

Particle Size Distribution and Morphology of in Situ Suspension Polymerized Toner

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A spherical polymerized toner with an average size around 10 μm and a span $(D_{0.9} - D_{0.1})/D_{0.5}$ of 1.5–2.0 is prepared directly by in situ suspension copolymerization of a mixture of styrene/*n*-butyl acrylate/iron black. The particle size distribution (PSD) and morphological properties of the toner are investigated. On the basis of the analysis of droplet breakage, coalescence, and growth in the preparation of the polymerized toner, several factors affecting the droplet size, PSD, and morphology of the toner, i.e., agitation speed, ultrasonic introduction, and addition of different types and amounts of surfactants and pigment, are experimentally studied. Surface treatments of the pigment are conducted by modification with coupling agents and in situ prepolymerization. It is shown that surface modification of the pigment particles with coupling agents destroys the stabilization of the droplet, resulting in unexpectedly large particles. However, the in situ prepolymerization treatment is capable of maintaining the required PSD.

1. Introduction

A toner is a dry developer widely used in copiers and laser printers. It is based on the electrophotographic process (or xerography) invented by Carlson in 1938.¹ Good quality toners should have average particle sizes around 10 μm , a low fixing temperature with wide latitude, and sufficient surface charge.² Commercialized toners are mainly composed of binder resin, colorant, and additives, and they are mostly manufactured by the melt-mixing method. In general, the preparation process is as follows: colorants such as carbon black (or iron black) are first dispersed uniformly by blending into a melted thermoplastic resin, then, by extruding and cryogenic air-jet grinding, these are classified into the desired particle size distribution (PSD), and finally, these are mixed with outer additives, such as fumed silica, to obtain the final product.^{3–7}

The grinding and classifying in producing toners are energy intensive and of low efficiency, and polymerization routes have been proposed recently. Patented polymerization methods for toner preparation include suspension polymerization, emulsion polymerization, dispersion polymerization, interface/free radical polymerization, and aggregation processes.⁸ All of these methods build the toner particle from droplets of monomers or micelles directly, which is distinct from the breaking down from bulk materials. Among them, the suspension polymerization method has the advantages of preparing toner particles with perfectly spherical shape and being less of the stabilizer adsorption in comparison to emulsion polymerization.^{9,10} Unfortunately, the particle size of suspension-polymerized microspheres is usually larger than 50 μm , which is far beyond the desired size of a toner. Therefore, a special apparatus, such as a high-speed mill, or homogenizer, is always employed in these patents to reduce the size of the droplets, which are both costly and of low efficiency. Even using these, unwanted large particles are still unavoidable if no specialized dispersants are

added to suppress the coalescence of droplets during polymerization. In most cases, specialized dispersants are multicomponent, and contain an ionic type emulsifier, like sodium dodecyl sulfate (SDS), which is often not easily removed from the final product. Fine powders such as SiO_2 and CaCO_3 are also used as stabilizers, but they also need to be removed from the final product by acid washing.^{11,12} To overcome these disadvantages, an in situ suspension polymerization method is used to prepare a toner directly in this paper.

2. Experimental Section

2.1. Experimental Materials. Iron black (IB) pigment of industrial grade (Wuxi Magnetic Materials Factory, China), with a rhombus shape and an average particle size of 0.2–0.3 μm , is used as the colorant. Analytical grade styrene (Beijing Fuxing Chemicals Factory, China) and analytical grade *n*-butyl acrylate (Beijing Yili Fine Chemicals Co., China) are used as comonomers after they are distilled at reduced pressure. 2,2'-Azobisobutyronitrile (AIBN) of chemical purity (Shanghai Fourth Reagent Factory, China) is used as initiator after purification by dissolving in absolute alcohol and recrystallization at a lower temperature. Bis(3,5-di-*t*-butylsalicylato) chromium (E81) (Oriental Co., Japan) and hexadecyltrimethylammonium bromide (CTAB) of chemical purity (Beijing Chemicals Factory, China) are selected as the negative charge control agents (CCA). Nigrosine of chemical purity (Beijing Chemicals Factory, China) is selected as the positive CCA. Poly(vinyl alcohol) (PVA1788) of chemical purity (Beijing Chemicals Reagent Co.), with 1700 degree of polymerization and 88% degree of hydrolysis, is chosen as the stabilizer. Synthesized poly[(ethylene oxide)-*co*-(propylene oxide)] (PDA) and sodium dodecyl sulfate (SDS) of chemical purity (Tianjin Nankai Chemicals Factory, China) are used as surfactants to control the PSD of the polymerized product. Other additives, such as KCl, silicon oil, etc., are also used to facilitate polymerization.

2.2. Toner Preparation. Purified styrene (50 mL) and *n*-butyl acrylate monomers (10 mL) are added to a 100 mL beaker. The ratio of styrene to *n*-butyl acrylate

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is selected to be 5/1 by volume. AIBN (3 g) is dissolved in the monomers completely as a free radical initiator. IB (17.5 g) and CCA (1.55 g) are also added into the monomers in the presence of ultrasonic (20 kHz, 100 W) energy at room temperature. Then, the monomers and pigments are well mixed and transferred to a 600 mL polymerization reactor in which PVA1788 (2.5%, 100 mL), PDA (1.28%, 80 mL), and other additives are previously dissolved in deionized water, and deionized water is added until the volume of the mixture reaches 400 mL. The polymerization reaction is carried out in a water constant-temperature bath at a setting temperature ranging 65–85 °C for 4–6 h. The final product is washed with deionized water until the supernatant is transparent, then filtered by vacuum, and dried at a reduced pressure to give the polymerized toner.

2.3. Sample Characterization. The size of the droplets and polymerized toner is measured by a Malvern Mastersizer (Micro-Plus) with a measurement range 0.050–555 μm . The droplet sample is sucked out from the suspension and quickly injected into a 5.0% (wt) PVA1788 solution to stop the polymerization and droplet coalescence for measurement. Calibration with an optical microscope shows that the size measurement of the droplets is reliable.

The morphological properties of the polymerized microspheres are observed by field emission scanning electron microscopy (JSM6301F, JEOL Co., Japan). The toner sample is coated with Au before it is observed by SEM. The inner structure of the toner is observed by transmission electron microscopy (Hitachi 800, Japan) with microtomed samples. A powder sample is dispersed into an epoxy and then solidified. After quenching with liquid nitrogen, it is sliced with a microtome.

Thermal gravity analysis is employed to determine the pigment content in the toner. The total content of pigment inside of a polymerized toner sample is measured by TGA directly. A sample is heated from room temperature to 750 °C with a ramp of 20 °C/min, under a nitrogen atmosphere with a flux of 90 mL/min. To determine the pigment amount inside of the toner, a sample is washed by H₂SO₄ of 24.5% concentration and ultrasonic treatment for 2 h. In this case, the pigment on the surface is removed by the reaction with acid. Thus, the inner side pigment content can be obtained by TGA analysis of the washed sample.

3. Results and Discussion

3.1. Droplet Size Distribution in Polymerization Process. The size growth model of a bead suspension polymerization proposed by Winslow and Matreyek¹³ indicates that the particle size is mainly determined by the droplet size in the lower conversion stage and the stability of monomer/polymer droplets in the high conversion stage. If the coalescence of monomer/polymer droplets is negligible during polymerization, e.g., due to protection by a stabilizer, the PSD of the polymerized toner is approximately the size distribution of the droplets of the monomer. Therefore, the PSD of the toner can be predicted by Hinze's theory,¹⁴ which is based on the dynamic balance between breakage and coalescence of dispersed droplets. If the coalescence of dispersed droplets can be neglected by using a stabilizer, the average size of a suspended droplet in a reactor can be estimated by eq 1, which is based on Kolmogoroff's

turbulence microscale theory.¹⁵

$$d = k_1(\sigma/\rho_c)^{3/5}\epsilon^{-2/5} \quad (1)$$

This equation indicates that decreasing interface tension (σ) and increasing power density (ϵ) and the density of continuous phase (ρ_c) are all advantageous for decreasing the average size of the droplets of the monomer. The power density has a relationship with the agitation speed in the stirring reactor:

$$\epsilon \propto k_2 n^3 \quad (2)$$

where n is the agitation speed and k_2 is a coefficient related with blade. Thus

$$d = k_3(\sigma/\rho_c)^{3/5}n^{-6/5} \quad (3)$$

It should be mentioned here that this equation is only valid in the case of noncoalescence and a nonpigment system.

If a surfactant is added, previous research^{16,17} has illustrated that (1) the droplet size will be smaller; (2) the power value of agitation speed in eq 3 will decrease with increasing surfactant concentration; (3) the power value of the surface tension is larger than ³/₅; and (4) the droplet size still follows the normal distribution. However, in small reactors, a bimodal distribution of droplet size is also often found.¹⁸ Chatzi's research^{19,20} indicates that there are two different types of droplet breakage, which are thorough breakage and erosive breakage. Normally, large droplets are stretched out and broken into a series of small droplets due to viscous shear force, fluctuations of pressure, or relative speed, which is known as thorough breakage. However, if the fluctuations in pressure or relative speed are high enough to make the edge of the droplet unstable, some small droplets peel off from the mother droplet, forming daughter droplets and some satellite droplets, which is known as erosive breakage. The concept of thorough breakage and erosive breakage explains the bimodal distribution of droplet sizes well.²⁰

If pigments, or more commonly, inorganic powders, are involved, published literature^{21–26} has shown the following general conclusions: (1) the particles should be well divided or loosely agglomerated; (2) the optimal stabilization effect can be achieved when the contact angle between a liquid–liquid interface and the particle surface is close to 90°; (3) and the hydrophilic particles prefer to stabilize oil-in-water emulsions and the hydrophobic particles prefer to stabilize water-in-oil emulsions. Still, knowledge about stabilized dispersion with a particle dispersant, e.g., the choice of the particles and dispersion of the particles, is still scant due to its complexity. It is believed that fine particles depress turbulence in the suspension by reducing the eddy size,²⁷ which consequently decreases the droplet size. Taguchi et al.'s research also illustrates that increasing the amount of inorganic powder results in a decrease in droplet size.²⁸

From this analysis, it is inferred that the droplet size can be decreased by increasing the agitation speed. Experiments with agitation speed ranging from 800 to 2000 rpm are conducted, and the results are shown in Figure 1A, in which the size distribution of the droplets against the agitation speed is plotted. It is shown that the average size of the corresponding droplets decreases

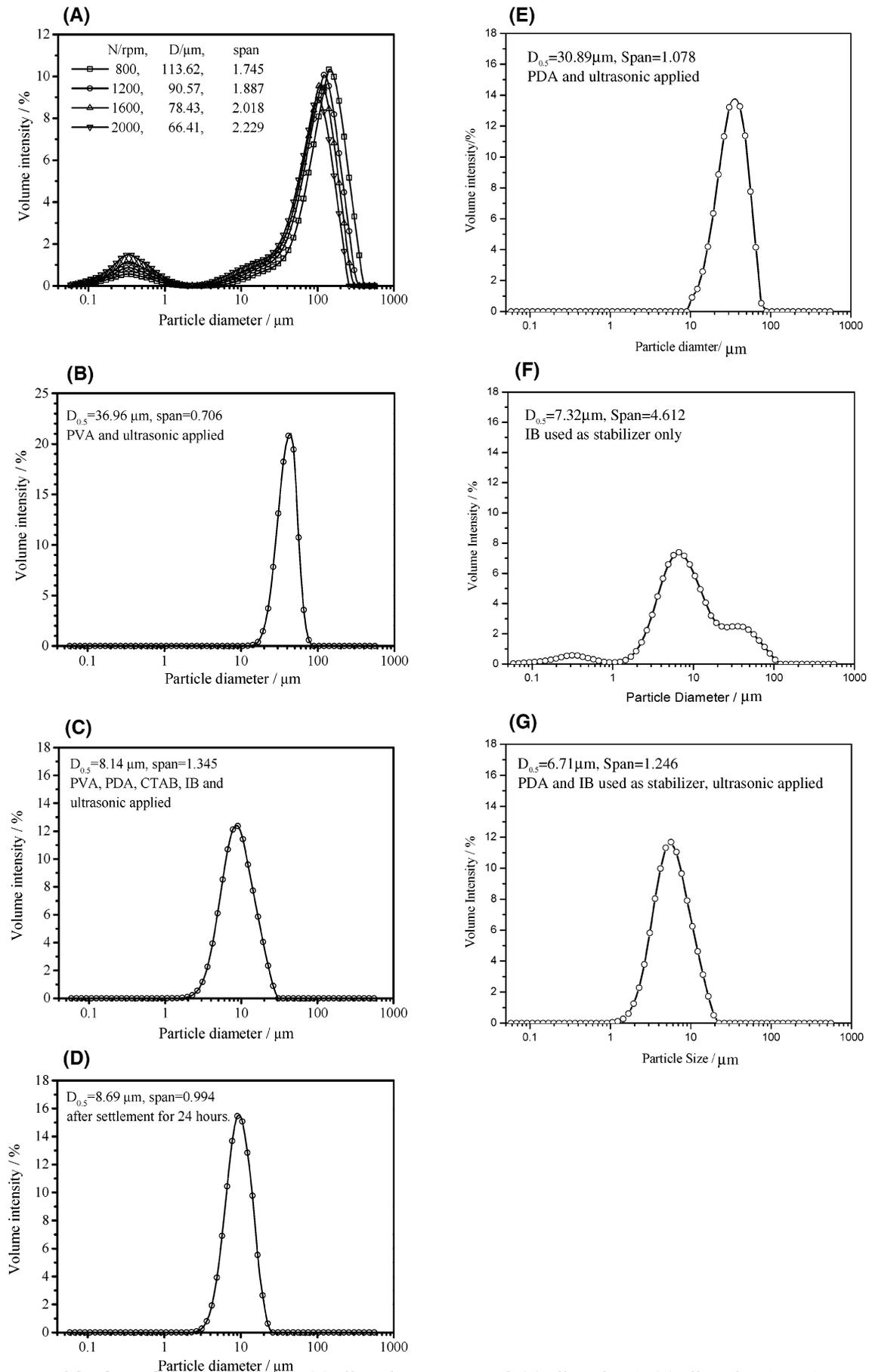


Figure 1. PSD of droplet at different conditions: (A) effect of agitation speed; (B) effect of PVA; (C) effect of PVA, PDA, CTAB, and IB, ultrasonic applied; (D) after settlement 24 h; (E) effect of PDA; (F) effect of IB; (G) effect of PDA and IB.

from 113.62 to 66.41 μm and all curves have two peaks, which are in the submicron range and the tens of microns range, respectively. It appears that erosive breakage prevails in the suspension due to the high speed of stirring, leading to the formation of submicron satellite droplets. It is also shown that although a high agitation speed can reduce the droplet size significantly, the average droplet size is still much larger than 10 μm .

When PVA1788 is added as a stabilizer, the droplet size distribution is shown in Figure 1B. It is shown that the average size of the droplets is reduced to 40 μm , and the size distribution (span) is also sharpened. The peak of submicron droplets disappears in Figure 1B, which indicates that thorough breakage predominates in the suspension. The change from Figure 1A to 1B seems caused by the adsorption of PVA molecular on the surface of droplets, which decreases the surface tension of the droplets and forms a protection film on the surface. The film may depress pressure fluctuations on the droplet and the relative velocity difference between the droplet and continuous phase; thus, erosive breakage no longer dominates in the suspension.

Since the droplet size is still too large for preparing a toner, ultrasonic (20 kHz, 100 W) treatment is applied to the suspension to reduce the droplet size. The experimental results show that ultrasonic energy does not obviously affect the droplet size when the droplet size is less than 50 μm . However, the final droplet with its size in the range 30–40 μm still cannot meet the requirement for toner preparation. Thus, another auxiliary surfactant is used to further lower the interfacial tension for reducing the droplet size. Although SDS has been considered as an effective surfactant for reducing surface tension, it is less useful here due to its strong ability to form micelles, which will lead to the formation of unwanted submicron particles. Apart from that, as an anionic surfactant, SDS will destroy the stability of the droplets and form a big chunk when cationic surfactant CTAB is used as negative CCA. Therefore, a desired surfactant should be capable of lowering the surface tension of droplets, free of formation of emulsion particles and compatible with CCA. After experimentation, PDA is chosen as the auxiliary surfactant, and the corresponding average droplet size is reduced to 20–25 μm with a span 1.5–2.0. Owing to PDA being a nonionic block copolymer consisting of a hydrophobic group (PPO) and a hydrophilic group (PEO), it may easily combine with PVA molecules to form a stable film to protect droplets from coalescence. Meanwhile, its extended PEO group and OH group may decrease interface tension to ensure fine droplet formation.

When IB particles are added, the droplet size is remarkably reduced to 7–12 μm . This is shown in Figure 1C. It is an exciting result because the droplet size is in the range required by toners and the stability of the suspension is excellent. Figure 1D shows that a better size distribution is obtained after 24 h of settling. Experimental results also show that when PDA is used as a stabilizer alone, the droplet size is about 30 μm as shown in Figure 1E. When IB particles are used as a stabilizer alone, the droplet size reduced to 10 μm with a wide size distribution (the span is 4.612) as shown in Figure 1F. But when PDA and IB particles are used together as a stabilizer, the droplet size is about 7 μm with a span of 1.246 as shown in Figure 1G, which is similar to the droplet size distribution as shown in Figure 1C. It implies that there probably exists a

Table 1. Particle Size Distribution of Polymerized Toner^a

sample	CCA (g)	IB (g)	<i>N</i> (rpm)	<i>D</i> _{0.5} (μm)	span
1	1.55 (Ni)	17.5	800	14.83	1.814
2	1.55 (Ni)	17.5	800	9.08	1.435
3	1.55 (Ni)	17.5	800	11.47	1.838
4	1.55 (Ni)	17.5	720	9.32	1.931
5	0.26 (Br)	17.5	720	13.76	1.581
6	0.51 (Br)	17.5	720	7.77	1.431
7	1.02 (Br)	17.5	720	9.62	1.956
8	1.55 (Br)	17.5	720	8.84	1.207
9	0.51 (Cr)	17.5	800	14.03	1.927
10	1.55 (Cr)	17.5	800	14.43	1.602
11	1.55 (Cr)	17.5	800	12.91	2.104
12	1.55 (Cr)	17.5	800	18.21	1.648
13	0	17.5	720	51.11	2.117
14	0	0	720	108.50	1.692

^a Ni: negrosine; Br, CTAB; Cr, E81; span = (*D*_{0.9} - *D*_{0.1})/*D*_{0.5}.

synergetic effect between PDA surfactant and IB particles in reducing droplet size. Gosa et al.²⁹ reached a similar conclusion with PEO–PPO–PEO block copolymers and silica used as the stabilizer. In this case, PDA's role can be regarded as a kind of PEO–PPO–PEO block copolymer. Finally, stable suspensions of droplets with an average size around 10 μm and PSD of 0.99 is obtained.

3.2. PSD of Polymerized Toner. Under the optimal conditions of forming the desired size distribution of the droplets in suspension, polymerization is initiated by increasing temperature. Dissolved initiator decomposes and produces free radicals to trigger the polymerization. As the polymerization of the monomer droplet proceeds, the viscosity within the particles increases rapidly. In this stage, droplets easily coalesce if a stabilizer cannot protect the droplet. This coalescence tendency is a predominant phenomenon until the viscosity is higher than a critical value for noncoalescence. Therefore, the PSD of polymerized toner is dependent not only on the size distribution of the droplets but also on the stability of the droplets.

Typical particle sizes of the polymerized toner with three kinds of CCA are shown in Table 1, in which the average sizes of *D*_{0.5} are all around 10 μm . However, compared with E81 and Nigrosine, the particle sizes of the toner are obviously smaller when CTAB is used as CCA. The reason is that CTAB itself is a kind of cationic surfactant, which can decrease the surface tension of the monomer. When the added amount of CTAB increases from 0.26 to 0.51 g, the average toner size of *D*_{0.5} remarkably reduces from 13.76 to 7.77 μm , but the span changes little, from 1.581 to 1.431. But adding more CTAB may result in the formation of submicron particles due to emulsion polymerization, which impairs the performance of the toner. For comparison, polymerization without IB or surfactants is conducted as well. The polymerized microspheres are of average sizes of 108.5 and 51.11 μm , respectively, which are all larger than the other toner sizes listed in Table 1. This also implies that there probably exists a synergetic effect between the surfactants and IB particles in reducing toner size.

The size distribution of the droplet changes with polymerization time is plotted in Figure 2. The average size of the droplet is reduced from 12.93 to 11.61 μm after 2.5 h of polymerization. This indicates that there is no obvious coalescence during polymerization and the droplet size shrinks during polymerization, which may be attributed to the density difference between the

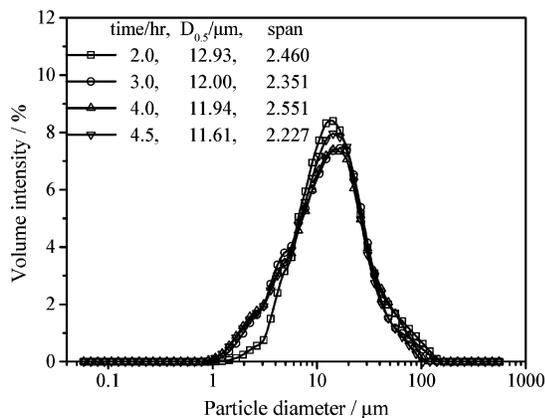


Figure 2. PSD of droplet change with polymerization time.

polymer and monomer. However, the shrinkage does not change the PSD much, and it is still useful to estimate the PSD of the toner by the PSD of the droplets. This also indicates that the assumption ignoring breakage and coalescence of droplets in the polymerization process is acceptable.

3.3. Morphology of the Polymerized Toner. The in situ suspension polymerized toner is spherical in shape as shown in Figure 3A. However, SEM images of individual particles in Figure 3B show that the surface of toner particles adheres many fine particles. Close-up images in Figure 3C indicate that the fine particles are rhombus IB particles and spherical polymerized particles.

Although some IB particles are exposed on the surface when droplet breakage occurs, the main contribution

to surface enrichment of IB particles may be attributed to Brownian movement of well dispersed IB particles, which bring particles from the inner side to the interface or even into the water phase.³⁰ The centrifugal effect due to the droplet's movement also drives more IB particles from the inner phase to the interface. The particles reaching the interface of a droplet and the water phase are easily localized due to the hydrophilicity of IB particles by minimizing the interface energy.^{26,29} The amount of particles that reach and stabilize on the surface is primarily determined by the cumulative diffusion length of the particles as expressed by eq 4

$$\langle L^2 \rangle^{1/2} = \left[\frac{k}{3\pi r} \int_0^t \frac{T dt}{\eta(t)} \right]^{1/2} \quad (4)$$

where $\langle L^2 \rangle^{1/2}$ is the diffusion length, k is the Boltzmann constant, r is the diameter of the additive particles, $\eta(t)$ is the zero shear viscosity, and T is the absolute temperature. This indicates that smaller particles more easily reach the surface and the diffusion tendency can be weakened by increasing the viscosity of the monomer droplets. When IB particles reach the surface, they will stabilize the monomer droplet together with the surfactant.

Since surfactants such as PDA, PVA, and CTAB are used in the suspension, micelles may form and react with free radicals decomposed from the dissolved initiator in the continuous phase, forming fine spherical particles by emulsion polymerization. Similar results are also obtained by Almog and Levy in their series research on suspension polymerization of polystyrene.³¹⁻³³

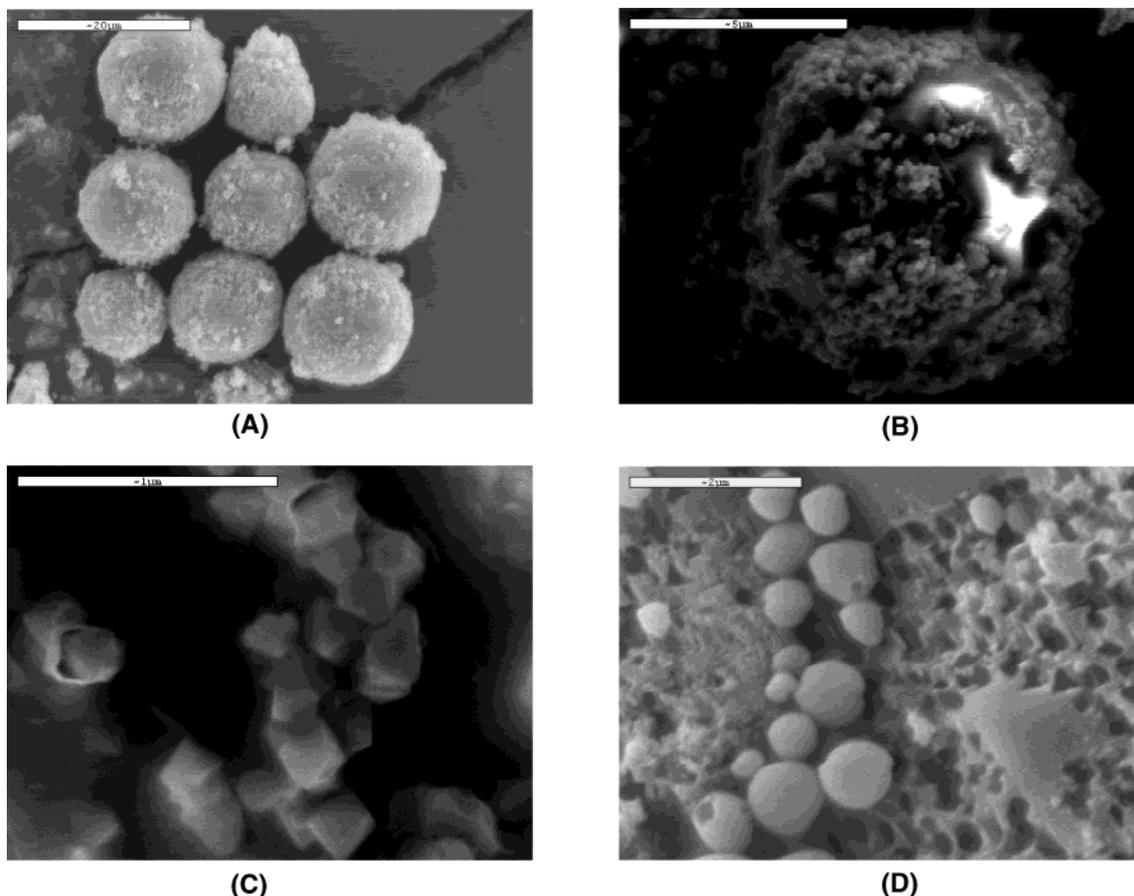


Figure 3. Morphology of polymerized toner at different magnification.

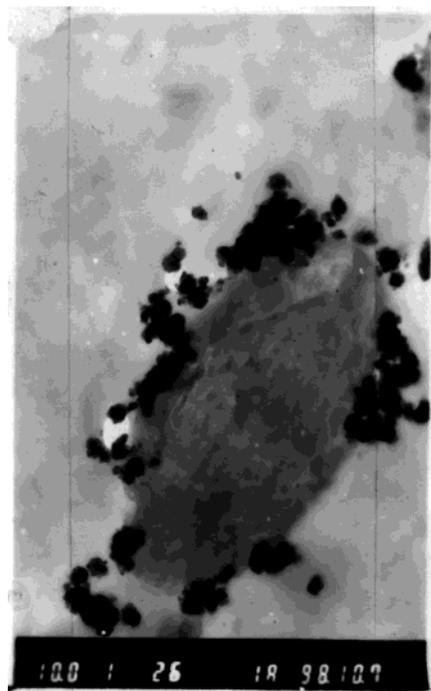


Figure 4. TEM image of polymerized toner.

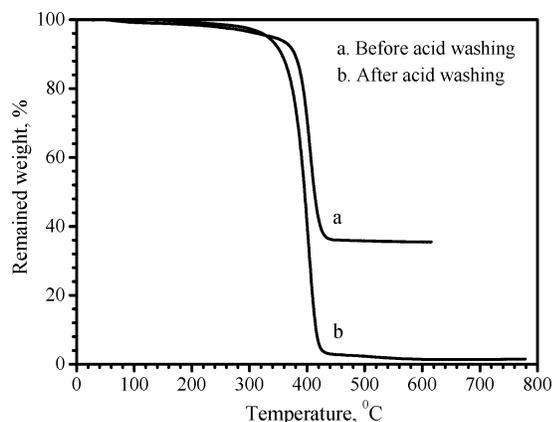


Figure 5. TGA curve of polymerized toner.

These fine particles prefer to locate on the surface of the toner for minimizing the surface energy. Figure 3D shows a surface image of a toner particle sample after acid washing. It is shown that surface enriched IB particles are dissolved forming small holes, and only those inert microspheres are left on the surface. The amount of fine microspheres is certainly dependent on the properties and quantities of the added surfactants.

Further inspection on the slice of a toner particle with TEM shows that most IB particles enrich on the toner surface as shown in Figure 4. A similar result was also obtained by Ochiai et al.,¹¹ and a similar result has also been found for carbon black filled polymerized toner.³⁴ Quantitative determination of the IB content inside of the toner is carried out by TGA analysis. The results from samples before and after acid wash treatment are shown in Figure 5. Before acid washing, the IB percentage in toner is 35.47% (wt); after acid washing, the IB percentage in toner is reduced to 1.52% (wt). This indicates that almost all IB particles enrich on the surface, and this is consistent with the TEM image shown in Figure 4.

Adhesion of fine particles on the toner surface will decrease the charge on the toner and deteriorate toner performance. Therefore, it is better to diminish the enrichment of IB particles on the toner surface. Previous research¹¹ indicated that this can be realized by improving the affinity between the particles and monomers. Thus, surface modifications utilizing coupling agents such as silane and titanate are conducted. Corresponding FTIR spectra of IB particles before and after modification indicated that their surface was successfully modified.³⁵ However, the polymerization results illustrate that the stability of the dispersion system is impaired or even destroyed; hence, large particles or even big chunks are produced. Since the system stability is built on the synergetic effect of hydrophilic IB particles and surfactants, the synergetic effect will be destroyed when the surface of IB particles is modified to be hydrophobic.²⁸

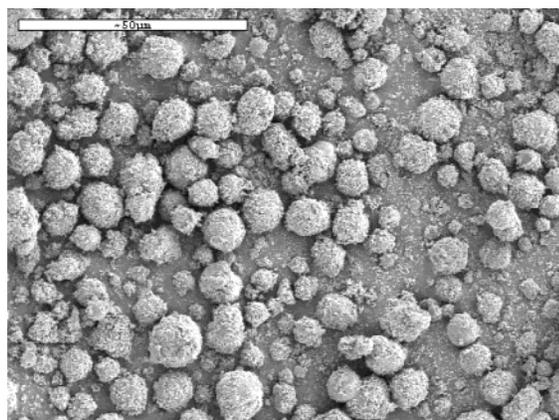
However, according to eq 4, increasing the viscosity of monomer can also reduce the cumulative length of the Brownian movement of inorganic particles. Thus, a prepolymerization method is carried out for reducing the surface enrichment of fine particles. The corresponding results are shown in Figure 6. The PSD of the toner changes little in comparison to the situation of nonprepolymerization, which indicates that the stability of the suspension is not influenced by prepolymerization. SEM images of individual particles indicate that the surface enrichment of IB particles is not reduced as much as expected.

Our previous research indicates that the added pigment has also a great effect on the polymerization reaction.³⁶ The added IB particles will speed up the polymerization reaction, which is shown in Figure 7.

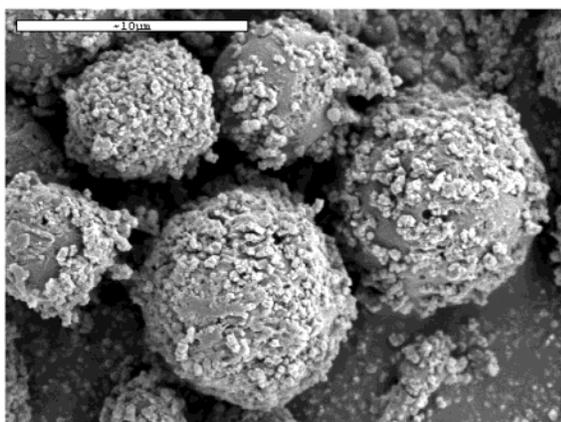
Although pigments such as iron black or carbon black adhered on the toner surface, their functions as colorant are less affected. Besides that, the charging behavior of polymerized toner can also be adjusted by adding either inner or outer charge control agent to meet toner's requirements. Thus, in situ suspension polymerization method is still a promising approach for toner preparation.

4. Conclusions

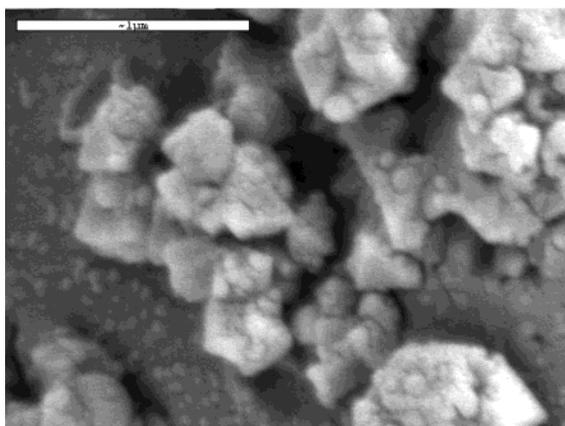
A spherical toner is prepared directly by in situ suspension copolymerization of a mixture of styrene/butyl acrylate in the presence of iron black. By optimizing agitation speed, surfactants, and pigments and introducing ultrasonic energy, droplets with average size of 10 μm and a narrow size distribution are obtained. There is a synergetic effect between surfactants and solid particles in reducing droplet size. After conducting in situ suspension polymerization, toners with average size around 10 μm and span of 1.5–2.0 are synthesized. The surface of the polymerized toner is partially covered by inorganic pigments and microspheres formed through emulsion polymerization. Surface pretreatments are also conducted using coupling agents and in situ prepolymerization. The corresponding experimental results illustrate that surface modification by coupling agents destroys droplet stabilization, resulting in large particles. However, in situ prepolymerization treatment is capable of maintaining the required particle size distribution and slightly reducing surface enrichment of fine particles.



(A)



(B)



(C)

Figure 6. SEM image of polymerized toner with prepolymerization at different magnification.

Notation

- ϵ = average energy dissipation rate per unit mass of vessel content ($\text{g}\cdot\text{s}^3/\text{cm}$)
 σ = interfacial tension (dyn/cm)
 n = impeller speed ($1/\text{s}$)
 ρ_c = density of continuous phase (g/cm^3)
 d = diameter of a droplet of volume (cm)
 k_1 = adjustable constant (–)
 k_2 = adjustable constant (–)
 k_3 = adjustable constant (–)
 $\langle L^2 \rangle^{1/2}$ = mean diffusion length (cm)
 k = Boltzmann constant (–)
 r = diameter of the additive particles (cm)

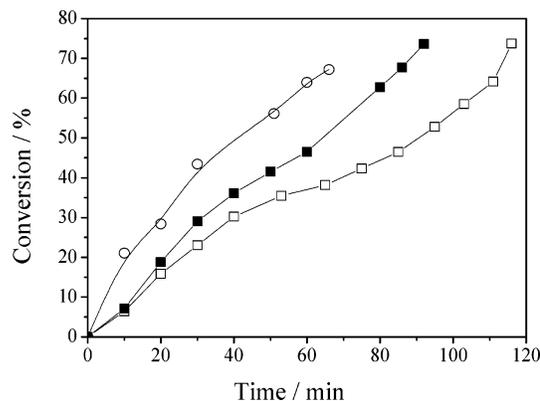


Figure 7. Styrene conversion as a function of time at different IB concentrations ($T = 80\text{ }^\circ\text{C}$, with ultrasonics): \square , $C_{\text{IB}} = 0\%$ (wt); \blacksquare , $C_{\text{IB}} = 5\%$ (wt); \circ , $C_{\text{IB}} = 15\%$ (wt).

$\eta(t)$ = zero shear viscosity ($\text{g}\cdot\text{cm}/\text{s}$)

T = absolute temperature (K)

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