

## Effect of Preparation Condition on Low-density PS Particle Size and Distribution

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**Abstract:** The preparation conditions were studied in order to obtain smaller, narrow size-distributed and low-density polystyrene (PS) micro-particles by suspension polymerization. The results show that some of preparation conditions, the shape and position of stirrers, and stirring rate etc., have important influence on the size and distribution of particles. The preparation conditions must be carefully designed and controlled in order to obtain high-quality PS beads. A bow-shaped stirrer is helpful to produce small-sized particles and narrow size distribution, and the upper edge of a stirrer should be set to the same level as the surface of mixture, and the stirring rate should be controlled in the range of 520–600 r/min.

**Key words:** low-density micro-particles; suspension polymerization; preparation conditions

Micro-particle polymers, with their particular function, are widely used in the fields of bioengineering, electronic industry and chemical industry etc.[1–3] and furthermore they still continue to expand their application range. For example, they can serve as carriers of certain substance floating in air. For this purpose they should have both smaller diameter and lower density. Among various synthesis methods suspension polymerization is chosen for easily controlling the shape and size of particles and lightly carrying out the industrial practices [4–5].

This paper deals mainly with the effect of preparation conditions on the size and distribution of low-density PS micro-particles synthesized by suspension polymerization.

### 1 Experimental

#### 1.1 Materials

The materials used in the experiment are: styrene (St), divinylbenzene (DVB), polyvinyl alcohol (PVA), and benzoyl peroxide (BPO) that all are used in the chemically pure state; gelatine is industrial products; gasoline (120#); sodiumdodecylbenzenesulfonate (SDBS) is industrial products; water is deionized. In order to remove an inhibitor St, DVB were washed with 5% sodium hydroxide solution before use. All other materials were used in their as-supplied state.

#### 1.2 Preparation and characteristic

A modified suspension polymerization was used to synthesize low-density polystyrene particles. The pol-

merization ingredients were added in the following way. First, PVA, gelatine, SDBS and deionized water were mechanically stirred in a 500 ml glass polymerization reactor–3-neck round-bottomed flask, which was placed in a thermostatic water bath ( $\pm 0.2^\circ\text{C}$ ) so as to heat the mixture aqueous phase up to the set temperature. Then the mixture of BPO, St, DVB and gasoline, organic phase, was added to the polymerization reactor and continuously stirred for a certain time. Then the newly-formed mixture was heated up to another given temperature and kept stirring until the polymerization was terminated. The reactor was then removed from the bath, allowed to cool to room temperature and beads were washed with 0.1 mol/L sodium hydroxide solution to remove gelatine, with deionized water to remove NaOH etc. and with acetone to remove gasoline etc. Then the particles were dried up and sifted. The basic formula and preparation conditions for polymerization are shown as following: styrene 10–40 ml, gelatine 1–6 g, DVB 5–20 ml, PVA 0.5–2 g, BPO 0.1–1 g, SDBS  $(1-5)\times 10^{-4}$  g, gasoline 5–40 ml, deionized water 100–300 ml, stirring rate 500–620 r/min, dispersion temperature  $65^\circ\text{C}$ , dispersion time 1.0 h, polymerization temperature  $82^\circ\text{C}$ , polymerization time 8 h.

The particle size and distribution were measured with LS-230 hondrometer.

### 2 Result and Discussion

The influence of preparation conditions on particle size and its distribution, including the shape and the position of a stirrer, the stirring rate, pre-dispersion tem-

perature and time, was discussed in this part. Keep the rest the same value when a certain condition is changed and examined.

**2.1 Effect of shape of stirrers**

The geometrical shape of a stirrer is an important factor to the size and distribution control of beads. It can be seen from the figure 1 that the size and distribution of beads becomes narrower in the order of (a)→(b)

→(c), and the average diameter decreases in the order of (b)→(a)→(c). It can be related to the flowing direction and rate of a liquid mixture. The straight upper edge of a stirrer makes less mixture flow axially, and the radial flowing rate of mixture changes uniformly so that narrowly size-distributed beads were produced (figure 1 (b), (c)). On the other hand, the round lower edge of a stirrer makes the radial flowing rate change

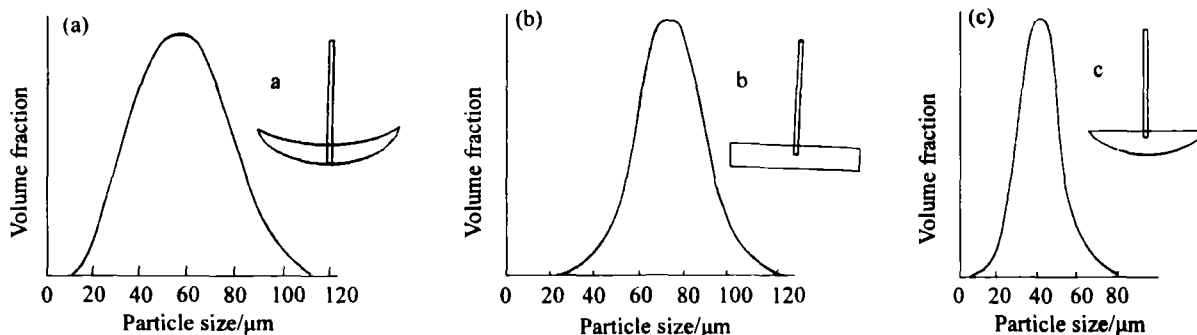


Figure 1 Schematic diagram showing the effect of the shape of stirrers on particle size and its distribution.

significantly so that smaller beads were formed (figure 1 (a), (c)). Therefore, stirrer c is a better choice to prepare PS particles.

**2.2 Effect of position of stirrers**

Figure 2 shows the plot of amount of those beads less than 40 μm against the relative position of a stirrer. The amount increases with the rise of the stirrer position as long as the upper edge of the stirrer is below the surface of the liquid mixture. It has something to do with the density of reactors and polymers. The organic phase used in the polymerization and the polymer, the final product, which contain some diluent, tended to rise to the surface of the liquid mixture during the stir-

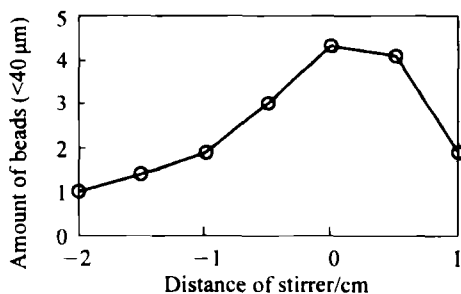


Figure 2 Dependence of amount of beads on the position of stirrers.

ring because of their lower density, less than 1 g/cm<sup>3</sup>. So the higher stirrer position was advantageous to produce the smaller-sized particles in the end.

**2.3 Effect of stirring rate**

Figure 3 shows the plot of average diameter of beads versus stirring rate. When the stirring rate is less than

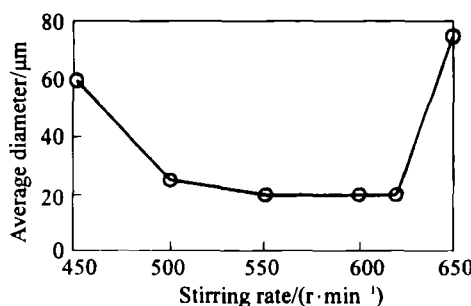
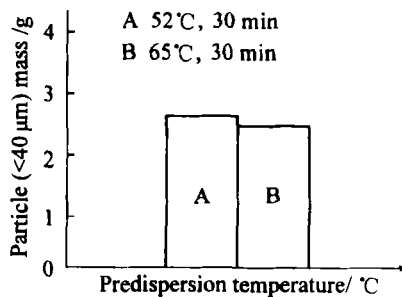


Figure 3 Dependence of particle size of beads on stirring rate.

500 r/min, the size of the beads decreases with stirring rate increase. And when the stirring rate is changed between 500 r/min and 620 r/min there is not much alteration in size of beads. When the stirring rate is over 620 r/min, the particle size increases with the stirring rate. Generally, it is resulted from the forces acting on the organic phase during the stirring. There are two kinds of forces acted on the organic phase. One of them makes the organic phase disperse into beads, while the other makes beads gather together. The smaller particles will be formed in the case of a larger dispersion force that is determined by the stirring rate, increasing with the stirring rate when it is less than 500 r/min. In the range of 500–620 r/min, the dispersion force and gathering force act on the beads almost get balance so that their average size remains the same. If the stirring rate is larger than 620 r/min, the final particles will have larger diameter because sticky particles will get together in the process of stirring. Therefore, the stirring rate of 500–620 r/min is suggested in order to get smaller beads.

## 2.4 Effect of pre-dispersion temperature

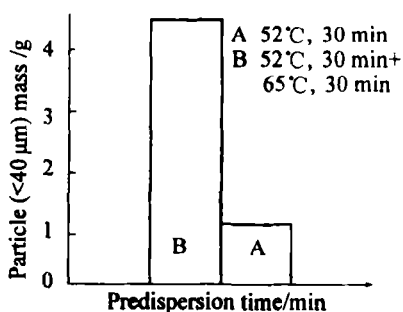
The polymerization will begin after the organic phase was dispersed into beads in the aqueous phase by stirring at the given temperature. **Figure 4** shows the influence of the pre-dispersion temperature on the particle size of beads. It can be seen from figure 4 that the amount of the particles less than 40  $\mu\text{m}$  almost remains constant when the pre-dispersion temperature increases from 52°C to 65°C. This is caused by the decrease of viscosity and surface tension of aqueous phase. Lower viscosity of the aqueous phase leads to the gathering of organic phases, which tends to disperse under lower surface tension of aqueous phase. Therefore, a higher pre-dispersion temperature should be considered in order to reduce heating time.



**Figure 4** Effect of predispersion temperature on particle size.

## 2.5 Pre-dispersion time

At the given dispersion temperature, pre-dispersion time is longer, the more those beads less than 40  $\mu\text{m}$  are obtained as shown in **figure 5**. However, there exists a balance point, at which the organic phase was dispersed



**Figure 5** Effect of predispersion time on the particle size.

into the aqueous phase and small beads were formed under the action of dispersion agent but these beads meanwhile tended to gather into large ones in the view-point of thermodynamics. Therefore, the balance will be reached between dispersion and gathering over a certain time. If the dispersion time is not long enough the balance can't be reached. As a result, large-sized particles were obtained. The amount of small-sized beads simply increases with dispersion time until the balance is reached. Therefore, enough time should be provided to disperse the organic phase into the aqueous phase and form small-sized particles as many as possible.

## 3 Conclusions

In order to obtain small and narrow size-distributed PS particles, the following preparation conditions are suggested:

- (1) The shape of stirrer c should be used.
- (2) The upper edge of stirrers should be on the same level as the surface of a mixture.
- (3) The stirring rate should be in the range of 500–620 r/min.
- (4) Pre-dispersion temperature should be set at about 65°C.
- (5) Enough pre-dispersion time should be given.

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