

## Effects of polymerization conditions on particle size distribution in styrene-graphite suspension polymerization process

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**ABSTRACT:** Suspension polymerization in the presence of graphite has been studied in order to determine the effects of some operational parameters on the particle size distribution (PSD). The results showed that, with increasing graphite content, the particle size of the polystyrene/graphite (PS/G) beads increased. Moreover, instability of the suspension polymerization system was found at high amounts of graphite. With increasing initiator concentration, the particle size of the polymer beads increased and the PSD became slightly narrower. Changing the concentration of the suspending agent proved to be an efficient way of controlling the particle size, although its increase led to a broadening of the PSD. Adding the suspending agent in two portions at different times decreased the particle size, maintained a lower concentration of suspending agent, and kept the suspension polymerization system stable. Adjusting the stirring speed proved to be a very efficient means of manipulating the PSD of the PS/G composite beads. The Sauter mean diameter decreased and the PSD was broadened with increasing stirring speed; 400 rpm was identified as an appropriate value to obtain polystyrene/graphite beads with desirable particle size and distribution. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44270.

**KEYWORDS:** composites; polystyrene; synthesis and processing

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### INTRODUCTION

Suspension polymerization is an important polymerization technique in industrial scale production, which is commonly used to manufacture many kinds of commercially important polymers including poly(vinyl chloride), expandable polystyrene, high impact polystyrene, poly(methyl methacrylate), poly(vinyl acetate), and copolymers thereof. It usually proceeds by a free-radical mechanism; a dispersed phase containing monomer and initiator is dispersed in an aqueous phase by the combined action of agitation and suspending agents (i.e., inorganic and/or water-soluble polymers). All of the reactants (i.e., monomer, initiator, etc.) reside in the dispersed phase. The polymerization reaction occurs in the monomer droplets, which are gradually converted into sticky monomer/polymer droplets and finally into rigid polymer particles.<sup>1</sup>

Polymerization reaction systems are kept stable through the addition of a suspending agent, stirring, controlled addition of the initiator, control of the oil/water ratio, and so on. If some operational parameters change, the balance of the reaction system may be destroyed, rendering it unstable, and the polymerization will be

interrupted.<sup>2</sup> Therefore, maintained stability of suspension polymerization systems is essential during the polymerization process.

As regards the final polymer particles prepared by suspension polymerization, the particle size distribution (PSD) is the most important property, which controls key aspects of the process and affects important product quality characteristics, such as insulation capability, storage, processability, mechanical resistance, bead impregnability, and morphology after expansion.<sup>3</sup> The PSD can be even more important for special applications such as ion-exchange chromatography, chromatographic separations, and biomedical engineering.

The PSD of a polymer is governed by a complex process of droplet coalescence and breakup during the polymerization process, which is affected by several operational parameters such as the type and concentration of suspending agent, the type of impeller and stirring speed, the type and concentration of initiator, the shape and size of the reactor, monomer/water ratio, reaction temperature, and so on.<sup>4,5</sup> It is very important to find key factors to effectively control the PSD in order to prepare desirable size beads in each polymerization. Moreover, polymer beads with distinct

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**Table I.** Preparation Ingredients of PS/G Composites Beads

Ingredients	Samples												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Styrene (g)	100	100	100	100	100	100	100	100	100	100	100	100	100
H <sub>2</sub> O (g)	250	250	250	250	250	250	250	250	250	250	250	250	250
Graphite (g)	0	1	2	3	4	4	4	4	4	4	4	4	4
TBPEH (ppm)	3500	3500	3500	3500	3000	4000	3500	3500	3500	3500	3500	3500	3500
Stirring speed (rpm)	400	400	400	400	400	400	400	400	400	400	400	250	550
TCP (g/L <sub>water</sub> )	8.0	8.0	8.0	8.0	8.0	8.0	8.0	6.0	10.0	6.0 + 4.0 <sup>a</sup>	6.0 + 2.0	8.0	8.0
TCP addition time(min)	0	0	0	0	0	0	0	0	0	0 + 120 <sup>b</sup>	0 + 120	0	0

<sup>a</sup> TCP was added in two portions, an initial 6.0 g/L<sub>water</sub> followed by a further 4.0 g/L<sub>water</sub>.

<sup>b</sup> In "0/120," "0" represents the time at which is prior to the reaction and "120" represents the time at which is after the reaction temperature reaching 90 °C.

average size should be able to obtain from batch to batch using the same reactor and with minimal process adaptation. Several experimental studies have been published on the effects of the above operational parameters on the PSD of polymer beads in suspension polymerization.<sup>6–10</sup> Moreover, predictions of the PSD and the dynamic evolution of the particle formation process by simulation methods have also been reported.<sup>11–15</sup> However, these previous studies were focused on the effects of operational parameters on PSD in pure monomer suspension polymerization systems, without additives.<sup>16–18</sup> Because the compatibility of the additives (such as Fe<sub>3</sub>O<sub>4</sub>, carbon black, montmorillonite) with styrene is not good generally, adding such additives can reduce the stability of the polymerization system.<sup>19–21</sup> Therefore, the manipulation of the PSD must be accomplished while keeping suspension stability.

As previously mentioned, suspension polymerization system are kept in equilibrium through stirring, controlled addition of suspension agent and initiator, monomer/water ratio, and so on. When an additive is deployed in a polymerization system, it will have an efficient effect on the PSD of the final polymer beads. Therefore, it is necessary to investigate the effects of operational parameters on PSD in the presence of additives.

Flake graphite has some excellent properties, such as conductivity, thermal stability, lubrication, chemical stability, flexibility, infrared reflectivity, and so on.<sup>22</sup> Therefore, it is widely used in many fields, such as electromagnetic shielding paint, thermal conductive polymers, wear-resistant polymers, and so on.<sup>23–28</sup>

Polystyrene/graphite (PS/G) composite can be prepared by suspension polymerization. Galewski and Glück prepared expandable polystyrene/graphite beads by suspension polymerization, which has low thermal conductivity because flake graphite can reflect infrared rays, and so it can be used as a good insulation material after expansion.<sup>29,30</sup> Xiao *et al.* synthesized PS/G nanocomposite by *in situ* polymerization, which exhibits higher glass transition temperature and the dielectric constant can reach as high as 136.<sup>31</sup> Low-density heat-resistant PS/G microspheres were successfully synthesized via *in situ* suspension polymerization, which possess

entirely feasible applications in oil exploitation as pure water carrying petroleum proppants.<sup>32</sup>

However, graphite is an inorganic material, and it is not compatible with styrene, thus, adding graphite can reduce the stability of the polymerization system.<sup>22</sup> Therefore, it is necessary to investigate the effects of graphite content on the PSD of the PS composite beads. Moreover, to the best of our knowledge, studies on the effects of the operational parameters on the PSDs of the PS/G composite beads have not hitherto been reported.

The main goal of this work was to investigate the effects of graphite and some operational parameters (such as initiator concentration, stirring speed, suspending agent concentration, and addition time) on the PSDs of the PS/G composite beads prepared by suspension polymerization. These operational parameters were chosen because they can be easily implemented on an industrial scale with minimal cost and process adaptations.

## EXPERIMENTAL

### Materials

Natural flake graphite was obtained from Shandong Xinghe Graphite Co., Ltd (China), the mean size of the powder is 5 μm. Styrene was obtained from Sinopharm Chemical Reagent Co., Ltd (China). *tert*-Butyl peroxy-2-ethylhexanoate (TBPEH) was purchased from Tianjin Fuchen Chemical Co., Ltd (China). Calcium trihydroxy phosphate (TCP) was supplied by Zhangjiagang Taihua Chemical Co., Ltd (China). The water used in this experiment was distilled followed by deionization. Styrene was distilled before being used to remove the inhibitor. Other reagents were of analytical grade and used as received.

### Polymerization Procedure

PS/G composites were prepared by suspension polymerization, following the basic methodology and recipe (Table I) described previously,<sup>17</sup> with some minor experimental adaptations.

Suspension polymerization reactions were carried out in a 500-mL jacketed glass reactor, under atmospheric pressure. First, graphite was added in styrene monomers by ultrasonic dispersion for 5 min,

and obtained styrene and graphite mixtures. Second, the reactor was loaded with deionized water, containing the specified amount of TCP. After that, started stirring, and then, a solution containing the desired amounts of initiator (TBPEH) and purified styrene monomers was added into the reactor. The system was kept under  $90 \pm 0.5$  °C for about 5–6 h, during the reaction process, the reactor was closed with its top lid, which was equipped with a reflux condenser. The polymerization reaction was terminated when the expected PS/G composite particles became hardened by sampling. The polymerization time was counted from the reaction temperature reaching 90 °C to the termination of polymerization reaction. The resulting product was filtered and washed with distilled water. The final polymer particles were dried at 50 °C.

### Characterization

Polymer particles were dried and sieved through 200, 400, 600, 800, 1000, 1250, 1430, 1600, 2000, and 2360  $\mu\text{m}$  mesh screens. Results are presented as histograms of retained mass percentages in each sieve. Sauter mean diameter ( $d_{32}$ ) and dimensionless standard deviation ( $\sigma$ ) were calculated using eq. (1) and eq. (2), respectively.<sup>8</sup>

$$d_{32} = \frac{\sum_{i=1}^n \Delta\phi_i}{\sum_{i=1}^n \frac{\Delta\phi_i}{\bar{D}_i}} = \frac{1}{\sum_{i=1}^n \frac{\Delta\phi_i}{\bar{D}_i}} \quad (1)$$

$$\sigma = \frac{\sqrt{\sum_{i=1}^n [(\bar{D}_i - d_{32})^2 \cdot \Delta\phi_i]}}{d_{32}} \quad (2)$$

where  $\Delta\phi_i$  is the mass fraction retained in the sieve  $i$ , and  $\bar{D}_i$  is the average diameter considering sieves  $i$  and  $(i + 1)$ .

## RESULTS AND DISCUSSION

### Effect of Graphite Content on PSD

Figure 1(a–e) shows the PSDs of the PS/G composite beads with different graphite contents. Figure 2 shows the Sauter mean diameter and dimensionless standard deviations of the PS/G composite beads. Supporting Information Figure S1 shows the photos of PS/G composite beads with different graphite contents. In this part, the graphite content is 1, 2, 3, and 4 wt %, respectively, and the other respective parameters are listed in Table I.

The results showed that, as the graphite content increased,  $d_{32}$  of the PS/G composite beads increased from 848  $\mu\text{m}$  for 1 wt % graphite content to 889  $\mu\text{m}$  for 4% graphite, as compared to 806  $\mu\text{m}$  for pure PS (Figure 2). However, the particle population in the range 800–1200  $\mu\text{m}$  increased with increasing graphite content. The particle size was mainly distributed in the range 800–1600  $\mu\text{m}$  at a graphite content of 4 wt %. Additionally, the dimensionless standard deviation ( $\sigma$ ) increased significantly with increasing graphite content. Broad PSDs are not desirable in industrial scale production, because they can lead to waste material, increased operational costs, and decreased processability.<sup>8</sup>

In previous studies, researchers have concluded that the PSD of polymer beads is related to the viscosity of the reaction system; the particle size increased with increasing the viscosity.<sup>33</sup> At an early stage, the initial monomer droplet size distribution is an

important parameter of the suspension polymerization process, which generally determines the final PSD of the polymer beads under the same operating conditions (e.g., dispersed phase volume fraction, temperature).<sup>13,34</sup>

Graphite is a hydrophobic material with a sheet structure. Graphite of flake size 5  $\mu\text{m}$  was chosen for this work. Prior to the suspension polymerization, graphite was first dispersed in styrene with the aid of ultrasonication, and then the dispersion was divided into numerous droplets by stirring and adding the suspending agent. According to literature reports, graphite can increase the viscosity of such polymerization system.<sup>35</sup> Therefore, in the initial stage, the viscosity of the monomer dispersion increased with the increasing graphite content, which led to larger size droplets under the same operating conditions. Finally, polymer beads with larger particles were obtained.

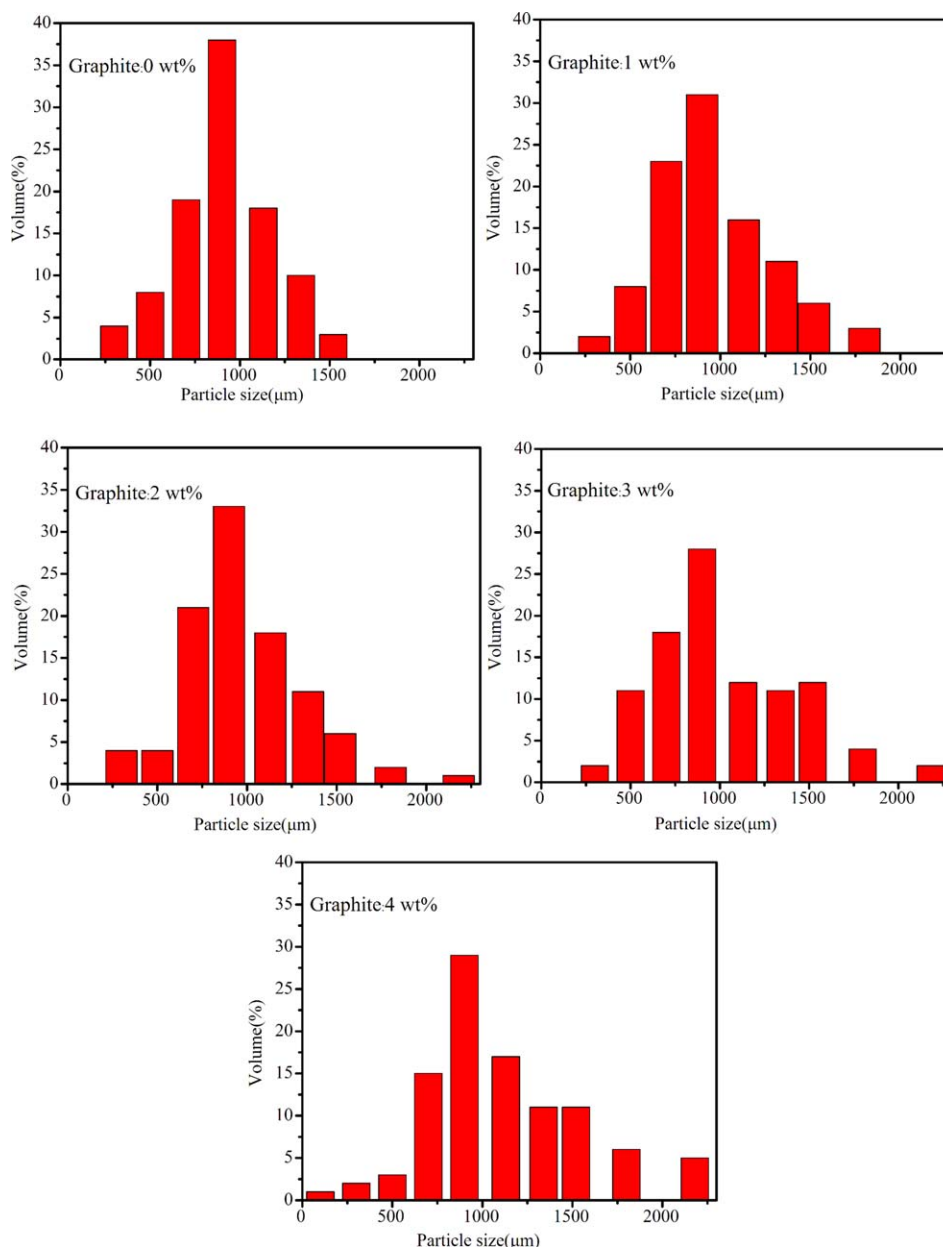
### Effect of TBPEH Concentration on PSD

Figure 3(a–c) shows the PSDs of the PS/G composite beads obtained by suspension polymerization with different TBPEH concentrations. Figure 4 presents the Sauter mean diameters and dimensionless standard deviations of the PS/G composite beads. Supporting Information Figure S2 shows the photos of PS/G composite beads with different TBPEH concentrations. In this part, the TBPEH concentration is 3000, 3500, and 4000 ppm, respectively, and the other respective parameters are listed in Table I.

As shown in Figures 3 and 4, the average size of the PS/G composite beads increased with increasing TBPEH concentration. The  $d_{32}$  of the PS/G composite beads increased from 806  $\mu\text{m}$  for 3000 ppm TBPEH to 1013  $\mu\text{m}$  for 4000 ppm TBPEH loading, indicating that the size of the PS/G composite beads increased significantly with more initiator addition. Moreover, the dimensionless standard deviation decreased with increasing TBPEH concentration. More primary free radicals produced from more initiators decomposition by heating, and more styrene/polystyrene nanodroplets can be produced by more primary free radicals. The larger surfaces areas of the nanodroplets have to be covered by the TCP in order to prevent the coalescence. Accordingly, for a same amount of TCP, the area of unprotected nanodroplets increases when the amount of initiator increases, and therefore, the coalescence is greater and the final size of the particles is higher. Moreover, at the same temperature, the polymerization rate of styrene is closely related to the decomposition rate of the initiator, which is directly proportional to the initiator concentration.<sup>36</sup> In other words, the initiator decomposes more rapidly as its concentration is increased, leading to rapid increases in the polymerization rate of styrene and the viscosity of the monomer droplets. Consequently, there is more coalescence between droplets, resulting in large particle sizes.

### Effect of TCP Concentration on PSD

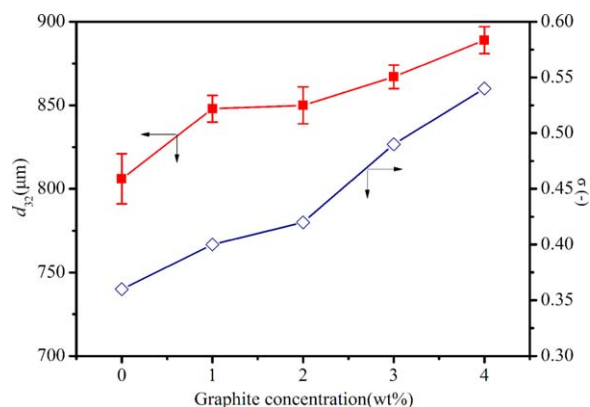
In suspension polymerization, the PSDs of polymer particles are significantly influenced by the suspending agent. In general, suspending agents fall into two categories. The first type comprise water-soluble organic macromolecules, such as hydroxymethyl cellulose, poly(vinyl alcohol), poly(vinylpyrrolidone), sodium polymethacrylate, and so on.<sup>37–41</sup> The second type comprise



**Figure 1.** Final PSDs of the PS/G composite beads with different graphite contents. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

inorganic suspending agents, such as calcium phosphate, magnesium carbonate, talcum powder, and so on.<sup>42,43</sup> In a suspension polymerization system, an inorganic suspending agent can assemble at the surface of the monomer, isolate the monomers, and hinder the collisions between monomer drops.<sup>6</sup> Figure 5(a–c) shows the PSDs of the PS/G composite beads with different TCP concentrations. Figure 6 shows the Sauter mean diameter and dimensionless standard deviation of the PS/G composite beads. Supporting Information Figure S3 shows the photos of PS/G composite beads with different TCP concentrations. In this part, the TCP concentration is 6.0, 8.0, and 10.0 g/L<sub>water</sub>, respectively, and the other respective parameters are listed in Table I.

The results show that on increasing the TCP concentration from 6.0 to 10.0 g/L<sub>water</sub>, the average size of the PS/G composite beads decreased from 1274 to 624 μm (Figure 6). As shown in Figure 5, when the TCP concentration was 6.0 g/L<sub>water</sub>, the diameters of the PS/G composite beads were mainly distributed in the range 1500–2360 μm. However, when the TCP concentration was increased to 10.0 g/L<sub>water</sub>, the maximum in the PSD shifted toward smaller particles. Moreover, the dimensionless standard deviation increased as the TCP concentration was increased. This was because the isolating role of TCP became more pronounced with more of it on the surface of the monomers, which resulted in the particle size reduction.



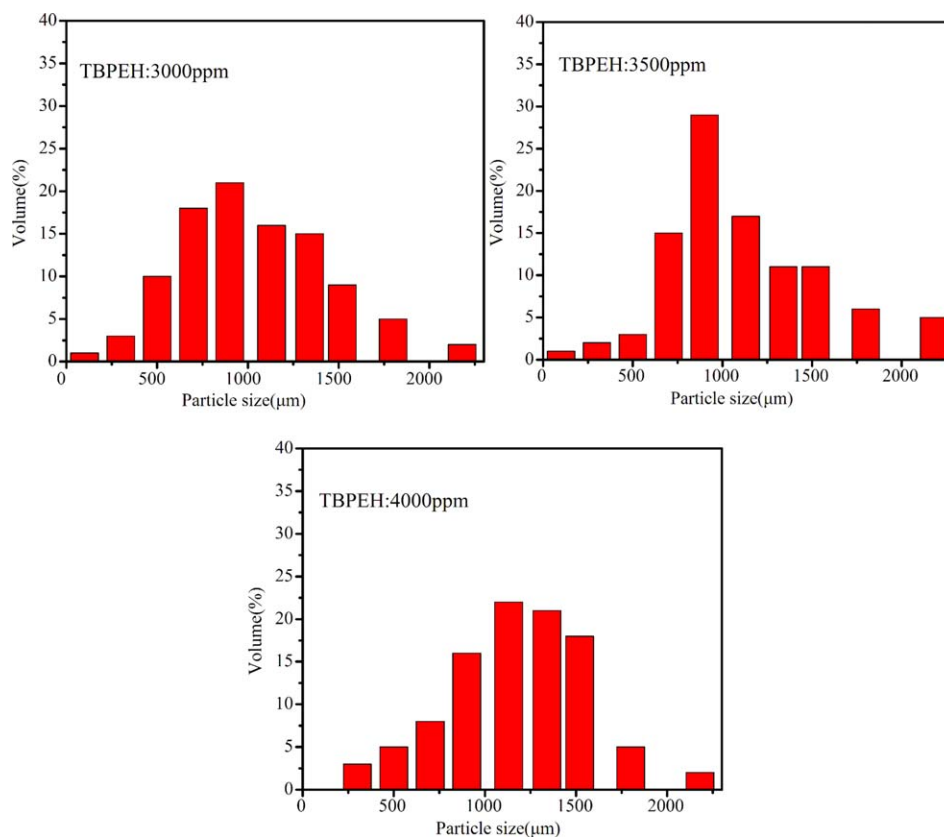
**Figure 2.**  $d_{32}$  and dimensionless standard deviation of PS and PS/G composites. (■)  $d_{32}$ -Sauter mean diameter and (◇)  $\sigma$ -dimensionless standard deviation. [Color figure can be viewed at wileyonlinelibrary.com.]

### Effect of TCP Addition Time on PSD

Table II shows the PSDs of the PS/G composite beads at different TCP addition time. Supporting Information Figure S4 shows the photos of the PS/G composite beads with different TCP addition time. In this part, TCP adding time and the respective parameters are listed in Table I.

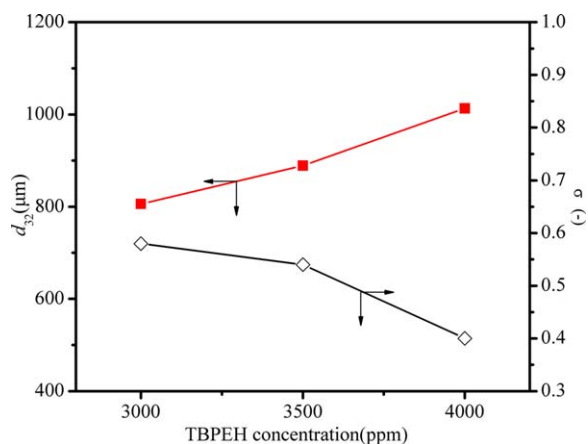
On an industrial scale, in order to maintain the stability of a polymerization system or to obtain polymer beads with

desirable particle size, adding a second portion of suspending agent after a given time is a common measure during suspension polymerization processes. As shown in Table II, compared with adding 6.0 g/L<sub>water</sub> TCP prior to the reaction, the particle size decreased and the PSD became narrower when a further 2.0 g/L<sub>water</sub> of TCP was added after polymerization system had been kept at constant temperature ( $90 \pm 0.5$  °C) for 120 min. The particle size was larger when the same amount of TCP was added in two portions as opposed to one. We also investigated the addition of 10.0 g/L<sub>water</sub> TCP in one and two portions, and a similar result was obtained. In the initial stage of suspension polymerization, with increasing concentration of the suspending agent, the sizes of the monomer droplets containing graphite decreased. In the middle to late stage of suspension polymerization, the viscosity of the monomer/polymer droplets increased significantly, and the coalescence rate exceeded the breakage rate between the droplets. The size of the monomer/polymer droplets increased rapidly. However, for the same total amount of suspending agent, single addition prior to the reaction can generate smaller monomer droplets than in two portions. In the latter case, the viscosity of the monomer/polymer was much higher than that with single addition in the initial stage, and the coalescence rate was very high. Later addition of a second portion of the suspending agent did not prevent the formation of larger polymer beads, even though the added suspending agent could decrease the coalescence rate of the monomer/polymer droplets.<sup>8</sup>



**Figure 3.** Final PSDs of the PS/G composite beads with different TBPEH concentrations. [Color figure can be viewed at wileyonlinelibrary.com.]

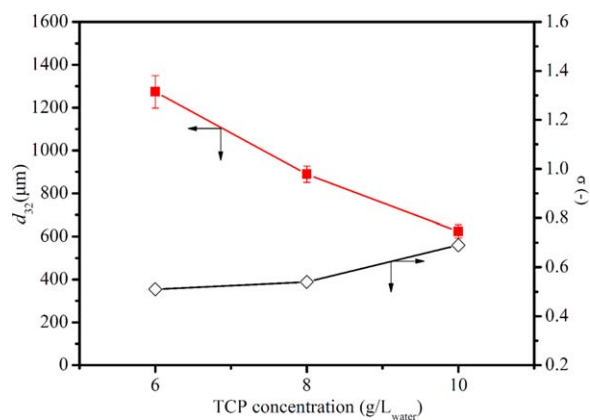




**Figure 4.**  $d_{32}$  and dimensionless standard deviation of PS and PS/G composites. (■)  $d_{32}$ -Sauter mean diameter and (◇)  $\sigma$ -dimensionless standard deviation. [Color figure can be viewed at wileyonlinelibrary.com.]

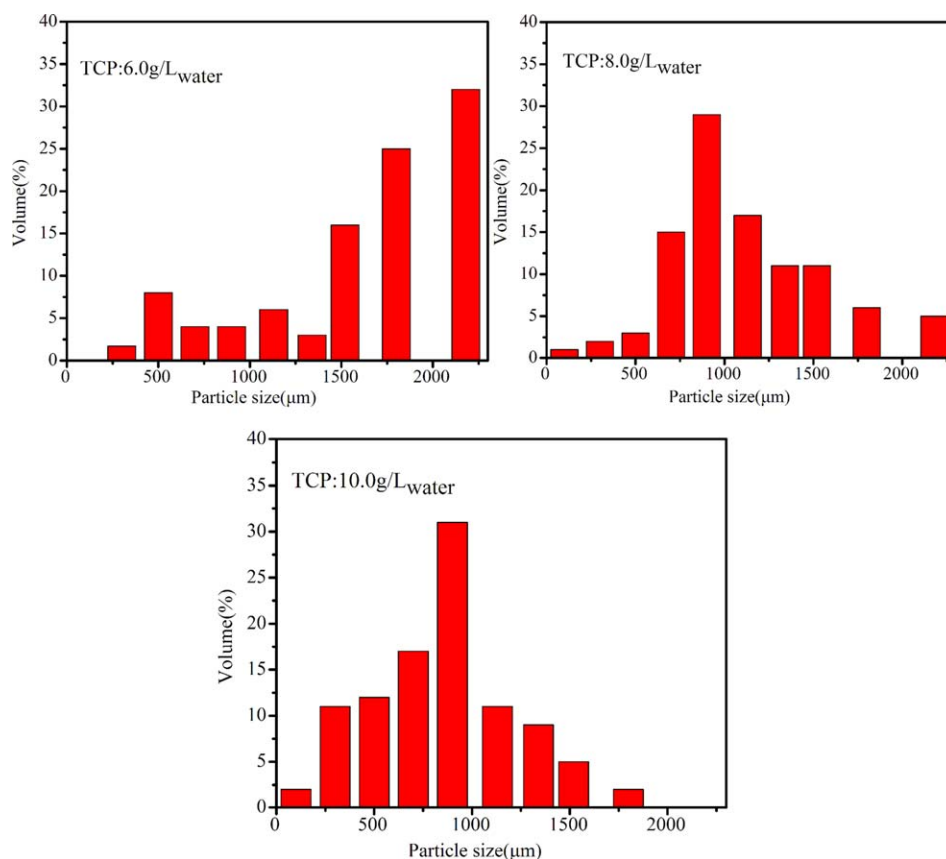
#### Effect of Stirring Speed on PSD

As expected, the stirring speed significantly affected the turbulence intensity and the initial monomer droplet size of the dispersion when the other operational parameters were kept constant as expected.<sup>2,44</sup> Figure 7 (a–c) shows the PSDs



**Figure 6.**  $d_{32}$  and dimensionless standard deviation of PS and PS/G composites. (■)  $d_{32}$ -Sauter mean diameter and (◇)  $\sigma$ -dimensionless standard deviation. [Color figure can be viewed at wileyonlinelibrary.com.]

of the PS/G composite beads with different stirring speeds. Figure 8 presents the Sauter mean diameters and dimensionless standard deviations of the PS/G composite beads. Supporting Information Figure S5 shows the photos of the PS/G composite beads with different stirring speeds. In this part, the stirring speed is 250, 400, and 550 rpm, and the other respective parameters are listed in Table I.



**Figure 5.** Final PSDs of the PS/G composite beads with different TCP concentration. [Color figure can be viewed at wileyonlinelibrary.com.]

**Table II.** Effect of TCP Addition Time on  $d_{32}$  and Dimensionless Standard Deviation of the PS/G Composite

Samples	TCP concentration and addition time				
	6.0 <sup>a</sup>	6.0 + 2.0 <sup>b</sup>	6.0 + 4.0 <sup>c</sup>	8.0 <sup>a</sup>	10.0 <sup>a</sup>
Sauter mean diameter ( $d_{32}$ ) ( $\mu\text{m}$ )	1274	1012	861	889	624
Dimensionless standard deviation ( $\sigma$ )	0.51	0.47	0.45	0.54	0.69

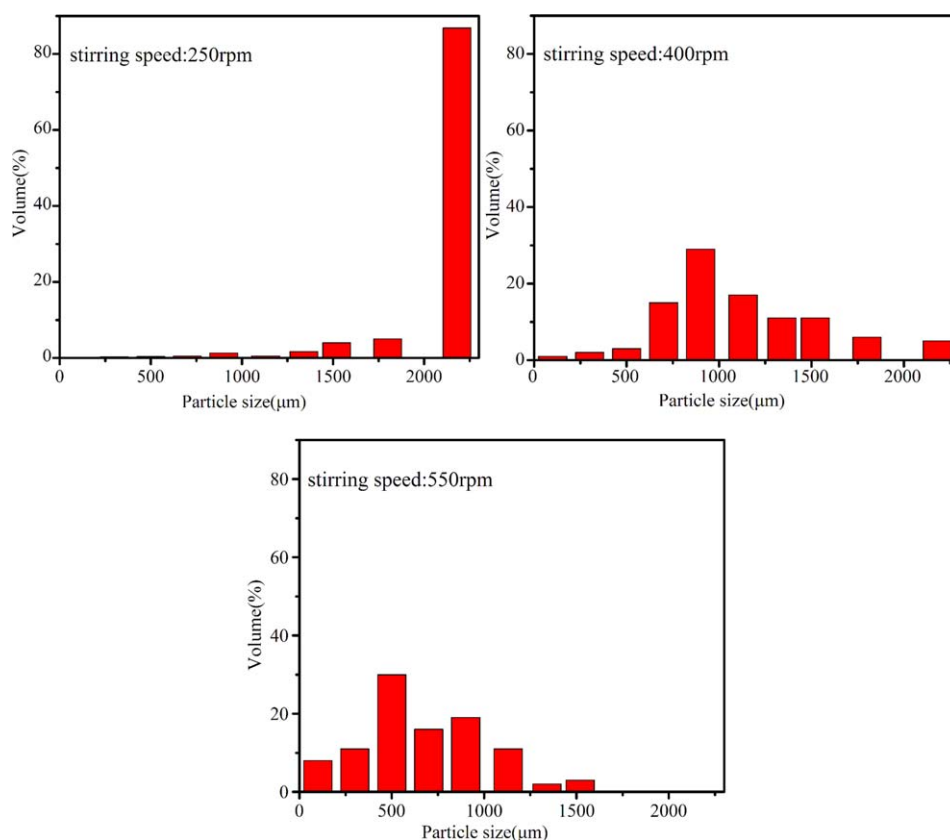
<sup>a</sup>TCP (6.0, 8.0, or 10.0 g/L<sub>water</sub>) was added in a single portion prior to the reaction.

<sup>b</sup>TCP was added in two portions, 6.0 g/L<sub>water</sub> prior to the reaction and a further 2.0 g/L<sub>water</sub> after the reaction temperature reaching 90 °C.

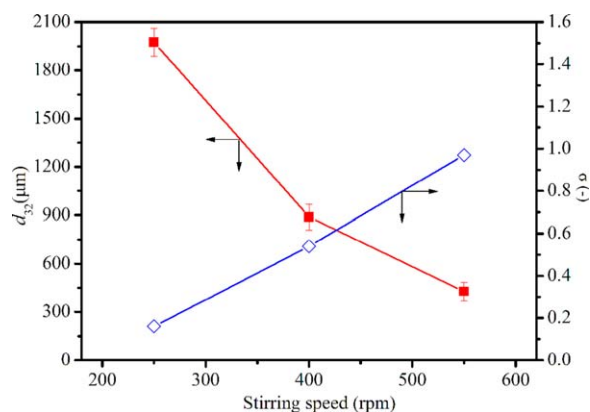
<sup>c</sup>TCP was added in two portions, 6.0 g/L<sub>water</sub> prior to the reaction and a further 4.0 g/L<sub>water</sub> after the reaction temperature reaching 90 °C and keeping constant temperature for 120 min.

The results showed that stirring speed had a significant effect on the PSDs of the PS/G composite beads. On increasing the stirring speed from 250 to 550 rpm, the particle size decreased from 1974 to 428  $\mu\text{m}$  (Figure 8). As shown in Figure 7, at a stirring speed of 250 rpm, most of the PS/G composite beads exceeded 2100  $\mu\text{m}$  in diameter. However, when the stirring speed was increased to 550 rpm, the peak of the PSD shifted toward smaller particle size and the suspension polymerization system became unstable. Moreover, the dimensionless standard deviation increased with increasing stirring speed. Based on the results in Figures 7 and 8, suitable stirring speed of 400 rpm was identified for producing PS/G composite beads with desirable PSD.

With increasing stirring speed, the size of the initial monomer droplets decreased, and hence the size of the final polymer beads particles decreased accordingly.<sup>45</sup> However, the PSD and average size of the final polymer beads were mainly determined by a balance between coalescence and breakup of the droplets.<sup>13</sup> As the suspension polymerization proceeded, the viscosity of the dispersed phase increased and the coalescence rate increased. A high stirring speed reduced the coalescence behavior. However, the suspension polymerization system became unstable at 550 rpm. In order to obtain polymer beads with desirable particle size, an appropriate stirring speed was necessary. In this work, a stirring speed of 400 rpm was identified as suitable for obtaining desirable polymer beads.



**Figure 7.** Final PSDs of the PS/G composite beads with different stirring speeds. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Effect of stirring speed on  $d_{32}$  and dimensionless standard deviation of PS and PS/G composites. (■)  $d_{32}$ -Sauter mean diameter and (◇)  $\sigma$ -dimensionless standard deviation. [Color figure can be viewed at wileyonlinelibrary.com.]

## CONCLUSIONS

Polystyrene composites containing graphite have been prepared by suspension polymerization. The results of a series of experiments showed that graphite had a significant effect on the PSD of PS/G composite beads. The particle size increased and the Sauter mean diameter range was broadened with increasing graphite content from 1 to 4 wt %. However, the suspension system became unstable when the graphite content exceeded 4 wt %.

The particle size increased and the dimensionless standard deviation became slightly narrower with increasing initiator concentration. However, an excessively high initiator concentration led to instability of the suspension polymerization system.

Addition of a suspending agent proved to be an efficient means of manipulating the PSD of the PS/G composite beads. As the concentration of suspending agent increased, the Sauter mean diameter decreased and the dimensionless standard deviation increased significantly. Moreover, adding the suspending agent in two portions exerted a significant influence on the PSD. When the same amount of TCP was initially added prior to the reaction, addition of a second portion decreased the particle size and narrowed the dimensionless standard deviation, which is desirable in the industrial processes. However, when the same total amount of TCP was added, the particle size with addition in two portions was larger than that with a single addition.

The Sauter mean diameter decreased and the distribution was broadened when the stirring speed was changed from 250 to 550 rpm. A stirring speed of 400 rpm was identified as an appropriate value to obtain PS/G composite with desirable particle size and distribution.

## REFERENCES

- Kiparissides, C. *Chem. Eng. Sci.* **1996**, *51*, 1637.
- Dowding, P. J.; Vincent, B. *Colloid. Surf. A: Physicochem. Eng. Asp.* **2000**, *161*, 259.
- Alvarez, J.; Alvarez, J.; Hernández, M. *Chem. Eng. Sci.* **1994**, *49*, 99.
- Machado, R. A. F.; Pinto, J. C.; Araújo, P. H. H.; Bolzan, A. *Braz. J. Chem. Eng.* **2000**, *17*, 395.
- Jahanzad, F.; Sajjadi, S.; Brooks, B. W. *Macromol. Symp.* **2004**, *206*, 255.
- Wolters, D.; Meyer-Zaika, W.; Bandermann, F. *Macromol. Mater. Eng.* **2001**, *286*, 94.
- Zhang, B.; Ma, Y.; Chen, D.; Xu, J. N.; Yang, W. T. *J. Appl. Polym. Sci.* **2013**, *129*, 113.
- Goncalves, O. H.; Nogueira, A. L.; Araujo, P. H. H.; Machado, R. A. F. *Ind. Eng. Chem. Res.* **2011**, *50*, 9116.
- Lin, J. F.; Zhang, H. Y.; Liang, J. Y.; Deng, J. P. *Macromol. Chem. Phys.* **2015**, *216*, 1963.
- Liu, C.; Luo, Y. F.; Jia, Z. X. *Polym. Compos.* **2014**, *5*, 856.
- Kiyoshi, S.; Mamoru, N. *J. Chem. Eng. Jpn.* **2003**, *36*, 1242.
- Bárkányi, Á.; Németh, S.; Lakat, B. G. *Comput. Chem. Eng.* **2013**, *59*, 211.
- Kotoulas, C.; Kiparissides, C. *Chem. Eng. Sci.* **2006**, *61*, 332.
- Bárkányi, Á.; Németh, S.; Lakatos, B. G. *Chem. Eng.* **2011**, *24*, 613.
- Saliakas, V.; Kotoulas, C.; Meimaroglou, D.; Kiparissides, C. *Can. J. Chem. Eng.* **2008**, *86*, 924.
- Wang, L. L.; Zhao, T. B.; Li, Y.; Ding, H. J. *China. Pet. Process. Petrochem. Technol.* **2016**, *18*, 73.
- Castor, C. A., Jr.; Pontier, A.; Durand, J.; Pinto, J. C.; Prat, L. *Chem. Eng. Sci.* **2016**, *145*, 279.
- Abedin, R.; Pojman, J. A.; Knopf, F. C.; Rice, R. G. *Ind. Eng. Chem. Res.* **2012**, *55*, 2493.
- Ferreira, G. R.; Segura, T.; de Souza, J. F. G.; Umpierre, A. P.; Machado, F. *Eur. Polym. J.* **2012**, *48*, 2050.
- Zheng, Z. H.; Li, W. J.; Sun, H. M.; Cheng, Z. Q.; Yan, J. T.; Wang, H. Y.; Cui, X. *J. Polym. Compos.* **2013**, *34*, 1110.
- Hwu, J. M.; Ko, T. H.; Yang, W. T.; Lin, J. C.; Jiang, G. J.; Xie, W.; Pan, W. P. *J. Appl. Polym. Sci.* **2004**, *91*, 101.
- Chung, D. D. L. *J. Mater. Sci.* **2002**, *37*, 1475.
- Al-Ghamdi, A. A.; El-Tantawy, F. *Compos. A* **2010**, *41*, 1693.
- Wu, J. H.; Chung, D. D. L. *Carbon* **2003**, *41*, 1313.
- Debelak, B.; Lafdi, K. *Carbon* **2007**, *45*, 1727.
- Pan, G. L.; Guo, Q.; Ding, J.; Zhang, W. D.; Wang, X. M. *Tribol. Int.* **2010**, *43*, 1318.
- Slatter, T.; Lewisa, R.; Jonesb, A. H. *Wear* **2011**, *270*, 302.
- Xiang, J. L.; Drzal, L. T. *Carbon* **2011**, *49*, 773.
- Galewski, J. M. U.S. Pat. 9,120,905 B2 (2015).
- Glück, G. U.S. 6,414,041 B1 **2002**.
- Xiao, M.; Sun, L. Y.; Liu, J. J.; Li, Y.; Gong, K. C. *Polymer* **2002**, *43*, 2245.
- Han, X. B.; Cheng, Q. X.; Bao, F.; Gao, J.; Yang, Y. D.; Chen, T.; Yan, C. J.; Ma, R. *Polym. Plast. Technol.* **2014**, *53*, 1647.
- Maggioris, D.; Goulas, A.; Alexopoulos, A. H.; Chatzi, E. G.; Kiparissides, C. *Chem. Eng. Sci.* **2000**, *55*, 4611.



34. Bao, Y. Z.; Brooks, B. W. *J. Appl. Polym. Sci.* **2002**, *85*, 1544.
35. Yan, J. T.; Miao, X. J.; Zhang, Q. Y.; Cui, X. J.; Li, J. F.; Wang, H. Y. *Polym. Eng. Sci.* **2011**, *51*, 294.
36. Brooks, B. W. *Chem. Eng. Technol.* **2010**, *33*, 1737.
37. Mendizabal, E.; Castellanos-Ortega, J. R.; Puig, J. E. *Colloid Surf.* **1992**, *63*, 209.
38. Lerner, F.; Nemet, S. *Plast. Rubber Compos.* **1999**, *28*, 100.
39. Georgiadou, S.; Brooks, B. W. *Chem. Eng. Sci.* **2005**, *60*, 7137.
40. Georgiadou, S.; Brooks, B. W. *Chem. Eng. Sci.* **2006**, *61*, 6892.
41. Chung, S. I.; Wasan, D. T. *Colloid Surf.* **1988**, *29*, 323.
42. Wang, Z. P.; Brooks, B. W. *Polym. Int.* **1992**, *28*, 239.
43. Li, B. Y.; Wang, Y. P.; Niu, X. B.; Liu, Z. M. *Chin. J. Polym. Sci.* **2014**, *32*, 123.
44. Chatzi, E. G.; Kiparissides, C. *Chem. Eng. Sci.* **1994**, *49*, 5039.
45. Jahanzad, F.; Sajjadi, S.; Brooks, B. W. *Chem. Eng. Sci.* **2005**, *60*, 5574.