

Preparation of Polymer Microspheres by Phase-Separation/Aggregation (PSA) Technique for Color Toner Applications

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Abstract

A particle formation method related to controlled phase separation of organic and aqueous phases, and limited aggregation/coalescence is reported. The method can be applied effectively to form microspherical polymer particles for use as electrophotographic toners. An organic solution containing a polymer resin dissolved in a solvent and an aqueous phase containing an anti-aggregation agent are prepared. The aqueous solution is added to the organic solution during vigorous stirring to facilitate aggregation of gel colloids and diffusion of solvent into the aqueous phase due to the partial aqueous solubility of the solvent. As opposed to the case when the organic phase is added to the aqueous phase under an extremely high speed of agitation ($>10,000$ rpm), this phase-separation/aggregation process only requires an agitation speed of 1,000–1,500 rpm. Furthermore, removal of solvents due to diffusion into the aqueous phase is in process at the same time as the formation of gel particles. The depletion of solvents in the organic phase results in solid particle formation. Fine control of particle size distribution can be achieved by careful adjustments of the viscosity values of both the organic and the aqueous solutions. This phase-separation/aggregation method offers numerous advantages for preparation of toners including fast production run and extremely sharp particle size distribution, with mean volume-averaged diameter to mean number-averaged diameter ratios d_v/d_n smaller than 1.1. The particle shape can also be tuned by the selection of different aqueous solubility of the solvents. Both styrene/acrylate based and polyester based materials can be applied for formation of microspherical particles by using the phase-separation/aggregation technique.

Introduction

Conventional toner production methods such as mechanical grinding and jet milling require certain levels of “brittleness” for the constituent resin materials[1]. Polyesters and polyamides, owing to their ductile properties, are not suitable for conventional toner production. In conventional milling methods, resin materials are mixed and kneaded with other constituents under high temperatures above resin’s transition points. Disadvantages related to high energy consumption and inefficient mixing and dispersion can not be neglected even in the advanced equipments using mechanical grinding or jetting processes. Although toner shape can be made spherical by advanced grinding or extra heat treatment, the limitation of broad size distribution still poses as a disadvantage and enormous amounts of electric energy and process time are required to classify the toner sizes. It is easily understood as toner sizes miniaturize the production costs of mechanical toner processes increase excessively.

Small particle sizes are desirable in regard to enhanced image resolution and thin coverage of toner layers. Sharpened particle size distribution leads to improved uniformity of tribocharges on individual toner particles, which is imperative to high-quality toner

image formation. Furthermore, spherical or pseudo-spherical particle shape is beneficial to toner flow, leading to better toner transfer efficiency from image-bearing photoreceptors to printing media. Spheroidization and narrow particle size distribution represent two major technical obstacles that need to be overcome in conventional mechanical grinding or jet milling processes.

For the improvements of toner properties and performance, wet processes employing chemical dispersions or solutions have been used to produce toner particles[2]. Due to the chemical synthetic characteristics in which particles are obtained through gradual growth from respective constituents, particle sizes and particle shape are relatively easy to control within the desirable specifications. As a result, chemical toners become popularly adopted in new color laser printers and color copiers to enhance the print quality. Widely commercialized chemical toners include suspension[3] and emulsion aggregation (EA)[4] toners.

Although both suspension and EA toners have been shown to exhibit enhanced characteristics of image formation, limitation still exists as the choice of polymer resin materials being constrained in styrene-acrylate based polymers. Both suspension and emulsion polymer reactions are used for addition-type polymerization where polyester based resins are not applicable. This paper reports a toner particle formation method utilizing commercially available resin materials, rather than starting from polymer synthesis of monomers. There are no constraints on selection of resins as long as they can be dissolved in suitable solvents. This method is based on controlled phase separation of organic and aqueous phases, and limited aggregation/coalescence to afford toner particles with extremely sharp size distribution and adjustable particle shape. Key parameters such as concentrations of the aqueous non-solvent phase, concentrations of the anti-aggregation agent, agitation speed, and concentrations of the organic phase are studied and analyzed for process optimization of toner particle growth[5].

Experimental

231.6g of styrene-acrylate resin (Sekisui), 144g of methyl ethyl ketone, 216g of cyclohexanone, 2.4g of salicylate-type CCA and 12g of wax were mixed under heating until wax was completely dissolved. The obtained solution was cooled and transferred to a jar containing 300g of 1-mm glass beads, and then 12g of a cyan pigment (PB-15:3) was added. The mixture was vigorously agitated and milled using a paint shaker for 48 hrs. After filtering to remove glass beads, a well-mixed methyl ethyl ketone/cyclohexanone solution was obtained, containing a solid content of 40 wt% which consists of 35.6 wt% of resin, 0.4 wt% of CCA, 2 wt% of cyan pigment and 2 wt% of wax.

20g of poly(vinyl alcohol) and 178g of de-ionized water were mixed and heated until complete dissolution of poly(vinyl alcohol). The solution was cooled to afford the aqueous non-solvent phase containing 10 wt% of poly(vinyl alcohol).

40g of the organic phase solution was added to a flask under a stirring speed of 1,200 rpm, and then the aqueous non-solvent phase was added to the mixture gradually. Phase separation of the organic and the aqueous phases occurred and continuous addition of the aqueous solution resulted in a phase-inversion state in which organic droplets were finely dispersed in aqueous solution. The total amount of the aqueous solution used was 70g in weight and duration time was 50 sec. The mixture was kept under agitation for 10 min to facilitate aggregation and coalescence of gel colloids. 200ml of de-ionized water was then added to the mixture to solidify the gel particles to afford solid particles. After filtering, the solid particles were washed repeatedly with water and then dried under vacuum to afford toner particles.

A particle formation method employing the phase inversion technique was also reported previously[6]. In the reported procedures, low air pressure and high heat were used to remove the organic solvent to obtain the solid particles. On the contrary, PSA method in this report allows spontaneous formation of solid particles owing to the hydrophilic solvent being extracted to the aqueous phase during the process.

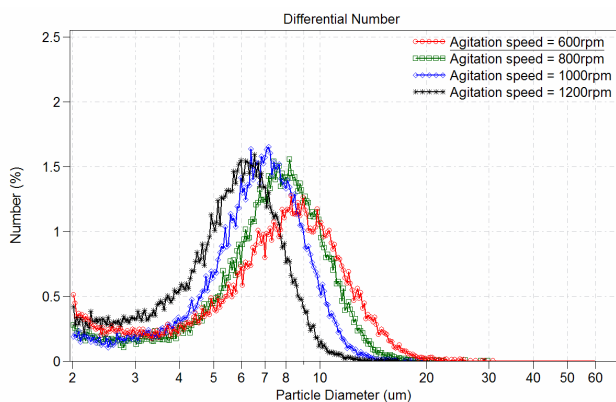


Figure 1: Particle Size Distribution Obtained by Various Agitation Speed.

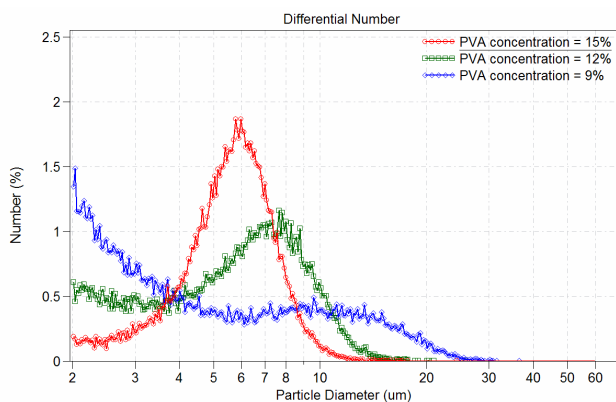


Figure 2: Particle Size Distribution at Various PVA Concentrations.

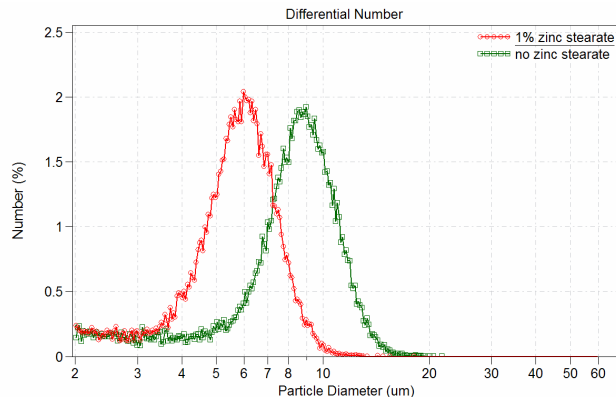


Figure 3: Effects of Zinc Stearate on Particle Size Distribution

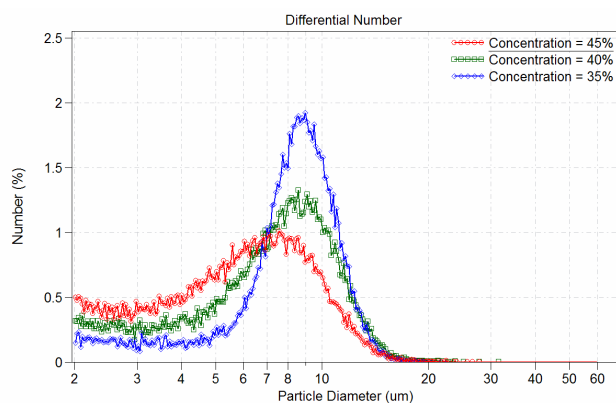


Figure 4: Particle Size Distribution Obtained from Various Concentration of Organic Phase.

To study the effects of concentration values of the non-solvent phase, stabilizing agent for phase transition (i.e. zinc stearate), stirring speed and concentration values of the organic phase on the particle size distribution, various parameters were adjusted and the resultant size distributions were analyzed and compared. The data are shown in Figures 1~4.

Results and Discussion

Key parameters for controlling particle size distribution and particle shape are identified and their effects are investigated as follows:

Agitation Speed: High agitation speed is effective for obtaining stabilized, finely-dispersed colloids from which small, uniformly sized particles can be achieved. Conversely, low stirring speed is prone to forming large particle sizes with a widened distribution. However, excessive stirring not only consumes a great amount of electric energy but also risks a possibility of overly aggregated particles due to increased collision frequencies of gel colloids, leading to enlarged particle size. In Figure 1, it is shown the optimal stirring speed is in the range of 1,000 to 1,200 rpm.

Concentration of the Aqueous Non-Solvent Phase: Figure 2 shows the particle size distribution curves obtained from

various concentration values of the aqueous phase. Non-solvent phase consisting of poly(vinyl alcohol), surface-active agent and water is shown to be capable of separating the organic solution into individual gel colloids and, equally important in terms of the functions, stabilizing the dispersion of organic gel colloids after phase separation. It is this stabilizing effect that allows the formation of small and finely dispersed gel particles with a uniform size distribution without the need of high-speed homogenizer equipment. In the meantime, a highly viscous non-solvent phase can suppress the depletion of organic solvent from the gel colloids, creating a pathway to control the shape and the size distribution of the particles after aggregation. It is possible to include a surface active agent, either ionic or non-ionic, in the non-solvent phase in addition to poly(vinyl alcohol). Surface active agents can reduce surface tension and therefore decrease the surface energy of gel colloids. Low surface tension is beneficial to formation of small, stable gel colloids. Various concentrations of the aqueous phase have been tested to adjust the viscosity values and the effects on particle size distribution are investigated. It is shown in Figure 2 that reduced viscosity of the non-solvent phase can lead to a broadened distribution or to a worse case, a flat distribution. Conversely, higher poly(vinyl alcohol) loadings or higher viscosity values can result in small sizes and narrow size distribution.

Stabilizing Agent for Phase Separation: The coalescence process of gel colloids can actually be divided into two stages, gel particle formation and gel particle growth. It is preferable that particle formation and particle growth be implemented consecutively instead of simultaneously in hope that the formation and growth can be regulated and controlled to achieve small sizes and narrow size distribution of the resultant solid particles. It is found the addition of a stabilizing agent, zinc stearate, can reduce the particle size and shift the distribution curve to the left as indicated in the data shown in Figure 3. The addition of zinc stearate has a dramatic effect on the particle size changing from an average value of 8.2 μm without zinc stearate to 5.7 μm in the presence of zinc stearate. The distribution curve also becomes narrow in the presence of zinc stearate. Zinc stearate seems to be able to stabilize the gel colloids in phase separation, achieving uniform size distribution of the gel colloids. The stabilizing agent, in combination with the use of highly viscous non-solvent phase, allows the coalescence process being separated into respective, individual stages of gel particle formation and gel particle growth. Adequate amounts of zinc stearate affect the particle size distribution favorably, achieving small sizes and narrow size distribution. Excessive amounts of zinc stearate, on the other hand, can lead to an increase of viscosity of the organic phase, creating an opposite effect of enlarging the particle size. Detailed mechanism of how zinc stearate assists the stabilization of phase separation is still subject to further investigations. One plausible scenario is that zinc stearate, being submicron particles dispersed in the organic phase, can act as seeds for heterogeneous nucleation and thus expedite the creation of small and uniform-sized gel particles.

Concentration of the Organic Phase: The stability of gel particles in phase transition is also affected by the concentration of the organic phase. As a result, the particle size

distribution can be modulated by changing the concentration of the organic phase as indicated in Figure 4. High resin concentrations with their high solution viscosities are prone to formation of enlarged gel particles and broadened size distribution, whereas low resin concentrations lead to stable, small, and uniform-sized particles. Nevertheless, production of toner particles operated at low polymer resin concentrations is not cost-effective given the consideration of low throughputs of products. It is therefore very important to optimize the process parameters to achieve an efficient toner production that is both certifiable in product quality and economically viable.

Figure 5 shows an SEM micrograph of toner particles prepared by PSA method using a styrene-acrylate based polymer resin. It is shown PSA toner particles can be made very spherical in shape which is advantageous for applications requiring excellent toner flow and high toner transfer efficiency.

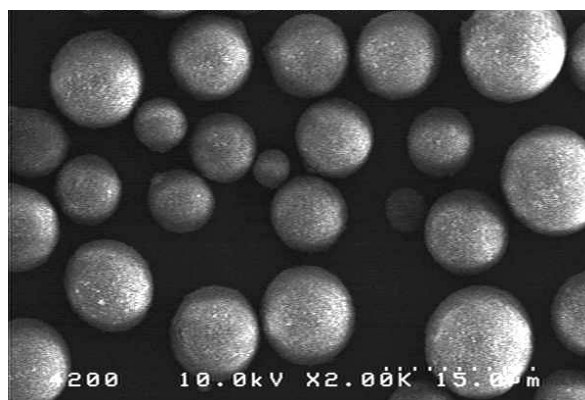


Figure 5: SEM micrograph of toner particles made with PSA method.

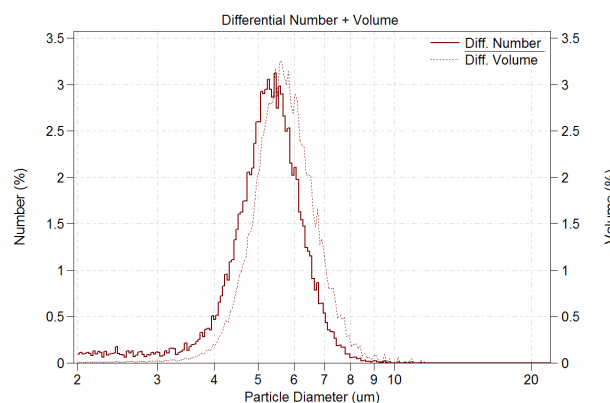


Figure 6: Particle size distribution of PSA toner particles made with a polyester resin.

To test the versatility of this phase-separation/aggregation method for toner production, other classes of resin materials were also used to prepare the organic phase solution. Both bis-phenol and non-bis-phenol type polyesters have been employed for the preparation of toner particles. Figure 6 shows the size distribution

of thus obtained toner particles, indicating a number-average size (d_n) of 5.25 μm and a volume-average size (d_v) of 5.76 μm . The size distribution is extremely sharp with the d_v/d_n ratio equal to 1.097.

Conclusions

A phase-separation/aggregation method has been demonstrated to provide an efficient process for production of color toners which exhibit narrow size distribution and a particle shape approaching spherical. Common toner constituent components including resin, pigment, CCA and wax are shown to be compatible with the process and can be applied in a wide range to afford toner particles for practical applications. Key process parameters such as concentration of the non-solvent phase, addition of a phase-stabilizing agent, agitation speed and concentration of the organic phase have been identified and studied to find the effects on the particle size and size distribution. This method has been shown applicable for both styrene-acrylate and polyester based resin materials.

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