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A review of recent progress in preparation of hollow polymer microspheres

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Abstract: The preparation methods of hollow polymer microspheres both at home and abroad are summarized, and their preparation mechanisms and developmental states are presented. These methods include the liquid droplet method, dried-gel droplet method, self-assembly method, microencapsulation method, emulsion polymerization method and the template method. Hollow polystyrene microspheres are the most extensively studied in the research of hollow polymer microspheres. Through comparison of the advantages and disadvantages of different preparation methods, it is concluded that microencapsulation method is most suitable for preparing polystyrene hollow microspheres.

Key words: Preparation methods, hollow polymer microspheres, preparation mechanism, polystyrene hollow microspheres, microencapsulation method

1 Introduction

With the characteristics of low density, optical scattering, high specific surface area, good heat-insulation and large useful inner spaces, hollow polymer microspheres have attracted more attentions (Dong et al, 2003). Hollow polymer microspheres are widely applied to inertial confinement fusion (ICF) targets, light weight fillers, high-performance opacifying coating, anti-ultraviolet filler, high quality insulating material, damping material, cosmetics, microcapsule and artificial cells and etc. (Tsuji and Ogushi, 1997; Yuan et al, 2006; Lin et al, 2004; Liang et al, 2003). Organic-inorganic composite hollow microspheres with a noble metal core are one type of catalyst being developed for the oil refining industry (Kim et al, 2002; Lin et al, 2004). A mixture of hollow glass microspheres and hollow polymer microspheres can be used as light weight fillers of cement slurry for oil and gas well (Wang et al, 2005). Hollow phenolic resin microspheres are used as an adsorbent for separating petroleum and petroleum products, and a heat insulation coating material for aerospace. In addition, they can also be used as a filler for oil and gas drilling mud (Li, 2006). Hollow polymer microspheres with different shell materials have their own applications. Many strategies have been reported for preparing hollow microspheres, such as the liquid droplet, dried-gel droplet and the self-assembly methods (Du and You, 1999; Liang et al, 2003). Many kinds of polymer materials, such as polystyrene (Zhang et al, 1999) and polydivinylbenzene (Okubo and Minami, 1997), have been successfully used to prepare hollow microspheres. By summarizing the recent progress in preparation of hollow polymer microspheres by different methods, this paper is aimed at comparing the advantages and disadvantages of different methods for preparing polystyrene hollow microspheres and intending to find the most suitable method.

2 Liquid droplet method

The liquid droplet method is one of the most widely-used methods to prepare hollow polymer microspheres (Zhang et al, 1999). The technological process is that when the droplets fall in the 4-5 m height vertical furnace with multi-temperature zones, the volatile organic solvent which has dissolved polymer evaporates, and hollow polymer microspheres are formed (Du and You, 1999). The advantages of the liquid droplet method are: 1) the diameter and wall thickness of the hollow polymer microspheres are of centralized distribution and are easy to regulate and control; 2) the sphericity and concentricity are high; 3) the spherical shell is compact and bubble-free. The disadvantage of the method is that the equipment and operation costs are high and the diameter of microspheres is relatively small (Qiu and Fu, 2002). The process for preparing polystyrene (PS) hollow microspheres by the liquid droplet method is shown in Fig. 1 (Du and You, 1999).

The process of preparing PS hollow microspheres is as follows: When the PS droplets fall into the high-temperature tube (approximately 200 °C) of the multi-temperature zones of the vertical furnace, the droplets firstly shrink due to the evaporation of the volatile organic solvent. With the gradual evaporation of the solvent, the concentration of PS on the

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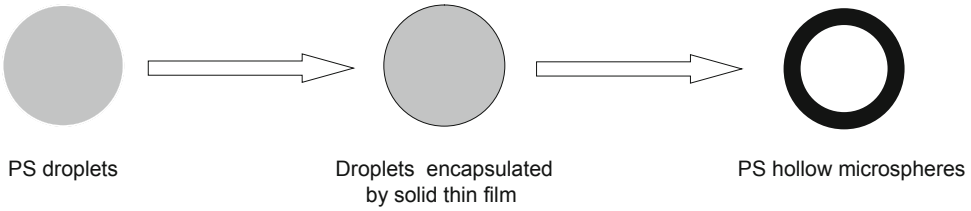

Fig. 1 Schematic representation of liquid droplet method for preparing PS hollow microspheres

droplets' surface increases. Then a thin solid film is formed on the surface of the droplets, evaporation is restricted and the temperature of the droplets begins to rise. When the droplets' temperature is higher than the boiling point of the organic solvent, bubbles begin to form in the droplets, and the spherical shell begins to expand rapidly. Finally PS hollow microspheres are obtained when the expanded droplets fall into the low-temperature zone of the vertical furnace (Qiu and Fu, 2002; Du and You, 1999).

3 Dried-gel droplet method

The dried-gel droplet method, which was firstly developed by Dorogotovstev and Akunets (1997), can be used for batch production of large diameter hollow microspheres (Wilkox et al, 1995), compared with the liquid droplet method. However, the costs of equipment and operation are high (Qiu and Fu, 2002). This method is mainly used to prepare PS hollow microspheres.

Both the liquid droplet method and dried-gel droplet method are conducted in the furnace tube. The difference is that the dried-gel droplet method uses the raw material of solid PS microspheres with a mass of several hundred micrograms. Before the experiment, 5-l0 wt% foamer is added to the solid PS microspheres. The dried-gel droplet furnace is a closed system filled with 2-10 kPa gas mixture of He and Ar, and its temperature is controlled at around 1000 °C. The quality of the PS hollow microspheres is good if the temperature of the PS microspheres is at 500-700 °C (Du and You, 1999).

The PS hollow microspheres with a diameter of 400-900 μm, wall thickness of 2-l0 μm and concentricity more than 95% are prepared with the dried-gel droplet method, and the process is shown in Fig. 2 (Wei et al, 2000).

The influence of the composition of He and Ar gas mixture in the dried-gel droplet furnace on the yield and quality of the PS hollow microspheres was investigated by Dorogotovtsev and Akunets (1997). The results show that with increasing of n_{He}:n_{Ar}, the yield of PS hollow microspheres increases. However, if the ratio of He is too high, the proportion cracked and deformed microspheres will increase. It is ascertained that the favorable ratio of n_{He}:n_{Ar} is 2:1, at which the yield and concentricity of PS hollow microspheres are both relatively high.

4 Self-assembly method

The amphipathic chain segments of the block copolymer can self-assemble into various shapes of micelles, such as spherical micelles, rod-like micelles and vesicle-like micelles, in the selective solvent. Self-assembly method makes use of vesicle-like or spherical micelles to prepare the stable hollow-structural microspheres by shell crosslinking reactions and then removal of their core (Liang et al, 2003).

Liang and his coworkers (2003) prepared hollow nanospheres by the self-assembly of block copolymer. First, polyisoprene-block-poly (2-cinnamoylethyl methacrylate) (PI-b-PCEMA) is used to self-assemble into vesicle-like micelles with a diameter of 38 nm in the selective solvent. Then, the micelles are induced by ultraviolet to make the PCEMA shell by crosslinking and ozone is used to oxidize and degrade the PI chain segments. Finally stable hydrophilic

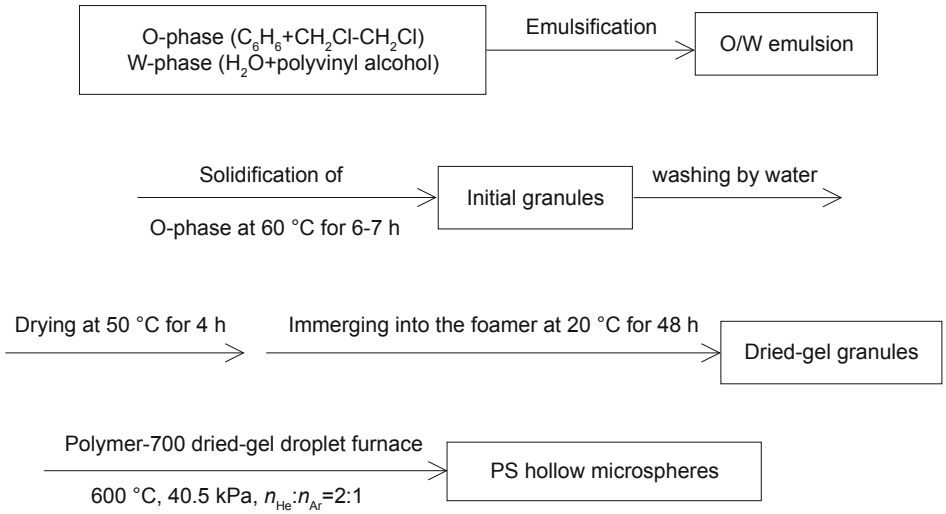

Fig. 2 Preparation of PS hollow microspheres with the dried-gel droplet method

and crosslinked hollow nanospheres are obtained. The process is shown in Fig. 3 (Liang et al, 2003).

Huang and his coworkers (1999) prepared the hollow microspheres by using block copolymer poly (isoprene-b-acrylic acid) in aqueous solution. The block copolymer self-assembles to form micelles, and then forms amphipathic crosslinked nano-microspheres via shell condensation of the micelles by using the polyacrylamide crosslinker. Then the core of polyisoprene is oxidized and degraded by ozone to obtain the hollow microspheres.

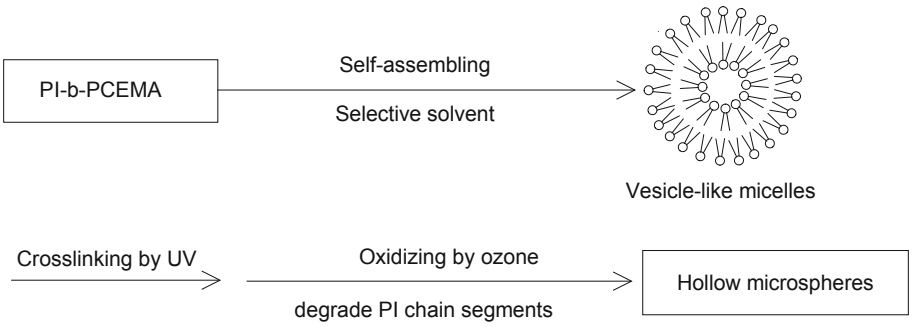

Fig. 3 Schematic diagram for preparing hollow nanospheres by self-assembly of block copolymer

He and his coworkers (2005) prepared hollow PS/melamine-formaldehyde (MF) composite polymer microspheres with a diameter of 10-100 μm by using PS sulphonate as raw material. The preparation process includes two steps. Firstly, the PS sulphonate particles aggregate on their surface. Secondly, MF prepolymer is added, and the mixture is stirred and heated, and then hollow PS/MF composite polymer microspheres are obtained.

Hollow microspheres prepared by the self-assembly method are of nanometer scale and their sphericity is high. However, the self-assembly method has strict requirements on the fabricating process. To prevent the polymer micelles from aggregating, the shell crosslinking reaction must be conducted in the micelles solution at very low concentration. This disadvantage restricts the self-assembly method for industrial application (Liang et al, 2003).

5 Microencapsulation method

The microencapsulation method is characterized by simple technology, simple operation and low cost (Zhang et al, 1999).

The following three different phases of solution are used with this method to prepare PS hollow microspheres (You et al, 2000).

W_1-phase: distilled water and surfactant

O-phase: PS and organic solvent

W_2-phase: distilled water and dispersion agent.

The technological process: the W_1-phase is poured into the O-phase while it is being stirred to obtain the W_1/O emulsion, which is then poured into the W2-phase to get the $W_1/O/W_2$ emulsion. Then, the $W_1/O/W_2$ emulsion is stirred at a constant temperature for hours to remove the organic solvent by evaporation. At last the product PS hollow microspheres are filtered, washed, vacuum-dried overnight and then stored at room temperature. The process of preparing PS hollow microspheres by microencapsulation method is shown in Fig. 4 (Zhang et al, 1999; Tsuji and Ogushi, 1997).

By using the raw material, PS, Zhang and his coworkers (1995) prepared PS hollow microspheres with diameters from 100 μm to 300 μm, and wall thickness from 2 μm to 8

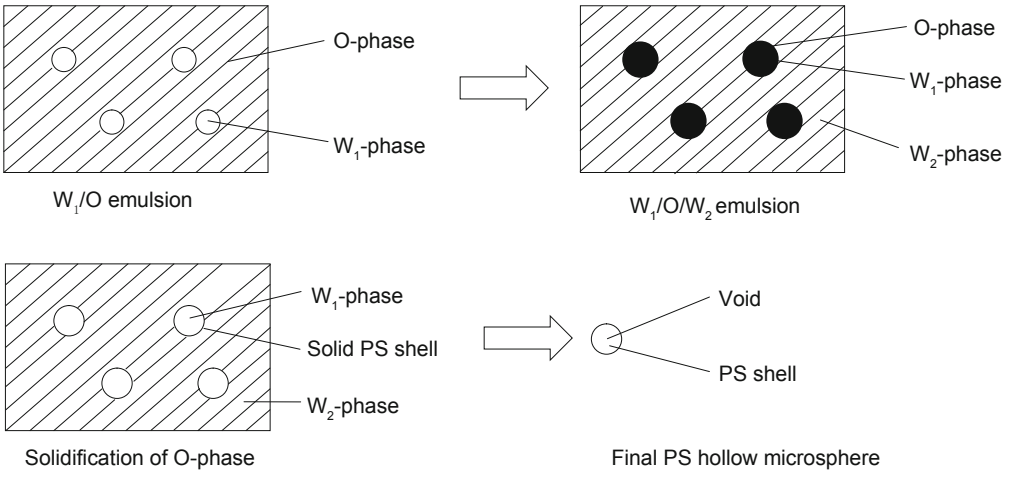

Fig. 4 Schematic diagram of microencapsulation method to prepare PS hollow microspheres

μm with the microencapsulation method. The sphericity and concentricity of the PS hollow microspheres are respectively more than 95% and 90%, and the surface roughness of them is less than 300 nm.

Tsuji and Ogushi (1997) prepared PS hollow microspheres with a diameter of about 520 μm for the inertial confinement fusion (ICF) experiments with the microencapsulation method. These microspheres adsorb high Z microparticles, on their inner surface, which could emit characteristic X-rays. There are two problems with these hollow microspheres prepared by this method. First, the concentricity and sphericity are not high. Second, a large number of small vacuoles on the micrometer scale exist within the shell (Du et al, 1998).

The density-matched microencapsulation technique is used to solve the problem of low sphericity and low concentricity by Takagi el al (1991), Boone (1998) and Zhang (2001). The principle of this technique is selecting an appropriate organic solvent to make the three phases have nearly the same density. If fluorobenzene (Zhang et al, 2001) or a solution of benzene and 1, 2-dichloroethane (1:1 by volume) (Du et al, 1998) were used as the organic solvent, the sphericity and concentricity of the hollow-structural microspheres, prepared by the density-matched technique, are respectively more than 99% and 98%.

The small bubbles inside the shell-wall are restricted by adding an inorganic salt to reduce the saturation vapor pressure of the solution. This reduces the diffusion of water into the oil phase in the W_2-phase (McQuillan et al, 1999). You and his coworkers (2000) selected the inorganic salts NaCl and $CaCl_2$ in the experiments, and proved that the two inorganic salts were able to restrict the formation of bubbles effectively.

Liu and zhang (2005) prepared hollow phenolic resin microspheres from commercial phenolic resin with the microencapsulation method. The following three different phases of solution are used to prepare them.

O_1-phase: pure vegetable oil

W-phase: ethanol solution with phenolic resin and polyethyleneglycol octyl ether (OP-15)

O_2-phase: vegetable oil with sorbitan stearate (Span 60)

The technological process: the O_1-phase is poured into the W-phase and stirred for about 15 minutes to obtain an emulsion. Then the emulsion is dispersed into the O_2-phase and stirred continually and heated to 80 °C to remove the solvent. After that the temperature is raised to 120 °C in order to solidify the phenolic resin. Finally the product hollow phenolic resin microspheres are filtered, washed, vacuum-dried overnight and then stored at room temperature (Liu and Zhang, 2005).

Liu and Zhang (2005) investigated the influences of parameters, such as the content of surfactant, content of O_1 phase in O_1/W latex, temperature of O_2-phase and the solidifying temperature of phenolic resin, on the structure of the hollow phenolic resin microspheres. The result shows that the conditions of the temperature of O_2-phase less than 70 °C, the mass fraction of surfactant of 5%-10%, the mass fraction of O_1-phase in O_1/W latex about 30% and the solidifying temperature of phenolic resin higher than 80 °C will be favorable for the phenolic resin to form and keep the hollow spherical shape.

6 Emulsion polymerization method

The emulsion polymerization method was first studied by Kowalski and his coworkers (1984) who applied for the patent of fabricating hollow polymer microspheres at Rohm & Hass Company. There are two commonly used emulsion polymerization methods.

6.1 Acid/alkali swelling method

The process of preparing hollow microspheres by the acid/alkali swelling method is as follows (Kowalski et al, 1984): Firstly, seed latex with carboxylic acid groups is prepared; Secondly, a hard permeable polymer shell is formed on the outer surfaces of the carboxylic core polymer particles; Thirdly, at around the glass transition temperature (Tg) of the shell, particles containing water and polyelectrolyte are prepared by neutralizing the carboxylic acid groups of the core polymer particles using volatile alkali.

The latex particles with a great number of carboxylic acid groups are first synthesized by several steps, and then neutralized by alkali and swelling. When the latex particles have swollen enough, they are acidified to make the outer layer shrinkage cavity close. Then the aggregated polymers, with an inner layer of polycarboxylate containing water and outer layer of carboxylic acid groups, are obtained. At last, the aggregated polymers are acidified to make the outer of latex particles case-hardened to form the hollow microspheres (Okubo and Mori, 1997; Okubo et al, 1996).

6.2 Dynamic swelling method

The steps of the dynamic swelling method are as follows: PS latex particles are first synthesized by seed polymerization, and then the latex particles are swelled in a toluene and divinylbenzene (DVB) mixed solvent, and the DVB is induced to polymerize. After the polymerization, toluene is removed and hollow microspheres with a polydivinylbenzene (PDVB) shell are formed. The mechanism is that PDVB deposits and accumulates on the surface of the latex particles, causing crosslinking of PDVB, and the soluble PS is gradually extruded into the inside of the latex particles by PDVB. After the polymerization solvent has evaporated, PS deposits on the inner wall of PDVB (Okubo and Minami, 1997).

In order to prove the above experiment, further studies were carried by Okubo and his coworkers (1998) using the method of suspension polymerization to polymerize the PS/DVB/toluene mixture solution in different proportions. They found that the hollow structure was affected by molecular weight and the concentration of PS, indicating that PS plays an important role in the dynamic swelling method.

7 Template method

The preparation steps with the template method are as follows: A polymer shell is formed on the surface of template particles and then the template particle is removed, and hollow polymer shells are obtained (Bai and Fang, 2004).

The template method is often used to prepare hollow polymer microspheres of different materials, and has been proven a very successful method (Li and Zhang, 2004). Its main advantage is the very simple process. The processes of the template method for preparing hollow polymer microspheres includes two steps. First, the polymer shell is formed on the interface between the template and the surrounding continuous phase due to the deposition or reaction of the solute on the surface of the dispersed templates. Second, the hollow structure can be obtained by removing the template materials (Yang et al, 2005; Li et al, 2004; Li et al, 2005). However, in despite of its simple process, the template method is limited because it requires a large amount of template, resulting in high cost. The schematic illustration of preparing hollow structure with the template method is shown in Fig. 5 (Wang et al, 2007).

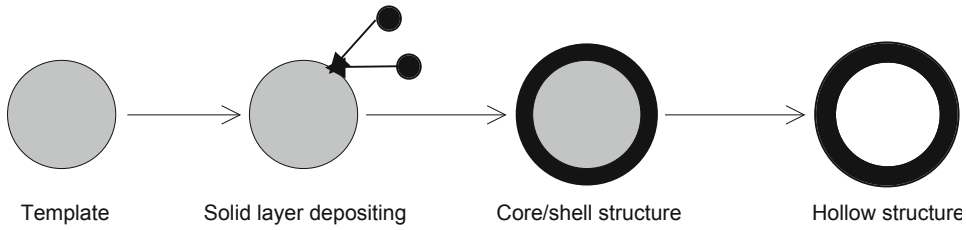

Fig. 5 Schematic illustration of formation process of hollow microspheres structure for template method

According to the synthesis mechanism the template method can be divided into two types: transcriptive synthesis and morphosynthesis (Bai and Fang, 2004).

7.1 Transcriptive synthesis

Transcriptive synthesis mainly refers to layer-by-layer (LBL) assembly technique. LBL is suitable for preparing microspheres with controllable wall thickness. With the LBL technique there many template materials could be used: latex particles of melamine-formaldehyde (MF) resin, erythrocytes, some inorganic salts, PS and poly (styrene-co-maleic anhydride) (PSMA) microspheres (Ding et al, 2006). The schematic illustration for preparing hollow structure microspheres with the LBL technique is shown in Fig. 6 (Sun et al, 2005).

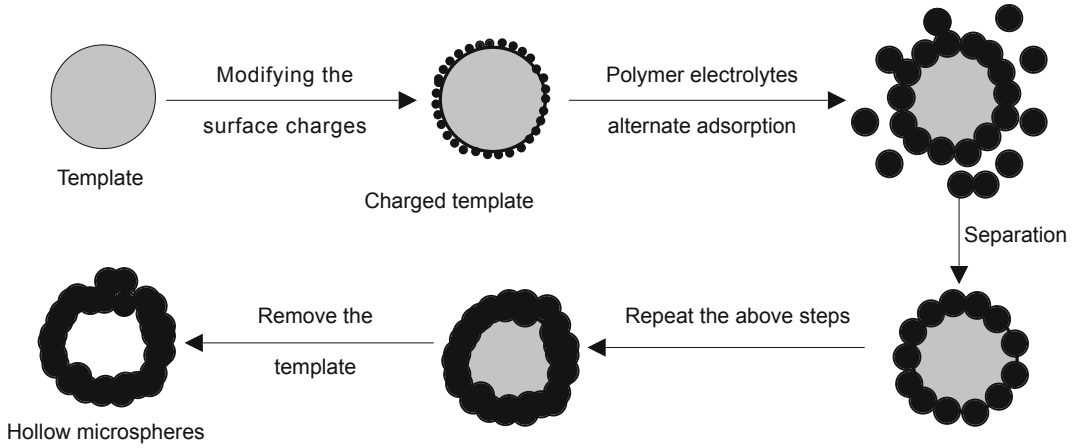

Fig. 6 Schematic representation of LBL for preparing hollow microspheres

A template with charges can be used directly to absorb the charged material, while a template without charges can be used after treatment with polyethyleneimine (PEI) or poly (4-styrenesulfonic acid sodium salt)(PSS). The hollow microspheres prepared by LBL possess uniform shell thickness and good spherical morphology, but this method is relatively complex, so its application is limited (Wang et al, 2007).

7.2 Morphosynthesis

The morphosynthesis method uses bubble capsule micelles shaped by surfactant etc. as template. McKelvey and his coworkers (2000) used cetyltrimethylammonium tosylate (CTAT)/sodium dodecylbenzenesulfonate (SDBS) or cetyltrimethylammonium bromide (CTAB)/sodium octyl sulfate (SOS) surfactants, styrene monomer and divinylbenzene (DVB) crosslinking agent to polymerize to prepare the hollow microspheres with a diameter of 60 nm and a wall thickness less than 10 nm.

PS hollow microspheres were prepared by Jang and Ha (2002) with the morphosynthesis method. They used surfactant of polyoxyethyene-polyoxypropylene-polyoxyethylene-[(EO)x(PO)y(EO)x] as template. The steps are as follows: Methyl methacrylate (MMA) monomer was

added dropwise to the surfactant solution and the solution was heated to 70 °C. Then, initiator azobisisobutyronitrile (AIBN) or potassium persulfate (KPS) was added into the surfactant/MMA solution and stirred at 70 °C for 2 h, and then quenched by using water to room temperature under stirring. Styrene and divinylbenzene (DVB) were dropped into the solution and heated to 70 °C again. Then, the initiator AIBN or KPS was added into the solution again. Styrene and DVB monomers were polymerized at 70 °C for 2 h. Methylene chloride was used to dissolve the PMMA core. The solution was transferred to a separation funnel, and ethanol was added to remove the surfactants. The solution was kept for 1 day, and PS hollow nanospheres were deposited. After the upper solution containing surfactants and PMMA was removed the product PS hollow nanospheres with a diameter from 15 nm to 30 nm, a wall thickness from 2 nm to 5 nm were obtained. The size of the hollow microspheres is controlled by the surfactant concentration and the weight ratio of surfactant to monomer.

8 Comparison of different methods for preparing PS hollow Microspheres

Table 1 is a comparison of different methods for preparing PS hollow microspheres. From Table 1, we can draw the conclusion that the microencapsulation method is most suitable for preparing PS hollow microspheres. However, hollow polymer microspheres with different wall materials need different methods and the influencing factors are different. Therefore, further studies are still necessary.

Table 1 Comparison of different methods for preparing PS hollow microspheres

Properties	Liquid droplet method	Dried-gel droplet method	Self-assembly method	Microenca-psulation method	Emulsion polymer-ization method	Template method
Equipment cost	High	High	Low	Low	Low	Low
Operation cost	High	High	Low	Low	Low	High
Micromanipulation	Yes	Yes	Yes	No	No	Yes
Batch production	Able	Able	Able	Able	Able	Able
Multiwalled product	No	No	Able	Able	Able	Able
Microsphere diameter, μm	500-1500	500-1500	≤0.5	50-700	≤20	≤5
Sphericity, %	≥97	≥99	≥99	≥99	≥99	≥99
Concentricity, %	≥90	≤90	≥99	≥98	≥98	≥99
Surface roughness, nm	<200	<200	<10	<300	<10	<5

9 Conclusions

Due to the unique properties and the promising applications, hollow polymer microspheres have become an important research direction in material science. At present hollow polymer microspheres with different compositions and properties can be prepared. However, only a few processes are successful for fabricating hollow polymer microspheres but these rarely achieve commercial application. How to prepare these materials more easily and feasibly needs to be further studied. Some shortcomings, such as time-consuming and complex fabrication processes, need to be overcome in the future. Development of a simple method suitable for industrial fabrication of hollow polymer microspheres is an important field for researchers in material science.

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