Fusing Study of Silica-Polymer Composite Particles for Toners

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Abstract

Toner fusing is a critical step which determines both the quality of printed image and the amount of energy consumed by a laser printer. Therefore, manufacturers of laser printers and toners constantly work on improving fuser units and designing new toner formulations. It turns out that the external additives, which are primarily used to improve toner electrostatic charging, flowability, and durability, also affect toner fusing [1]. For instance, when used at relatively high loading treated silica affects toner melt flow behavior by increasing viscosity of melted toner. If viscosity of melted toner is high this results in inefficient flow of toner and poor fusing. Some toner manufacturers have begun using new external additives which enable fusability at low fusing temperatures.

Silica composite particles - a new class of materials that was developed by Cabot Corp. for application in laser printer toners [2-4]. At the NIP29, we discussed how this material is synthesized and how it improves toner durability [5]. In this paper we demonstrate that the model toner formulations containing silica composite additives have better fusability than the formulations containing colloidal silica.

1. Introduction

In recent years, with the technology improvement in digital printers and copiers, there is a strong demand for high reproducibility of latent images and high resolution, as well as durability in long-run use and reduced energy consumption.

In order to satisfy the requirements described above, how to engineer the new toners having high durability, high stability and low-temperature fusability has been a popular study topic. For example, to improve toner durability in long-run use, Cabot Corp. has developed silica composite particles - a new class of materials for application in toners.

Size of silica composite particles can be tuned from approximately 60 nm to approximately 500 nm. The particle surface could be rendered hydrophobic by treating it with different silanes. The primary function of silica composites, is to act as a spacer protecting additives with smaller particle sizes from becoming embedding into the toner surface. Because the particles have irregular shapes and multiple contact points, they adhere well to the toner surface and don't "roll" like a ball; due to its density being ~20-25 % lower than the density of colloidal silica, silica composites show lower "drop-off" from toner surface than similar size colloidal silica.

In this paper, we demonstrate that silica composite particles can also improve toner performance in low-temperature fusability.

2. Experimental

2.1. Materials

The silica composite particles used in this study were produced by Cabot Corp. and sold under commercial name ATLAS™ 100. Particles of this material have raspberry-like morphology and they consist of an acrylic polymer core and a colloidal silica shell. The surface of these particles is hydrophobic due to the treatment with hexamethyldisilazane (HMDZ). Particles used in this study have an average size of ~80 nm.

Hydrophobically treated colloidal silicas are widely used in toner formulations as spacer additives. Two colloidal silicas with the particle sizes of 85 nm and 105 nm, both treated with HMDZ, were used in this study as the reference materials.

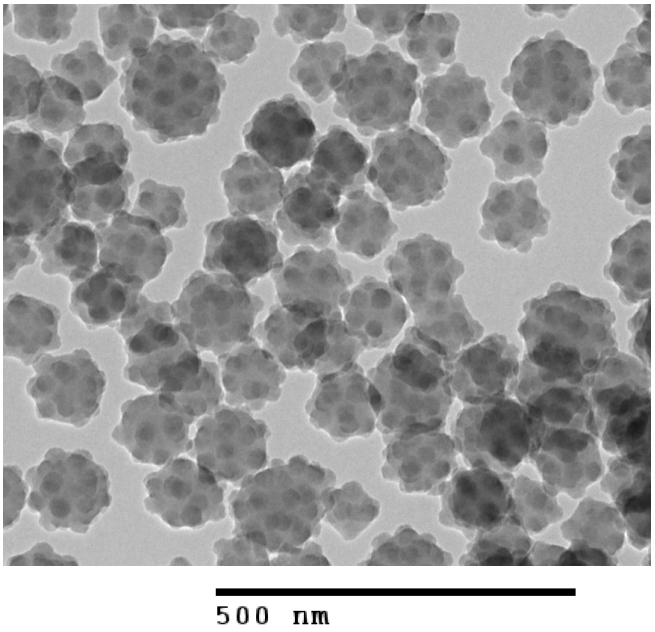

Figure 1. TEM image of ATLAS™100 silica composite particles.

2.2. Particles Characteristics

2.2.1. 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 silica-polymer composite particles in 20 mL of MEK and sonicating the dispersions for 15 minutes using a Misonix XL2020 Sonicator at a power setting of 6.

Table 1. Particle size and surface area data for silica-polymer composite particle and colloidal silicas used in this study.

Sample	d10 (nm)	d50 (nm)	d90 (nm)	BET SA (m^2/g)
Atlas™100	70	95	135	65
TG-C110	80	104	132	30
EP-C210	57	87	125	45

2.2.2. Thermal property

Thermal diffusivity of colloidal silica and silica composites were measured using HyperFlash apparatus LFA 467 manufactured by NETZSCH. In this method, a powder sample is compressed into a thin self-supporting pellet and one side of this pellet is heated by a short energy pulse from a Xenon lamp. From the resulting temperature rise at the rare surface of the pellet measured with the infrared detector, the thermal diffusivity is determined.

All measurements were performed at 25˚C. Samples were compressed into the pellets under constant pressure of 368 psi. Thickness of the pellet made of silica composite particles was 1.41 mm while thickness of pellet made of the colloidal silica was 0.82 mm.

2.3. Toner formulations

A Universal IKA mill M20 was used to mix additives with a commercial 9 µm negative magnetic toner. Depending on toner formulation, colloidal composites (ATLAS™ 100, available from Cabot Corp.) and colloidal silica (TG-C110 and EP-C210, developmental materials) were loaded at 1, 1.2 or 4 wt%; fumed silica (TG-308F, 200 m^2/g fumed silica surface treated with silicone oil, available from Cabot Corp.) was loaded at 0.6 wt% (Table 2). To prevent the toner from overheating and melting, mixing was performed in three 15 s pulses separated by 15 s cooling intervals.

Table 2. Model toner formulation (Additives)

	Colloidal silica	Colloidal Composite	Fumed Silica
1	EP-C210: 4%		
2		ATLAS™100: 4%	
3	TG-C110: 1.2%		TG-308F: 0.6%
4		ATLAS™100: 1.0%	TG-308F: 0.6%

2.4. Toner performance

2.4.1. Fusability Measurement

Prints were made with a commercial HP laser printer with black magnetic toner on a commercial A4 paper. Paper with toner deposited on it was removed from the printer without fusing. Toner fusing was done separately in an oven. The oven temperature was varied between 90 ˚C and 110 ˚C while fusing time was always 5 minutes.

Scotch® 810 tape manufactured by 3M (width 19 mm) was attached to the fused image using a controlled pressure (500 g weight). The tape was pulled from the paper at a very slow speed. Image density of the paper before and after the removal of the tape was measured. The change in image density of before and after the taping represents the fusability.

$$\text{Fusability} = (\text{I. D.}_{\text{before}} / \text{I. D.}_{\text{after}}) \times 100\% \quad (1)$$

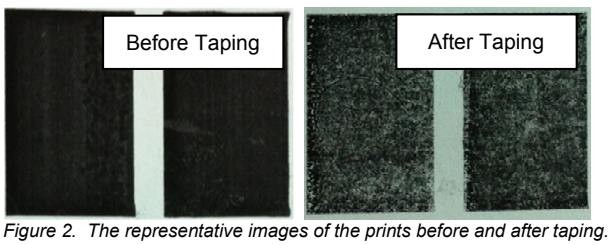

Figure 2. The representative images of the prints before and after taping.

2.4.2. Electron Microscopy

SEM images of toner fused to paper were collected using ZEISS Ultra Plus field emission scanning electron microscope. Before the imaging, the samples were coated with a thin layer of gold to reduce the electrostatic charging.

3. Results and Discussion

3.1. Thermal diffusivity of colloidal silica and silica composites

Depending on the design of the fusing unit, the toner typically is fused at temperature range from 130 to 180 °C under a pressure range of 300-700 kPa and it stays in the fuser zone for 10-20 ms [6]. The dynamics of the fusing process is complex. It involves heat transfer and interactions between different types of materials present in the toner all happening during a very short time.

It is known that thermal diffusivity of a material is a measure of how fast the material transfers heat. It is possible that thermal diffusivity of external additives affects thermal diffusivity of toner and its volumetric heat capacity, which, according to some reports [1], affects quality of toner fusing. Therefore we decided to measure thermal diffusivity of the new material – silica composite and compare it with thermal diffusivity of colloidal silica which is currently widely used in toner formulations. Results of our measurements are summarized in Table 3.

The collected thermal diffusivity data indicate that silica composite particles have significantly higher thermal diffusivity than colloidal silica.

Table 3. Thermal diffusivity for silica composite particle and colloidal silica)

Sample ID	Measurement temp. (°C)	Density (g/cm^3)	Thermal Diffusivity (mm^2/s)
TG-C110	25	2.2	0.083 ± 0.006
ATLAS™100	25	1.7	0.142 ± 0.005

3.2. Toner fusability

Toner warming, softening, and melting are the 3 stages of the fusing process shown in Figure 3. When temperature of the toner increases above its glass transition temperature toner particles start softening, cohere, and melt. Application of pressure by the fuser roll results in adhesion of the melted toner to the paper.

Figure 3. Schematic representation of toner fusing steps as a function of temperature. A good fusabiltiy requires toner to melt rapidly as temperature increases.

In the first set of experiments image density was measured for prints made with a commercial HP1020 printer using toner formulations containing EP-C210 colloidal silica and ATLAS™ 100 silica composites. Ten pages of paper were printed for each toner formulation and 9 measurements of image density before and after taping were made at different areas of each printed page. Averaged results are plotted in Figure 4. The collected data clearly

shows that formulation with ATLAS™ 100 silica composites affords prints with much higher image density than formulation with colloidal silica of similar size. The smaller decrease of image density upon taping in case of formulation with ATLAS™ 100 is an indication of a better fusing.

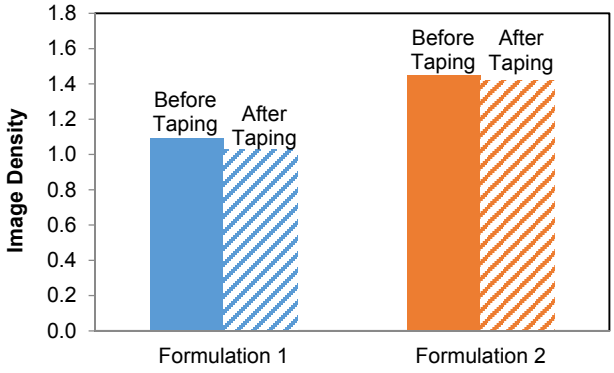

Figure 4. Results of image density measurements before and after taping for prints made with toners containing colloidal silica and silica-polymer composites. The prints were made with a commercial HP1020 model printer with a fuser operated at 180 °C.

In the second set of experiments we decided to test whether the trend for better fusing for toner formulation with silica composites would preserve at the lower fusing temperatures. In order to do this we turned off the printer fuser and performed fusing in an oven at a set of pre-defined temperatures in the range between 90 and 110 °C. Results of fusability measurements obtained in these experiments are plotted in Figure 5. The collected data suggests that the toner containing silica composite particles shows faster increase in fusability with temperature than the toner containing colloidal silica.

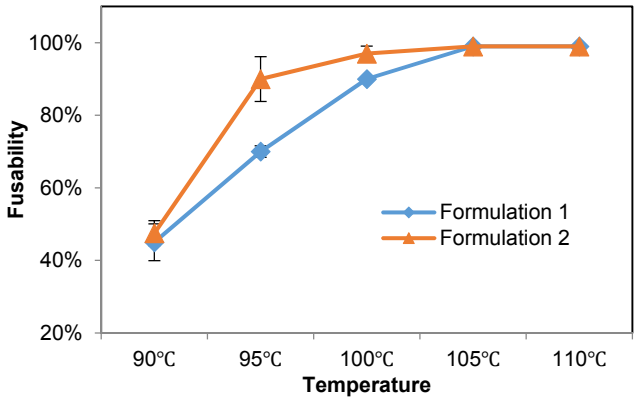

Figure 5 Results of toner fusability measurements as a function of fusing temperature. Toner fusing was done in an oven for 5 min.

In the third and final set of experiments low-temperature fusability measurements were performed for a fully formulated toner where loading of silica composites and colloidal silica were at a more "realistic" levels of 1 and 1.2 wt%, respectively, and high surface area fumed silica was added to enhance toner free flow. The difference between the loading of silica composites and colloidal silica is to reach the same toner coverage and compensate for a difference in skeletal densities of these materials.

Results of fusability measurements presented in Figure 6 again show that formulation containing silica composites has better fusibility.

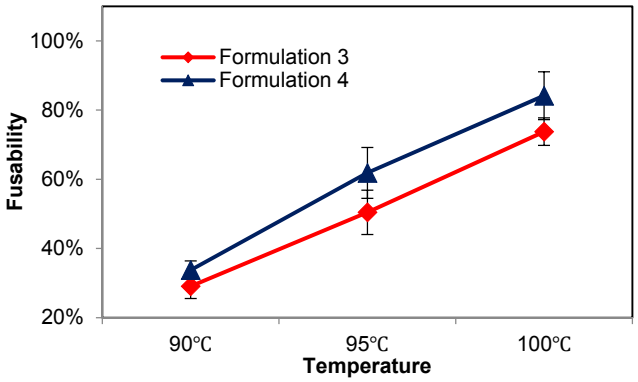

Figure 6. Fusability as a function of temperature for the fully formulated toners.

SEM images of fully formulated toner (Formulations 3 and 4) containing silica composites and colloidal silica fused to paper at 180 °C are shown in Figure 7.

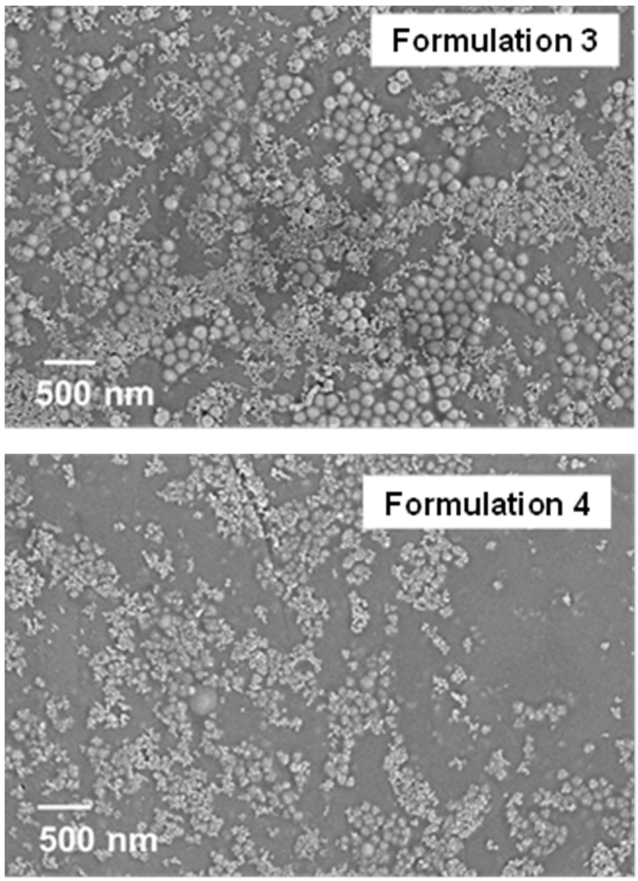

Figure 7. SEM images of fully formulated toner fused to paper.

Aggregates of many TG-C110 spacer additives can be clearly seen on the surface of fused toner while only few ATLAS™ 100 particles could be observed on the surface. The reason for this difference is not clear. It could be that the polymeric component of the silica composites has better affinity to toner polymer and this helps composite particles to distribute more uniformly within the layer of fused toner.

4. Conclusion

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

(1) Collected data demonstrates that the model formulations containing silica composite additives show better fusability than the formulations containing colloidal silica of similar size.

(2) Thermal diffusivity of silica composites measured at 25 °C is significantly higher than thermal diffusivity of colloidal silica.

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Author Biography

Li Cheng obtained his master degree at Qingdao University of Science and Technology in the field of polymer material process in 2008. Then he joined in Cabot and worked in Application Development lab. He is working as Application Development Specialist for toner in Cabot, including Carbon black for pigment and treated silica for external additives for toners.