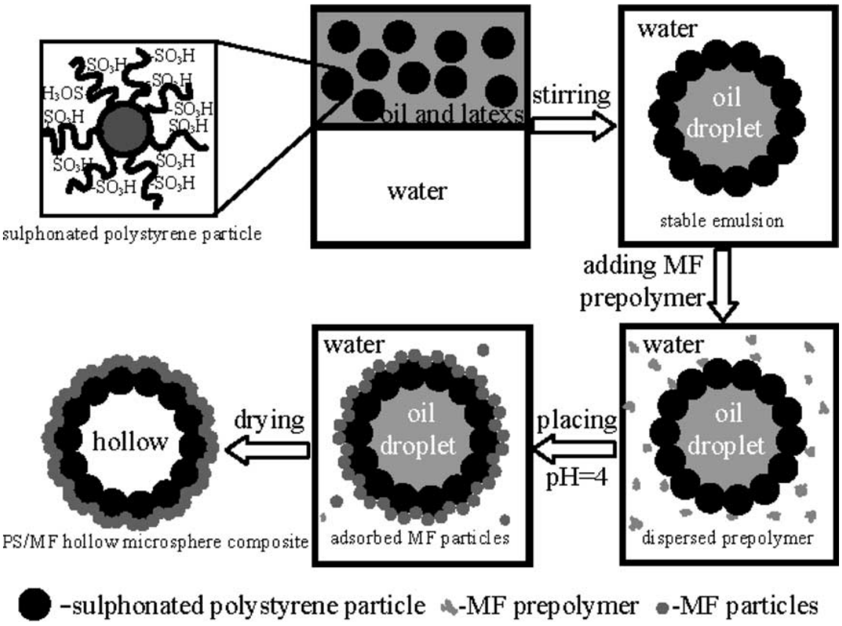
A variety of techniques have been developed to fabricate hollow particles. The water-in-oil-in-water emulsion polymerization [4], the layer-by-layer technique [5], and vesicles method [6]. Especially, the micelles of self-assembled block copolymer has been researched and used to prepare hollow particles [7–9]. However, despite the enormous progress in encapsulation technologies, these methods are often limited in their applicability, in the range of materials that can be used, in the uniformity of hollow sizes, or in the ease of synthesis and yield. A feasible and versatile technique should provide efficient encapsulation structures whose size, mechanical strength, and compatibility can be easily controlled. Ideally, it should be feasible to construct these capsules from a wide variety of inorganic, organic, or polymeric materials to provide flexibility in their uses. Recently, there has been increased interest in using self-assembled colloids at emulsion droplet interface to form microcapsules for controlled delivery applications [10–15]. In this method, emulsion droplets are used as 3D colloidal 'templates' whose size and shape determine the morphology of the obtained particle aggregates. The capsule surfaces are composed of a close-packed layer of colloidal particles, linked together to form a solid shell. After the particles are self-assembled and fixed, the emulsion droplets are dissolved and the particle aggregates are extracted as a colloid suspension. This method presents a flexible approach for the preparation of hollow and elastic capsules of different types of colloid particles, with sizes ranging from micrometers to millimeters and with easily adjustable and controlled permeability and elasticity.

Following these studies, methods were further developed

---

* Corresponding author. Tel.: +86 551 360 1586; fax: +86 551 532 0512.
E-mail address: xwge@ustc.edu.cn (X.W. Ge).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.06.015



Scheme 1. Schematic representation of the preparation procedure of PS/MF hollow microspheres composite.

to improve the mechanical stability of the particle aggregates. One way of doing so is to fabricate aggregates with more than one colloid component–composite aggregate. The composites usually incorporate a combination of metallic/organic [16], oxide/organic [17–20], or two types of organic particles [16]. The emulsion droplets provide an environment for the assembling of composite aggregates from different types of colloid species, when a second type of colloid particles is adsorbed on the out layer surface of the particle aggregates. This may be regarded as a variation of the layer-by-layer adsorption process [5,21]. The electrostatic attraction between the underlying oppositely charged aggregate layers leads to a compact and mechanically stable composite aggregate. Velev et al. have described such an example of using latex particle-packed-droplets as a core for the fabrication of composite aggregates [11]. Two different types of composite assemblies, one with a full core and one with a hollow core, were prepared. However, the thickness of the composite shells was nonuniform, and the shapes of the composite aggregates were uneven, especially for the hollow core sample.

In this study, we report the preparation of PS/MF hollow microsphere composite by the self-assembling of PS latex particles at the emulsion droplet interface. The preparation procedure is shown in Scheme 1. The polystyrene latex particles were sulphonated to increase hydrophilicity of the particles surface so that the modified particles can be stabilized at the oil–water interface. The influential factors that control the self-assembly of the latex particles at the emulsion droplet interface were studied. In order to improve the mechanically stability and composite properties, MF prepolymer was added into the emulsion and its crosslinking reaction was catalysed by the sulfogroup. The crosslinked product spontaneously shrinks into conglobation. Because of their weak positive charges, the so-formed MF particles will be adsorbed and fixed on the surface of sulphonated PS particle aggregates. As a result, PS/MF composite shell was formed with uniform thickness, and the shape of the composite aggregates is spherical. The composite aggregates can be conserved for long period of time in aqueous solution without any change of their physical and chemical properties. After removing the oil cores, hollow microsphere composites were obtained as mechanically stable dry materials.

2. Experimental

2.1. Materials

Styrene (St) monomer was purified by vacuum distillation before used. The 1-octanol, toluene, concentrated sulfuric acid, ethyl alcohol, polyvinylpolypyrrolidone, melamine, and formaldehyde were used as received.

2.2. Preparation of sulphonated polystyrene latex particles

Monodispersed polystyrene (PS) particle powder of 560 nm in diameter was prepared by dispersion polymerization as described elsewhere [22]. The polystyrene particles were sulphonated in concentrated sulfuric acid at 40 °C. The degree of sulphonation could be controlled by the reaction time. After diluting, the sample was repeatedly centrifuged and washed with ethanol–water, then dried in vacuum.

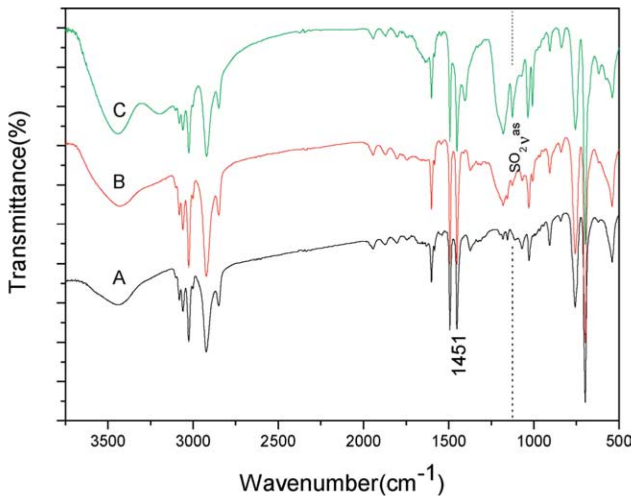


Fig. 1. FTIR spectra of sulphonated PS particles after different sulphonation time: *A* (0 h), *B* (8 h) and *C* (30 h).

2.3. Preparation of melamine-formaldehyde prepolymer dispersate

Two gram of melamine and formaldehyde (1/3 mol/mol) mixture was stirred continuously with magnetic agitator at 60 °C for 20 min, then was transferred into 2 kg deionized water under stirring at 60 °C for 7 min. The product was used immediately in the following synthesis.

2.4. Typical preparation procedure for hollow microsphere composite

The process is divided into two steps. The first step is an interfacial assembly of sulphonated polystyrene particles: 0.05 g sulphonated PS latex particles were first added into 2.5 ml oil phase (toluene/octanol 90/10 v/v). The mixture was briefly homogenized to form a transparent solution. Then 7.5 ml deionized water was introduced and stirring was continued by using lower shear. The mixture changed from turbid into creamy-white in appearance gradually. The emulsification took about 5 min to complete.

The second step is the fabrication of PS/MF composite aggregates: 7.5 ml of the 1 g/l MF prepolymer was added to 17.5 ml of above step emulsion under slow stirring. This mixture was placed at room temperature for 60 min with occasional shaking and then centrifuged for 30 min at 1000 rpm to separate the composite aggregates from the solution. The composites were collected and redispersed in 25 ml deionized water, then centrifuged again. The final products were dried in a vacuum at 25 °C for 24 h to obtain the hollow microsphere composite.

Table 1
Stability of the emulsions stabilized by PS latex particles with different sulphonation time at 25 °C (conductivity $\kappa = 185$ µS/cm for 2 wt% aqueous latex and pH = 4)

Sulphonation time (h)	FTIR	
	I_{1126}/I_{1451}	Emulsion stability after 24 h
1	0.00207	100% Coalescence
3	0.00386	30% Coalescence; cream
5	0.00552	9% Coalescence; cream
7	0.00693	5% Coalescence; cream
9	0.00801	Creaming only
11	0.00993	Creaming only
15	0.01537	Creaming only

2.5. Characterization

The obtained emulsions were examined by optical microscopy equipped with a high-resolution digital CCD camera in transmitted illumination. The morphology and size of the assembled microspheres were observed by a Nicolet SEM X-65 scanning electron microscopy (SEM) and a Hitachi Model H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 keV. Fourier transform infrared (FTIR) spectroscopy was carried out on a Bruker Vector-22 FTIR spectrometer using a KBr pellet. Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50H instrument under a stream of nitrogen. The sample was heated at 10 °C/min from 20 to 600 °C. The measurements of electrophoretic mobility were carried out using a Zetasizer Nano ZS ζ-potential analyzer. The ζ-potentials are calculated from the obtained electrophoretic mobility by using the Smoluchowski equation. At least 10 repeats were counted in each measurement.

3. Results and discussion

3.1. Effect of sulphonation time on emulsions stability

The polystyrene latex particles in their original state cannot be adsorbed at the oil–water interface. Therefore, it is necessary to modify their surface properties (i.e. electrostatic charge and hydrophilicity). The ideal modification of the latex surfaces should not cause the flocculation of the particles in the suspension and 2D coagulation after the particles were adsorbed to the interface. Furthermore, emulsion type (O/W, or W/O), preferred drop sizes, and emulsion stability (with respect to creaming, sedimentation and coalescence) were all crucially depend on the hydrophilicity of the particles [23].

The hydrophilicity and electrostatic charge of the PS particles surface can be modified by sulphonation. The FTIR spectra of two representative sulphonated PS particles and PS particles are shown in Fig. 1. The spectra of both B and C reveal well-defined characteristic bands (3060, 3026, 2924, 2850 cm^{-1}, and 1601, 1492, 1451 cm^{-1}) of styrene unit. The characteristic peaks at 1126 and 1039 cm^{-1} are

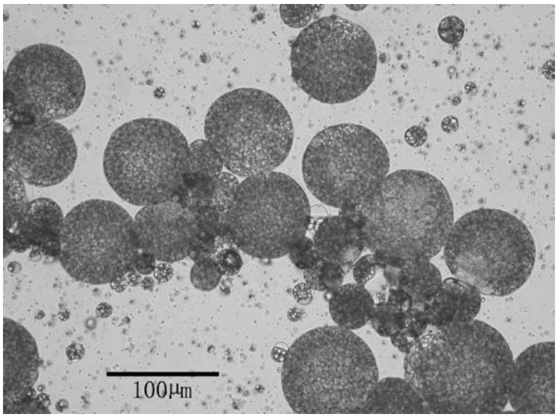


Fig. 2. Optical microscopy image of self-assembled oil-in-water emulsion stabilized by sulphonated PS latex particles for 30 h.

attributed to SO_3H groups [24]. With prolonged sulphonation time, the intensity ratio of the vibration band (peak area integral) at 1126 cm^{-1} to that at 1451 cm^{-1} (I_{1126}/I_{1451}) increased from 0.00751 to 0.04306, suggesting that more SO_3H groups were incorporated into PS.

During the emulsification process, oil droplets were gradually covered with sulphonated PS latex particles. The stability of the emulsions stabilized by PS latex particles with different sulphonation time is summarized in Table 1. Emulsion stability at 25 °C was assessed in graduated vessels by monitoring the movement of the oil–emulsion and emulsion–water interfaces with time.

Clearly, minimum sulphonation time was required for a stable emulsion. When sulphonation time exceeded 9 h, all the emulsions were completely stable to coalescence. Typically, 2 wt% of the sulphonated PS particle was sufficient to produce emulsions.

An emulsion sample stabilized by sulphonated PS latex particles for 30 h was shown in Fig. 2. The colours of the latex particles packed-droplets changed from light color into black. This indicates that a close-packed layer of sulphonated PS latex particles was formed on the surface of the oil droplets. The size of packed-droplets was polydisperse and typically ranged from 10 to 100 μm in diameter.

Table 2
ζ-Potentials of the 30 h sulphonated PS latex particles during neutralizing at 25 °C (0.4 wt% aqueous latex and conductivity $\kappa = 5$ μS/cm)

pH	4	5	6
ζ-Potential (mV)	−26.0	−30.3	−36.8

3.2. *Effect of sulphogroup on the self-assembly of sulphonated PS latex particle*

To assemble latex particles at emulsion droplet interface, the reportorial methods were typically done via a complex multi-step process [10–12]. The particles need to be sensitized and the surface charge need to be carefully adjusted to meet the conditions for adsorption. However, for the sulphonated PS latex particle, further modification steps are not requisite for the self-assembly. Here, the sulphogroup plays a key role in the self-assembling. When SO_3H group was neutralized, the latex particles are no longer packed closely on the droplets surface and emulsion becomes unstable. The earlier experiments conducted by Croll et al. indicated that the presence of some succinic acid groups on the surface of cross-linked poly (divinylbenzene-*alt*-maleic anhydride) microspheres could facilitate the self-assembly process at interface [13]. When the sulphonated PS latex particle appeared at the oil–water interface, ionization of the surface SO_3H groups would form the electric double layer around the particles surfaces, and the SO_3H groups will orient toward water phase. Comparatively, the SO_3H group brings lesser charge (ζ-potential = −26 mV and pH = 4, Table 2) to the particle surface. When the sulfogroups was neutralized, the particle surface charge increased, which lead to a strong electrostatic repulsion between the particles. As a result, the self-assembly of the latex particles became unstable.

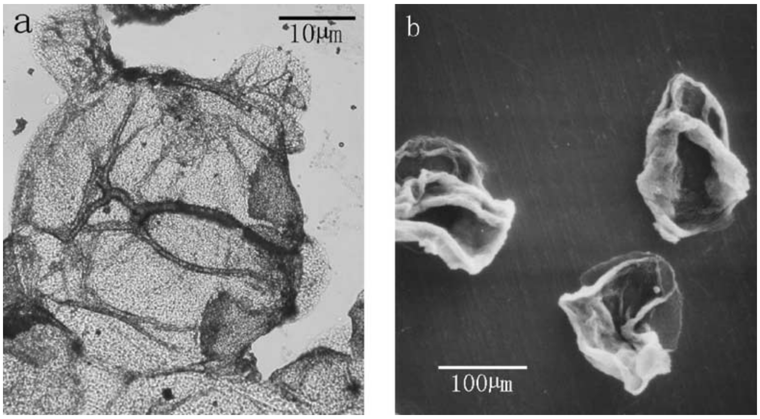


Fig. 3. Optical microscopy image (a) and scanning electron micrograph (b) of the self-assembled polystyrene particle aggregates after drying (PS particles were sulphonated for 30 h).

Table 3
Adsorption of the latex particles on the droplet interfaces with different oil phase composition at 25 °C (conductivity $\kappa = 185$ μS/cm for 2 wt% aqueous latex and pH = 4)

	Toluene/octanol ratio (v/v)					
	5/0	4/1	3/2	2/3	1/4	0/5
Hildebrand δ (MPa$^{1/2}$)	18.20	18.01	17.83	17.64	17.46	17.27
Particles adsorption	○	●	●	▣	○	○

○, No adsorption; ▣, poor adsorption; ●, compact adsorption.

3.3. Effect of the oil phase composition

The oil phase composition also affect self-assembly of latex particles at droplet interface. It is apt to work when latex particles and emulsion droplets were modified to possess opposite surface charges [11]. In the oil phase, the octanol is negatively charged. So the negative potential of the sulphonated latex particles will be repelled from the oil phase. The SO_3H groups make the particle surface becoming hydrophilic and attracted by the external water phase. Toluene is compatible to hydrophobic polystyrene particles and holds particles in oil phase. When the SO_3H groups content remains constant, adjusting toluene/octanol ratio of the oil phase can balance the opposite forces and control the sulphonated PS particles assembling at the oil–water interface.

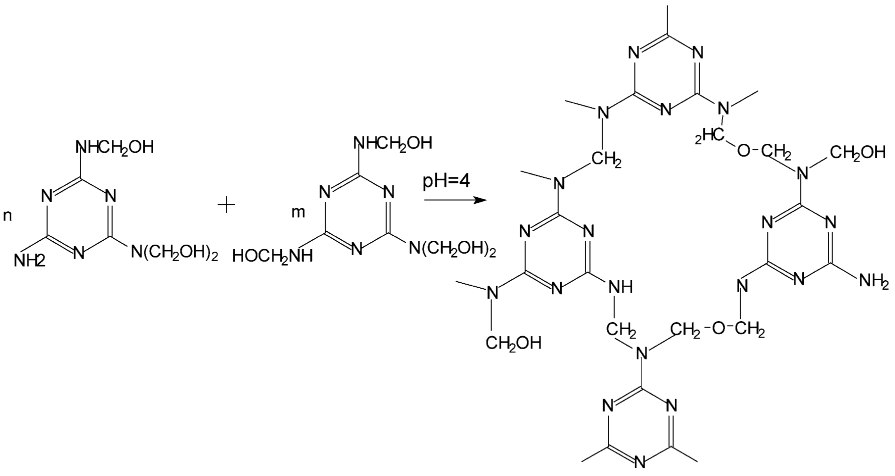
For polystyrene latex particles sulphonated for 30 h, the effect of the oil phase composition on the adsorption of the particles at the droplet interfaces was summarized in Table 3. By adding octanol into the system, the solubility parameter δ decreases, which means the change of compatibility of oil phase to PS particles, and the negative potential of oil phase increases. Initially, the particles pack-density increases with decreasing toluene/octanol ratio. However, when the ratio exceeds a certain value, particles became loosely adsorbed at the interface and unstable emulsions were obtained again. The appropriate toluene/octanol ratio for a stable emulsion is 4/1–2/3 (v/v) and the solubility paramater δ is around 18.0–17.6 MPa$^{1/2}$.

3.4. Characterization of PS/MF composite aggregates

When the sulphonated PS latex particle-stabilized emulsion was dried, collapsed capsule with a continuous shell of conglutinative latex particles were observed from optical microscopy and SEM (Fig. 3). The conglutination of latex particles is because of swelling of PS monomer chain by toluene. The result indicates that the self-assembly of the sulphonated PS latex particles at the emulsion droplets interface is insufficient to maintain the initial spherical structure after the removal of the oil phase.

In order to improve the mechanical stability and composite properties, a MF composite layer was added onto the surface of PS particle aggregates. In the MF prepolymer, the amidogen hydrogens of melamine monomer were partially or completely displaced by methylol. Through polycondensation reaction at acidic condition between methylols or between methylol and amidogen or imine group, the prepolymer was crosslinked either by ether linkage or methylene as shown in Scheme 2. The product spontaneously shrinks into conglobation. Because the molecular chain ends contain amidogen and imine group that will ionize to possess weak positive charges in aqueous solution, the crosslinked MF particles were expected to adsorbed and fixed on the surface of negatively charged sulphonated PS particle aggregates.

The FTIR spectra of sulphonated PS particles, MF prepolymer and PS/MF composite aggregates are shown in Fig. 4. The spectra of MF prepolymer revealed strong



Scheme 2. Schematic crosslinking reaction of MF prepolymer.

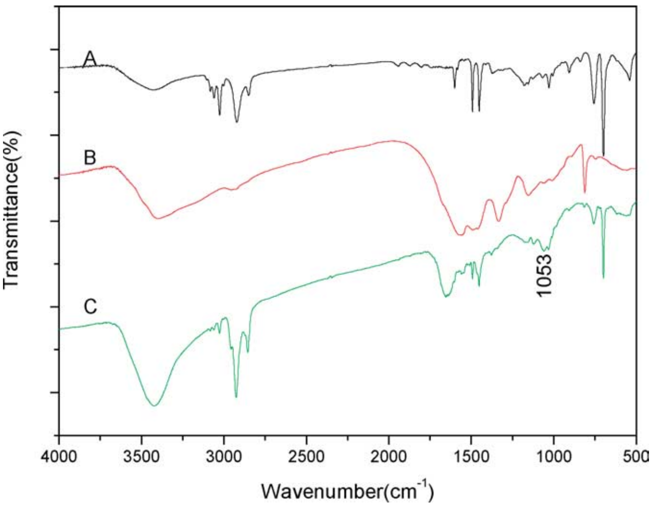


Fig. 4. FTIR spectra of sulphonated PS particles (A), MF prepolymer (B) and PS/MF composite aggregates (C).

vibration bands of amidogen at 1560, 1334 and 1153 cm^{-1} and methylol at 1010 cm^{-1}. The spectra of PS/MF composite aggregates not only revealed well-defined characteristics of MF but also showed the characteristic bands of the sulphonated PS unit. The appearance of ether linkage peak at 1053 cm^{-1} implied the polycondensation reaction of the MF prepolymer.

After placing in air for 24 h, the sulphonated PS particle aggregates and PS/MF composite aggregates were investigated by TGA in nitrogen atmosphere (Fig. 5). For both samples, the mass loss at temperature below 100 °C was due to the evaporation of adsorbed water and the mass loss between 100 and 200 °C was attributed essentially to the evaporation of the toluene and octanol. The two samples showed a mass loss of approximately 50–60% in this range. For the sulphonated PS particle aggregates (curve A), the steep mass loss between 320 and 450 °C was attributed to the decomposition and evaporation of the PS latex particles. However, for the PS/MF composite aggregates, besides a mass loss of 23.7% between 320 and 450 °C, a new mass loss of 4.15% between 224 and 320 °C was observed and maximal mass loss rate was found at 284 °C as indicated by the DrTGA curve (Fig. 5). This mass loss was attributed to the decomposition and evaporation of the MF polycondensate. Although having partial overlapping of decomposing region, it could still be estimated that the mass ratio of MF polycondensate and PS particles in the composite aggregates is about 1/6 (wt/wt).

Once the PS/MF composite aggregates formed, they could be concentrated and purified by centrifugation. The mechanical stability of the composite shells improved dramatically, as revealed from the SEM analysis of the dry material (Fig. 6(a)). The electrostatic attraction between the underlying oppositely charged layers gives the composite shells compactness and mechanical stability. The shell structure was found to be approximately continuous. The composite aggregates maintained effectively the initial hollow spherical structure after the removal of the oil cores. Furthermore, the hollow spherical structure was confirmed by the TEM analysis as shown in Fig. 6(b). The composite shell has an uniform thickness of around 1.2 μm. Interestingly, most hollow microspheres have a pore as shown in SEM and TEM. It was found from experiments that solvent evaporation rate has significant effects on the pore formation. Pore exists at quick evaporation rate and disappears at slow evaporation rate.

Compared to the reportorial materials and methods, the self-assembling of sulphonated polystyrene latex particles at emulsion droplet interface is much more facile and convenient to conduct. The sulphonation of PS latex particles not only improves hydrophilicity of particles surface but also brings lesser charge to the particle surface. Instead of adding oppositely charged latex particles directly to prepare composite aggregates, we added MF prepolymer into the system. As a result, composite aggregates with uniform shell thickness and spherical morphology were obtained.

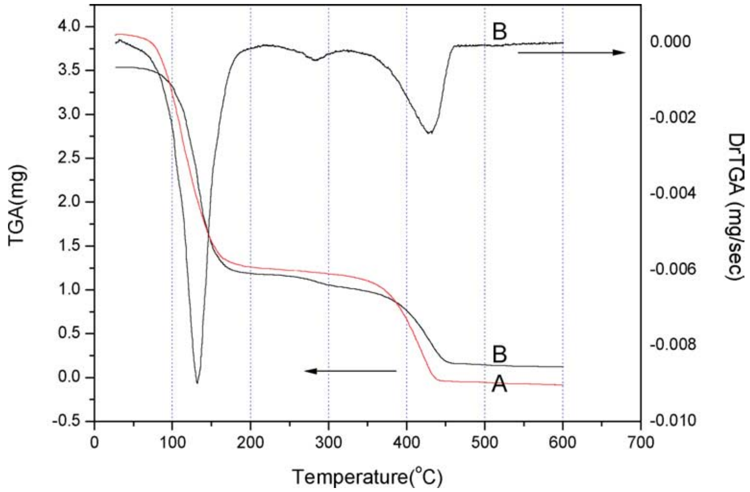


Fig. 5. TGA curves of the sulphonated polystyrene particle aggregates (A) and the PS/MF composite aggregates (B).

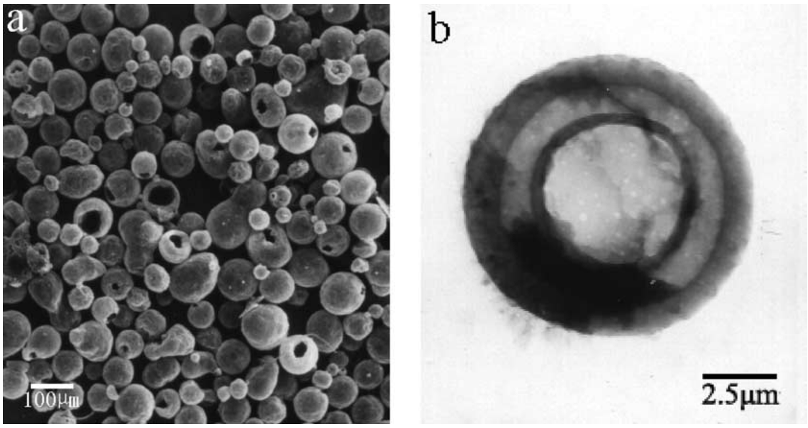


Fig. 6. SEM (a) and TEM (b) of the PS/MF hollow microsphere composite.

4. Conclusions

We have prepared the polystyrene hollow spheres successfully by self-assembling of sulphonated polystyrene latex particles at an oil-in-water droplet interface. A closely packed layer was formed at the droplet interface by selecting appropriate sulphonation time for PS latex particles and by controlling the composition ratio of the oil phase. The MF composite layer was used to keep the primal morphology of the PS particle aggregates after drying. In general, this research provides a novel and effective method to fix particle aggregates. The effect of the composite layer on the ordering of the underlying PS particle aggregates will be further examined in our future study.

Acknowledgements

The authors thank Natural Science Foundation of Anhui Province for financial support (No: 01044804 03044803).

References

[1] Wilcox Sr DL, Berg M, Bernat T, Kellerman D, Cochran Jr JK, editors. Hollow and solid spheres and microspheres: Science and technology associated with their fabrication and application. MRS proceedings, vol. 372. Pittsburgh: Materials Research Society; 1995 [Part A].

[2] Yin Y, Lu Y, Gates B, Xia Y. Chem Mater 2001;13:1146.

[3] Aoi Y, Kambayashi H, Kamijo E, Deki S. J Mater Res 2003;18:2832.

[4] Kim JW, Joe YG, Suh KD. Colloid Polym Sci 1999;277:252.

[5] Frank C, Marina S, Andrei S, Michael G, Rachel AC. Chem Mater 2001;13:109.

[6] McKelvey CA, Kaler EW, Zasadzinski JA, Coldren B, Jung HT. Langmuir 2000;16:8285.

[7] Yao J, Ravi P, Tam KC, Gan LH. Polymer 2004;45:2781.

[8] Park C, Yoon J, Thomas EL. Polymer 2003;44:6725.

[9] Thurmond KB, Huang H, Clark Jr CG, Kowalewski T, Wooley KL. Colloid Surf B: Biointerf 1999;16:45.

[10] Velev OD, Furusawa K, Nagayama K. Langmuir 1996;12:2374.

[11] Velev OD, Furusawa K, Nagayama K. Langmuir 1996;12:2385.

[12] Velev OD, Nagayama K. Langmuir 1997;13:1856.

[13] Croll LM, Stöver HDH. Langmuir 2003;19:10077.

[14] Mouaziz H, Lacki K, Larsson A, Sherrington DC. J Mater Chem 2004;14:2421.

[15] Dinsmore AD, Hsu MF, Nikolaides MG, Marquez M, Bausch AR, Weitz1 DA. Science 2002;298:1006.

[16] Honda H, Koishi M. In: Koishi M, editor. Construction of very small particles. Tokyo: Kogyo Chosakai Publishing Co; 1987. p. 127–203.

[17] Kawahashi N, Matijevic EJ. Colloid Interf Sci 1990;138:534.

[18] (a) Furusawa K, Nagashima K, Anzai C. Colloid Polym Sci 1994;272:1104.
(b) Furusawa K, Anzai C. Colloid Surf 1992;63:103.

[19] Honda H, Kimura M, Honda F, Matsuno T, Koishi M. Colloid Surf A 1994;82:117.

[20] Otsubo Y, Kazuya E. J Colloid Interf Sci 1994;168:230.

[21] Frank CA, Rachel C, Helmuth M. Chem Mater 1999;11:3309.

[22] Xu XL, Zhang ZC, Zhang MW. J Dispersion Sci Technol 1999;20:1647.

[23] Binks BP, Lumsdon SO. Langmuir 2001;17:4540.

[24] Xing XY, Cheng SL, Yao SY. Practical manual of infrared spectrum. Tianjin: Science and Technology Press; 1992. p. 294–7.