Silica-Polymer Composite Particles for Toners: Synthesis, Characterization and Performance

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Abstract

Evolution of toner technology together with a demand for faster printing puts new requirements on external additives used in toner formulations. Spacer particles, which are added to protect the toner surface from mechanical stress resulting from collisions with the particles of carrier or the doctor blade, have become a progressively more important part of the additives packages.

Polymeric particles, colloidal silica, and low surface area fumed silica are usually used as spacers. However, each of these materials has significant drawbacks. For instance, triboelectric charging properties of polymeric particles are not always optimal, large colloidal silica often drops off from toner surface, and low surface area fumed silica typically has broader than desired aggregate size distribution.

At the NIP28 conference we introduced the organic/inorganic composite spacer additives which combine benefits of polymeric and colloidal silica spacer additives [1]. We demonstrated that the new particles have lower drop off from the toner surface than colloidal silica additives.

In this paper we demonstrate how the new material particle size and shape could be controlled and present results of a print test where a model toner was formulated with the silica-polymer composite spacer additives.

Introduction

Colloidal organic/inorganic composite particles are a new class of materials that have been developed by Cabot Corporation for application in digital printing. These particles can be tuned in size from approximately 60 to 500 nm in diameter, have raspberry-like morphology with colloidal silica protruding from the surface and a particle core made of an acrylic polymer. A representative image of the colloidal composite particles obtained using a He ion microscope is shown in Figure 1. The ~25 nm colloidal silica particles protruding from the surface of the composite particles are clearly observed.

The primary function of colloidal composite additives is to act as a spacer particle and improve durability of the toner by protecting other additives present on toner surface from being embedded into the toner during the development and, as a result, improve the durability of image density, especially in formulations with low T_g toners.

In this paper we demonstrate that the composite particle size can be tuned by changing the size of colloidal silica or by using different silica to monomer ratios. Performance of the new material in a 10,000 page print test in a formulation with a model toner also will be discussed.

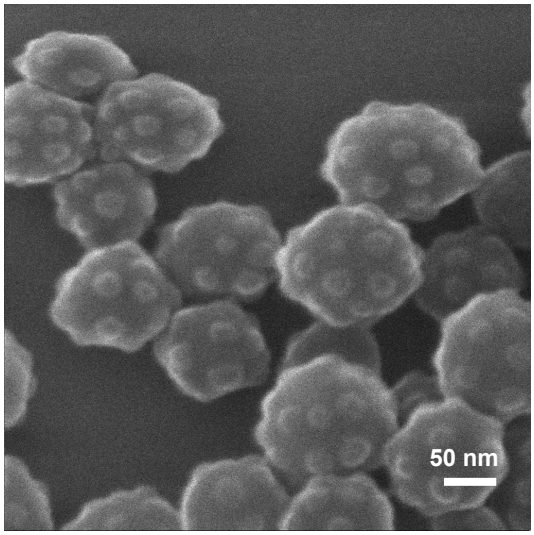

Figure 1. *A He ion microscope image of the colloidal composite particles. The 25 nm colloidal silica particles are protruding from the surface.*

Experimental

Synthesis of colloidal composites

Preparation of oil-in-water emulsions containing methacrylate monomers stabilized with colloidal silica particles has been described in the literature [2, 3]. We extended this process and adapted it towards synthesis of hydrophobic dry powders suitable for applications in toners [4].

At a high level, the material's synthesis procedure includes formation of a colloidal silica stabilized emulsion of methacrylate monomer in water, thermally initiated free-radical polymerization of the monomer, hydrophobic surface treatment of the obtained silica-polymer composite particles, and drying and de-agglomeration of the final product.

In this study, three sets of samples, **1**-**4**, **5**-**8**, and **9**-**11** were prepared using colloidal silicas CS-1, CS-2 and CS-3, respectively. The colloidal silica surface areas, measured by BET method, and the mean particle sizes, provided by the supplier are presented in Table 1.

Four different monomer to silica mass ratios R1, R2, R3, and R4 were used during the syntheses with R1<R2<R3<R4.

Table 1. Surface area and particle sizes of colloidal silicas used in the synthesis of 1-11.

Colloidal silica	Particle size (nm)	BET surface area (m^2/g)
CS-1	25	128
CS-2	15	243
CS-3	7	318

In the sets of **1-4** and **5-8** the monomer to silica ratios were varied from R1 to R4, while in the set of **9-11** the ratios were varied from R2 to R4.

Table 2. Colloidal silicas and the monomer to silica ratios used in the synthesis of 1-11.

Sample	Type of silica	$M_{monom.}$ / M_{silica}	Sample	Type of silica	$M_{monom.}$/ M_{silica}
1	CS-1	R1	**7**	CS-2	R3
2	CS-1	R2	**8**	CS-2	R4
3	CS-1	R3	**9**	CS-3	R2
4	CS-1	R4	**10**	CS-3	R3
5	CS-2	R1	**11**	CS-3	R4
6	CS-2	R2			

Characterization

Particle size measurements

The particle size distributions were measured by dynamic light scattering using Nanotrac 250™. The samples were prepared by dispersing ~0.02 g of composite particle in 20 mL of MEK and sonicating the dispersions for 15 minutes, using a Misonix XL2020 Sonicator at power setting of 6.

Electron microscopy

The SEM images of selected samples dispersed on the surface of a model polyester toner were collected at Cabot's Electron Microscopy laboratory.

Performance testing

Preparation of developers with toner

A Universal IKA mill M20 was used to mix **1-11** with a commercial 9 µm black polyester chemical toner containing no other external additives. Colloidal composite particles were loaded at 4 wt%. To prevent the toner from overheating and melting, mixing was performed in three 15 s pulses separated by 15 s cooling intervals.

Developers were prepared by mixing the formulated toners with a Cu-Zn ferrite carrier coated with a silicone resin (carrier particle size 60-90 µm; Powdertech Co., Ltd.). The developers contained 2 wt% of toner and 98 wt% of carrier.

Before the measurements of triboelectric charge, the developers were conditioned for several hours at 30 °C /80 % RH (further in the text abbreviated as HH) conditions.

After conditioning at HH the triboelectrostatic charge was developed by rolling the jars containing the developers on a roll mill for 30 min at 185 rpm. The triboelectric charge was measured using the blow off method [5].

Measurements of triboelectric charge

Triboelectric charge measurements were performed using a Vertex T-150 tester (Vertex Image Products, Inc.).

1 g of charged developer was placed in a Faraday cage and the toner blow off from the carrier was performed for 1 min using ~20 psi air jet. The electrostatic charge on the toner remaining in the Faraday cage carrier was measured by the electrometer built in Vertex T-150 tester and the mass of blown off toner was determined as a difference between the weights of the Faraday cage before and after the blow off.

Print test

The print test was performed using Samsung ML-1710 laser printer. A commercial 9 µm black polyester chemical toner containing no other external additives was formulated with 0.6 wt% of hydrophobic fumed silica CAB-O-SIL TG-308F (Cabot Corporation) and 2 wt% of composite particles, sample **1**, or a 100 nm treated colloidal silica, CS-4. The calculated toner surface coverage in case of **1** is 40 % and in case of CS-4 is 30 %. The printing speed was set at 17 ppm and 10,000 pages were printed.

Results and Discussion

Eleven samples, **1-11**, of colloidal composite particles with three different colloidal silicas and four monomer to silica ratios were prepared and the particle sizes of these samples were measured by dynamic light scattering, Figure 2. The collected data show that the size of colloidal silica and the monomer to silica ratio could be used independently to tune the size of the composite particles. In the case of composites prepared with 25 nm colloidal silica, **1-4**, the range of sizes accessible by changing the ration from R1 to R4 spans from 90 to 260 nm. This range is 2-3 times wider than the analogous ranges for 15 or 7 nm colloidal silica particles.

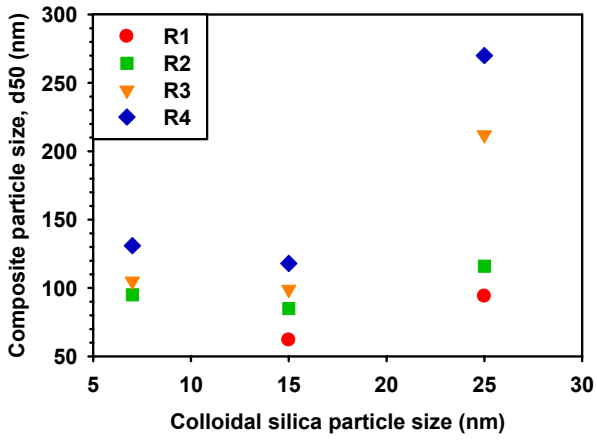

Figure 2. *Mean size of composite particles as a function of size of colloidal silica and monomer to silica ratio.*

The data also show that composites with smaller particle size, down to 60-70 nm, could be prepared using 15 nm silica than the composites prepared using 25 nm silica. We were able to produce composite particles as small as about 90 nm in the latter case.

We found that lack of the monomer in the reaction prevents effective synthesis of well-defined particles in the formulations where the ratio is significantly smaller than R1.

The TEM images of **2** and **6** are shown in Figure 3. The images show that 25 nm colloidal silica particles protrude from the surface of **2** and affect the particle shape making it less spherical. The 15 nm silica (Figure 3B) and 7 nm silica (TEM image not shown), do not significantly affect shape of composite particles.

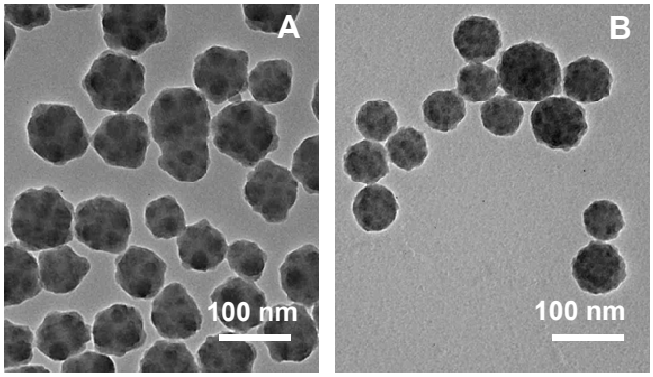

Figure 3. *TEM images of **2** (A) and **6** (B).*

Results of the triboelectric charge measurements for a model toner formulated with **1-11** are shown in Figure 4 and 5. The data presented in Figure 5 demonstrate that within each of the three sets of samples made with different silicas the absolute value of tribocharge decreases with the increase of monomer to silica ratio. At the same time there is no clear trend in the electrostatic change for the samples with the same ratio and different silicas.

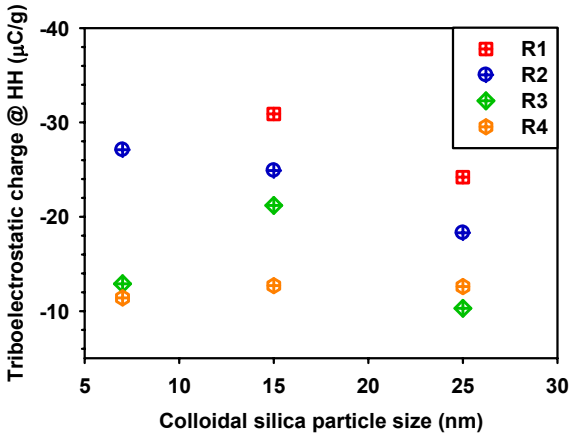

Figure 4. *The effects of colloidal silica size and monomer to silica ratio on triboelectric charge of **1-11**.*

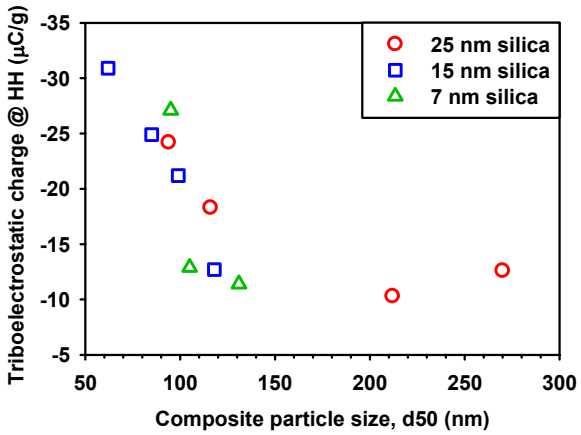

Figure 5. *Triboelectric charge (HH) of the model toner mixed with **1-11** as a function of composite particle size. Additive loading is 4 wt%.*

Data plotted in Figure 5 illustrate the relationship between the composite particle size/surface area and the electrostatic charge. The absolute value of the electrostatic charge changes from -32 µC/g down to -12 µC/g upon increase in particle size from 60 to 130 nm. This drop in the electrostatic charge is likely related to the decrease in additive surface area and, as a result, decrease in toner surface coverage from ~110 % to 55 %. The charge does not fall below -10 µC/g for 210 and 270 nm additives probably because the toner surface coverage in this case drops to ~30 % and the charge is largely determined by the charging properties of the toner itself.

Sample **1** was selected for print test because it provided a good combination of relatively high triboelectric charge and ~95 nm particle size. Colloidal spacer additives with such particle size are widely used in modern formulations of toners. As a reference material, a 100 nm HMDS treated colloidal silica, CS-4, was used, Table 3.

Table 3. Particle size and surface area data for 1 and CS-4 used in the print test.

Sample	d10 (nm)	d50 (nm)	d90 (nm)	BET SA (m^2/g)
1	70	95	135	65
CS-4	80	104	132	30

Changes of the image density as a function of the number of printed pages for toners formulated with **1** and CS-4 are shown in Figure 6. While the formulation containing **1** showed minimal decrease in the image density during the test, from 1.4 to 1.3, the image density for formulation containing CS-4 decreased by approximately 50 %, from 1.2 to 0.6.

Results of the triboelectric charge measurements for the freshly formulated toners and for the toners which remained in the cartridge after 10,000 prints are presented in Table 4.

Table 4. Results of the triboelectric charge measurements for fresh and old, i.e. remaining in the cartridge after 10,000 prints, toners formulated with 1 and CS-4.

Sample		HH (μC/g)
1	Before printing	-24.0±2.5
	After printing	-26.4±2.0
CS-4	Before printing	-15.1±0.8
	After printing	-6.6±0.5

The data demonstrate that the toner formulated with **1** has much better durability than the toner formulated with CS-4. A more than 50 % decrease in triboelectric charge was observed for the toner formulated with CS-4 while no significant change was registered for the formulation containing **1**.

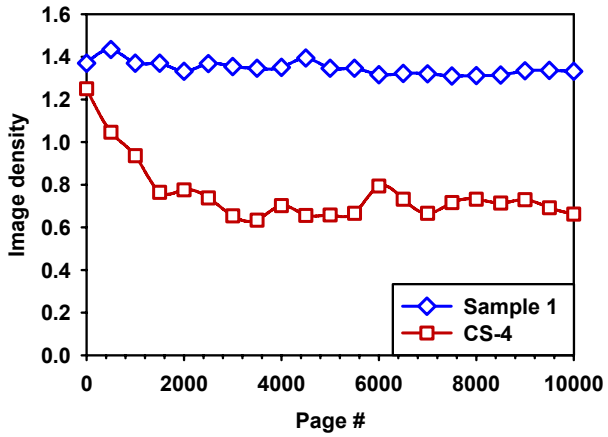

Figure 6. *Image density as a function of number of printed pages for toner formulations containing **1** and CS-4.*

The SEM images of the toner remaining in the cartridge after the print test show that toner formulated with **1** preserved its shape much better than the toner formulated CS-4, Figure 7. Particles of the latter toner became more irregular and show more sharp edges. Overall, shape of toner particles changed from potato to gravel-like. Furthermore, the SEM images collected at higher magnification, Figure 8, show that the surface of toner formulated with **1** has noticeably smaller number of dimples than the surface of toner formulated with CS-4.

The SEM images of the fresh toners were also recorded. The low magnification images of the freshly prepared toners mixed with **1** and CS-4 (not shown) look very similar to Figure 7A. The high magnification image of the toner mixed with **1** (not shown) looks similar to Figure 8A, while the high magnification image of the fresh toner formulated with CS-4 shows that the toner surface is smooth and does not have many dimples (Figure 9).

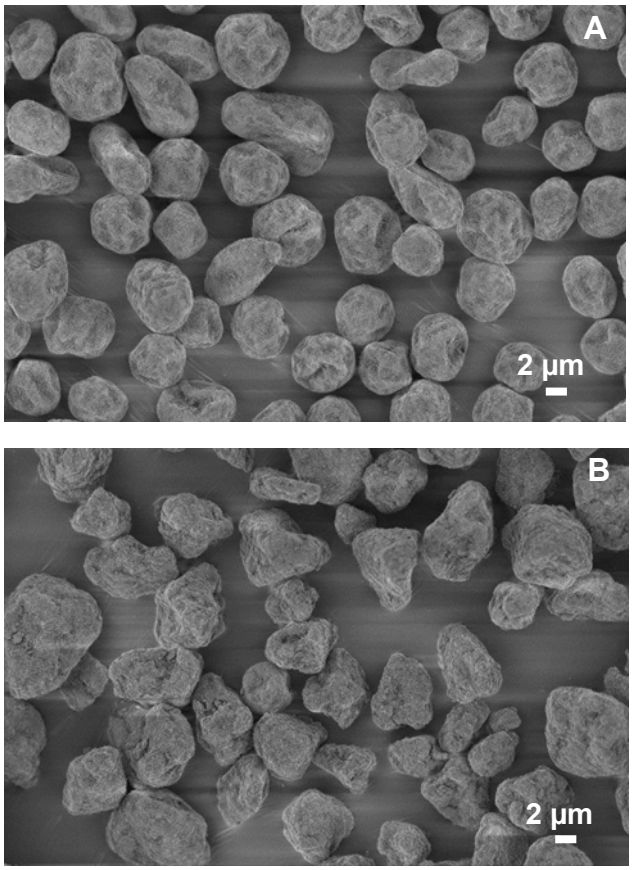

Figure 7. *SEM images of the toner remaining in the cartridge after 10,000 prints. Upper image (A) shows toner formulated with **1** and lower image (B) shows toner formulated with CS-4.*

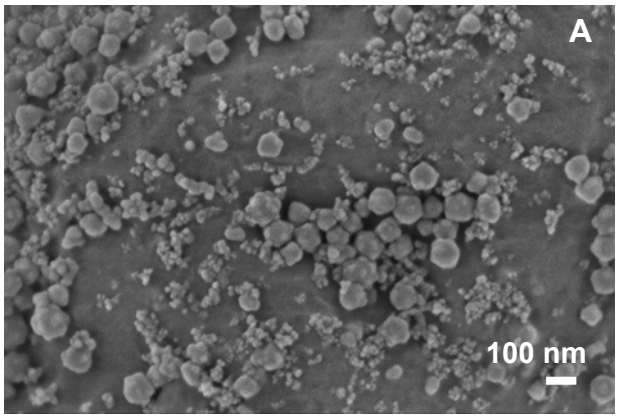

Figure 8A. *High magnification SEM image of the toner formulated with **1** and remaining in the cartridge after 10,000 prints.*

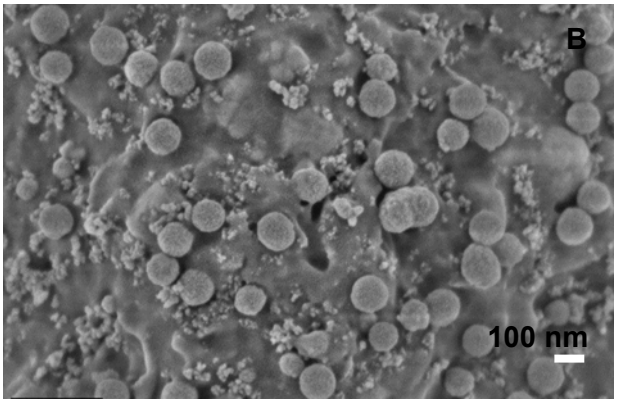

Figure 8B. *High magnification SEM image of the toner formulated with CS-4 and remaining in the cartridge after 10,000 prints.*

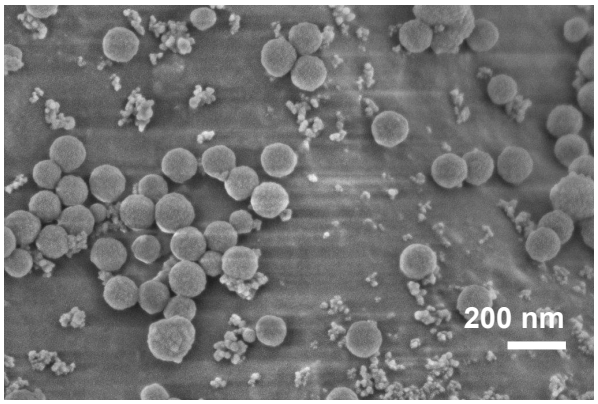

Figure 9. *High magnification SEM image of the toner formulated with CS-4 before the print test.*

Conclusions

The following are the primary results and conclusions from the work presented in this paper:

(1) A flexible method for the synthesis of colloidal silica-polymethacrylate composite particles suitable for application in toners has been developed.

(2) Three sets of colloidal composite samples, **1**-**4**, **5**-**8**, and **9**-**11**, containing 25, 15 and 7 nm silica particles were prepared and characterized by particle size measurement and electron microscopy methods.

(3) It has been shown that composite particle size can be tuned by: (a) by changing the size of colloidal silica used in the synthesis or (b) by changing the monomer to silica mass ratio.

(4) The collected data indicate that triboelectric charge of the new additives scales with the particle size/surface area and does not depend on the size of colloidal silica.

(5) Results of the print test show that a toner formulated with the new additive, **1**, maintains constant image density over 10,000 pages while the image density for the toner formulated with colloidal silica, CS-4, decreases by 50%.

(6) The triboelectric charge data and analysis of the SEM images of toners remaining in the cartridge after 10,000 prints show that **1** is significantly more effective in maintaining toner durability than CS-4.

References

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