Control of Particle Shape by Adjusting Solidification Rates in Aggregation of Dispersed Gels

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Abstract

This paper reports a chemical method, phase-separation/ aggregation (PSA), to prepare CPT particles with surface morphology tuned by adjusting the process parameters during aggregation and coalescence of the particles. It is shown a highly hydrophilic organic solvent favors the formation of spherical particles due to the facile gel formation and expeditious solidification. Deviations of spherical particle shape can be achieved by inclusion of a less aqueous-soluble organic solvent in which the viscosity of gel colloids is increased gradually, allowing shear force of the non-solvent phase to apply its effect on the particle shape. The particles can be made potato-shaped or elliptically shaped by adjustments of the aqueous solubility of the organic solvent. The effect of shear force can also be magnified by increasing the speed of stirring during particle coalescence, with a finding showing a distorted, elliptical shape as a result of increasing agitation speed. The viscosity or the solid content values of the aqueous non-solvent phase solution are also found to have effects on the particle shape. It is found a dilute aqueous phase solution is prone to forming spherical particles, whereas a concentrated aqueous phase allows the particles to become non-spherical. These parameters are studied to elucidate the interplay of viscosity and surface tension, and to understand their effects on the particle shape. The results of this paper show that the particle shape obtained from the PSA method can be fine tuned by modulating the process parameters.

Introduction

Particle shape and size distribution of toner particles are important factors in determining the performance for electrophotographic printing machines, especially for advanced high-resolution and color laser printers. More importantly, the particle shape affects toner tribocharge, flowability, readiness for wiper blade cleaning and particle stacking, all related to print performance on the media. Rugged toner particles made with conventional grinding or jetting methods tend to exhibit high tribocharge and good blade cleaning efficiency. But the rugged surface structure also results in inferior particle flow, and uneven toner stacking and thus non-uniform prints. Whereas, toner particles with smooth surface structure, spherical shape and narrow size distribution tend to exhibit low tribocharge and decreased blade clean-ability, but their uniformity in tribocharge and print density is enhanced.

Since particle shape is extremely important for print performance, a lot of development efforts have focused on the control and manipulation of shape factors in toner production. There are two shape factors (shape factor, SF) used extensively to define particle shapes:

$$SF_1 = \left(\frac{length^2}{area}\right) x \frac{\pi}{4} x100 \quad \text{----------(1)}$$

$$SF_2 = \left(\frac{perimeter^2}{area}\right) x \frac{1}{4\pi} x100 \quad \text{----------(2)}$$

in which SF_1 is related to the sphericity of the particle shape. An SF_1 value of 100 represents a perfectly spherical shape and a larger deviation from 100 means the shape is less spherical. SF_2 is used to describe the roughness of surface structure. An SF_2 value of 100 represents a perfectly smooth surface, whereas a larger deviation from 100 means the surface is more rugged.

Modulating the shape factor by adjusting process parameters in toner production is important for achieving optimized properties and performance of toner particles. Toner particles with different size values would acquire different electric charge values after tribicharging in cartridge motion. Excessively small toner particles would acquire a high Q/M value and thus are not easy to be transferred for image development. Furthermore, non-uniform tribocharging tends to create problems in image registration, resulting in blurred image development. Either non-uniform size distribution or irregular particle shape can lead to loose stacking of toner layers, and thus requiring thick piles of toner layers to meet the print density requirement. This would increase toner consumption and the printed paper is prone to becoming curled. Conversely, uniform toner size facilitates a dense packing of toner layers and thin piles would be enough to afford required print density. The resultant images are transparent under light and appear as vivid color outputs. Moreover, thin and efficiently stacked toner layers are advantageous for expeditious image fixing at fusing units and thus enabling low-energy, high-speed printing.

Dry toner technology has been used in printing machines such as laser printers, copiers and multi functional printers. There are a sequence of imaging processes in which toner development, implementing the transfer of toner from toner hopper to latent image-bearing photoreceptor and the following transfer of toner from photoreceptor to paper, is an essential element for image formation[1]. Toner particles produced from chemical routes, owing to the sharpened particle size distribution and uniform particle shape, are beneficial to an efficient, economical toner development. Newly introduced desk-top printing machines are gradually adopting chemical toner technology to fulfill small footprint, yet fully functioned and high-quality performance. Widely commercialized chemical toner products include suspension[2-3] and emulsion aggregation (EA)[4-5] toners.

Both suspension and EA processes have constraints in the choice of resin materials due to characteristics of the respective polymerization reactions. It is also very difficult to manipulate the control and tuning of particle shape, in which sphericity is the most common shape obtained from suspension and EA processes.

Although EA process has been shown to allow adjustment of toner shape, its procedure is not easy to operate. This paper reports a shape-adjusting method based on phase-separation/aggregation of particles in which the creation of gel colloids and the ensuing aggregation and coalescence of colloids can be controlled effectively, resulting in fine control of the particle shape.

Experimental

To a flask the resin and organic solvent were added and the mixture was heated and stirred until complete dissolution of the polymer resin. The solution, after being cooled, was transferred to a jar containing a color pigment and glass beads of 0.8~1.0 mm in diameter. The jar was then subject to milling by a paint shaker for 48 hrs. After filtering to remove glass beads, an organic phase solution was obtained.

Adequate amounts of poly(vinyl alcohol) were mixed with water in a flask and the mixture was heated until complete dissolution of the polymer. After being cooled to room temperature, an aqueous non-solvent phase solution was obtained.

X grams of the organic phase solution were placed in a reaction flask under stirring, then the non-solvent phase solution was added at a constant rate. As the addition of non-solvent phase continued, the organic phase and the non-solvent phase became phase separated and finally a dispersion of gel colloids of the organic phase in the aqueous phase was obtained. In total, Y grams of the aqueous non-solvent phase solution were used. After forming the gel colloids, stirring was continued for 10 min to facilitate aggregation and coalescence of the gel colloids. Plenty of water was then added to the mixture to solidify the gel particles. During the mixing of the organic and aqueous phases, solidification occurs spontaneously due to partial solubility of the organic solvent in water. After repeated washing with water and filtering, solid particles were obtained and then dried in vacuum to afford dry toner particles. Figure 1 shows the schematic diagram of the phase-separation/aggregation (PSA) process[6] and detailed constituent compositions of the experiments are listed in Table 1.

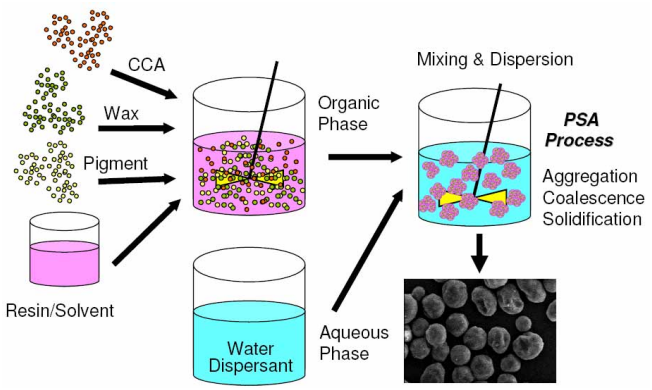


Figure 1: *PSA Process.*

Table 1: Compositions and Process Parameters. (SA : styrene-acrylate resin)

	organic phase(weight%)					process parameters			shape factors	
test	solid content, %	polymer resin	pigment	solvents MEK/EAc	dispersant PVA	organic phase, X g	aqueous phase, Y g	stirring speed (rpm)	SF_1	SF_2
1	40%	SA-1 35%	PB15:3 5%	1/1	15%	100	200	1000	149	130
2	40%	SA-1 35%	PB15:3 5%	7/5	15%	100	200	1000	128	121
3	40%	SA-1 35%	PR146 5%	1/1	15%	100	200	1000	132	128
4	40%	SA-1 35%	PR146 5%	3/2	15%	100	200	1000	126	115
5	45%	SA-2 40%	PB15:3 5%	1/1	15%	500	1000	1000	122	114
6	45%	SA-2 40%	PB15:3 5%	1/1	15%	500	1000	1400	203	126

Particle size distribution was measured by Multisizer 3 Coulter Counter, using a 100-µm test cell for size measurements of 2~60µm. The measurement was started with a calibration test of the standard solution; the sample solution was then added until an intensity reading of 10%. A total counts of 30,000 particles was set to complete the measurement which lasted about 10~30 sec. The data were presented as both number-averaged and volume-averaged particle size.

Particle shape was analyzed by ImageJ image analyzer on the CCD images from an optical microscope. The software calculates the longest diameter, cross sectional area, and perimeter values, from which the shape factors, SF_1 and SF_2, are determined according to equation (1) and (2).

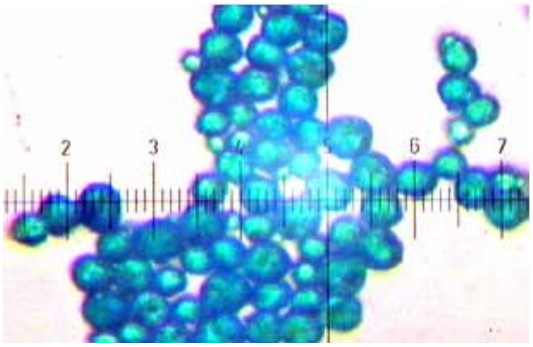
Results and Discussion

During the mixing of the organic and aqueous phases in PSA processes, three different stages can be observed and identified. They are: completely miscible organic and aqueous phases with the organic being the continuous phase; phase separated organic and aqueous phases with the organic being the continuous phase; and separated organic and aqueous phases with the aqueous being the continuous phase. It is in the third stage where a dispersion of gel colloids, precursor for solid particles, is formed. The aggregation and coalescence process consists of firstly the creation of gel colloids, secondly controlled aggregation on a limited scale, and finally coalescence.

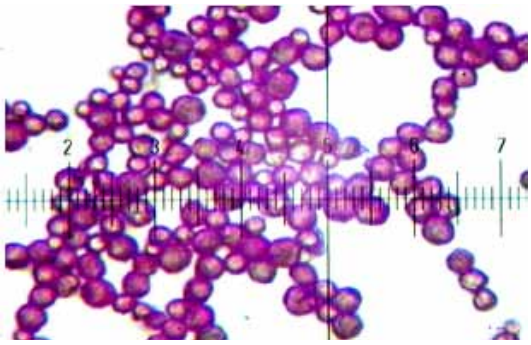
In the following, the variations of particle shape obtained by

adjusting process parameters are shown to elucidate the interplay of different parameters and the resultant shape factors:

Aqueous Solubility of The Organic Solvent: As shown in Table 1, weight ratios of the binary solvent system, namely relative amounts of methyl ethyl ketone (MEK) and ethyl acetate (EAc), were varied to change the hydrophilic characteristics of the solvent system. Solid particles are formed as a result of solvent depletion in the gel colloids which in turn is a result of diffusion of solvent to the aqueous phase. Consequently, the aqueous solubility of the solvent is a determining factor affecting the rate of solidification. The whole PSA process can be best described as dynamic aggregation and coalescence procedures.



(a) Particle shape of test 2



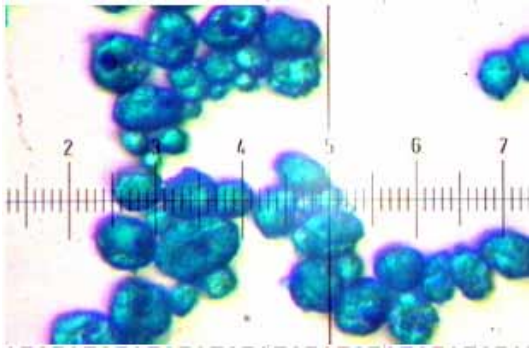
(b) Particle shape of test 4

Figure 2: *Particle shape for system with a high aqueous-soluble solvent, methyl ethyl ketone.*

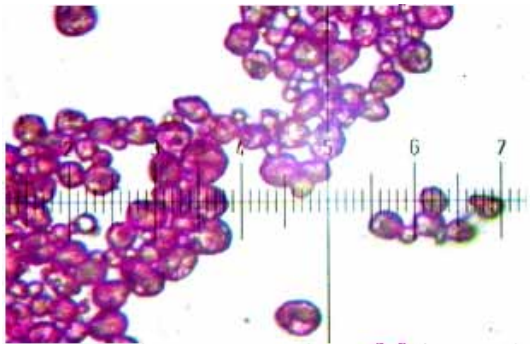
In Figure 2 and 3 it is shown a highly aqueous-soluble solvent, methyl ethyl ketone, favors spherical particle shape. Conversely, if more ethyl acetate, a less aqueous-soluble solvent, is used the particle shape tends to be non-spherical.

In aggregation and coalescence, the gel particles of the organic phase experience a dramatic change of viscosity as depicted in Figure 4 in which EF denotes elastic force, SF represents shear force, ST represents surface tension, and VF is viscous force, respectively. Curve A represents a case when a highly water-miscible solvent is used in the organic phase; curve B indicates a case which includes a medium solubility of solvent in water; curve C is a case when a poor aqueous-soluble solvent is used in the organic phase. For example, in case of curve B when viscosity increases and becomes greater than a critical viscosity, μ_1, viscous force (VF) becomes dominant compared to both shear force (SF) and surface tension (ST). The gel particles are no longer shrinkable by cutting with the shear force induced by stirring and therefore these particles enter into the period of particle growth due to the collision and aggregation of otherwise small particles. As the solvent being continuously extracted or diffused into the aqueous phase, the viscosity reaches above μ_2 and the particles become stabilized without any further change in size due to the elastic behavior of the gels.

In cases of test 2 and test 4 (Table 1 and Figure 2), highly aqueous-soluble MEK is extracted rapidly and its change of viscosity is mimicked as in the case of curve A in Figure 4 where viscosity increases instantaneously, leading to an expedient particle growth and quick stabilization of particle size. As a result, the particle shape approaches spherical. In cases of test 1 and test 3 (Table 1 and Figure 3), a higher content of ethyl acetate, a less aqueous-soluble solvent, leads to a prolonged period of particle growth and the particle shape is affected more by the shear force induced by stirring. As a result, the particle shape approaches non-spherical.



(a) Particle shape of test 1



(b) Particle shape of test 3

Figure 3: *Particle shape of system using 1:1 methyl ethyl ketone/ethyl acetate as solvent.*

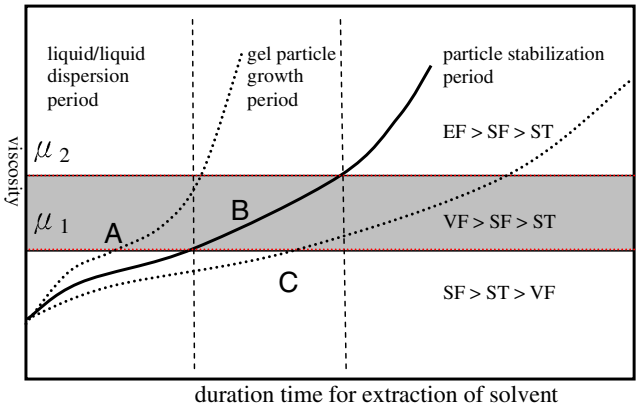
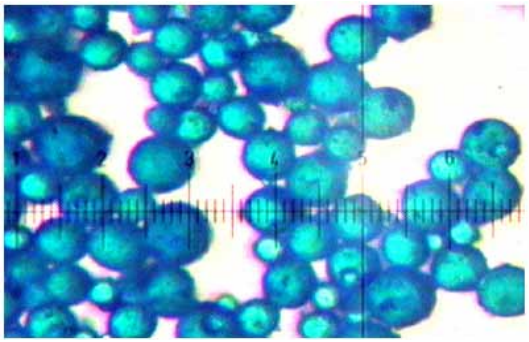


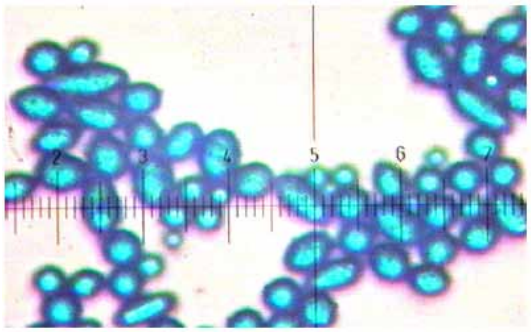
Figure 4: *Schematic diagram for the change of viscosity during aggregation and coalescence of particles.*

Shear Force: The effect of shear force on the particle shape was determined by varying the speed of stirring while maintaining the same compositions. It is shown in Figure 5 and Table 1, a higher shear results in elliptical or oval shape due to distortion by the shear force as compared to more spherical shape at a lower speed.

In essence, the variation of solution viscosity and its effects on the particle shape can be explained as a schematic drawing shown in Figure 6:



(a) Particle shape of test 5 at a stirring speed of 1,000 rpm



(b) Particle shape of test 6 at a stirring speed of 1,400 rpm

Figure 5: *Effect of shear force on the particle shape.*

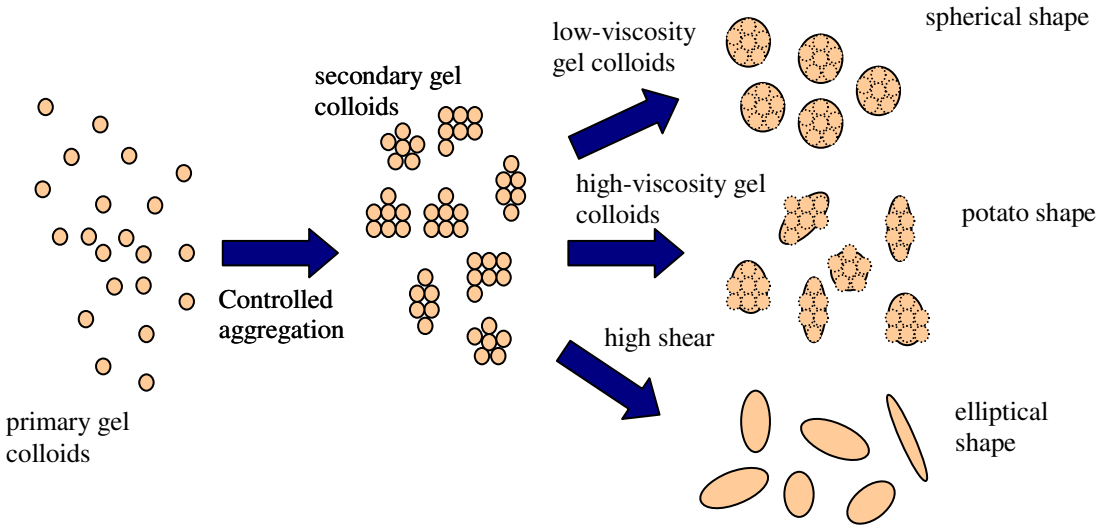


Figure 6: *Schematic diagram indicating relationship between viscosity variation and particle shape.*

Gel colloids with low viscosity values exhibit a high tendency towards cohesion owing to the dominant role of surface tension which leads to smooth, spherical shape of the particles. Conversely, high viscosity values result in potato-shaped, rugged surface domain consisting of incompletely fused surface structure. Furthermore, secondary gel particles under the influence of high shear force are prone to forming distorted, elliptical-shaped particles. In general, the particle shape is a result of the interplay of three forces, i.e. surface tension (cohesion), shear force applied by the viscous non-solvent phase under stirring and viscous force

within the organic phase. These three forces can be correlated with the process parameters and their relations can be categorized as two cases. The first is for the case when shape is controlled by surface tension and viscous force within the organic phase. The second is related to shape controlled by shear force induced by stirring. In the first case, the variation of viscous force and relative importance of surface tension can be adjusted by changing the extraction rate of solvent into the aqueous phase which in turn can be achieved by the selection of different solvents. In the second case, shear force can be manipulated by changing the speed of stirring or by changing the viscosity of the aqueous solution.

Conclusions

A particle formation method based on phase-separation/ aggregation process is reported to prepare toner particles exhibiting narrow particle size distribution and controlled particle shape. Key process parameters such as the aqueous solubility of the solvent and stirring speed have been identified and studied for tuning the shape factors to optimize the toner properties and performance.

Acknowledgment

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Author Biography

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