Aggregation Behaviors of Colloidal Particles for Production of Polyester-Based Chemically Prepared Toner

Sung Yul Kim, Bo Young Kim, Kyung-Yol Yon Advanced materials R&D Center, Samsung Fine Chemicals Co., Ltd. Daejeon, South Korea

Abstract

High performance, full color electrophotographic printers are gaining acceptance in many office environments. In this study, we controlled the aggregation of three different colloidal dispersions using four different multivalent metallic coagulants over a wide pH range to develop a polyester-based chemically prepared toner (CPT). The quantity of the each metallic coagulant required to achieve a narrow particle size distribution at the target mean aggregate size reached an optimum operation limit that, when exceeded produced a viscous, inoperative, sludge in the reactor. The optimal pH condition for each coagulant system was mainly dependent on the electrostatic balance produced by the deprotonation of the exposed carboxylic acid groups on the polyester resin particles at a pH between 5.5 and 6.5. Additional electrostatic interactions between the polyester colloidal dispersions and the monovalent cation ($M1^+$) metallic coagulation system at high electrolyte concentrations created a favorable environment to reproduce core-toner particles with a narrow particle distribution at the target mean size.

By manipulating the aggregation process, the individual nano-dispersions coalesced in an aqueous environment to form a polyester-resin based chemical toner that was uniform in particle size and had low total VOC level. The printing and image performance of this toner using a color laser printing system meet the specifications of major OEM printer engine manufactures.

Introduction

Use of polyester as binder resin in toner is usually desired because of a unique melt flow and mechanical toughness at low melt viscosity, which is highly desirable in high-speed digital printing applications. The alternative vinyl polymers are quite brittle at low molecular weights that is necessary to achieve high gloss and color saturation. As a consequence, most styrene-acrylate based toners have higher melt viscosity and provide lower gloss prints than polyester based toners [1].

However, manufacturing methods of polyester based CPT are not introduced much and many of the commercially available methods are solvent based process including Suspension of Polymer/Pigment Solvent Removal (Fuji-Xerox), Polyester Polymeration (PxP, Sanyo and Ricoh), and Chemical Milling (CM, DPI solutions). Emulsion aggregation (EA) process is the most widely used method in styrene-acrylated based CPT production. Also, the method is known highly reproducible and known to be environmentally friendly because the overall process is conducted in aqueous phase. Therefore aggregation behaviors of polyester colloidal particles could be helpful to prepare the polyester-based CPT.

Understanding the interaction forces between colloidal particles and the aggregation behavior is crucial not only for industrial application but also for biomedical application [2]. By manipulating the various matrix environments including ionic strength, pH, temperature, viscosity, shear forces, zeta potentials and etc., the aggregation and controlled growth of polyester colloidal particles in aqueous phase can be induced to achive toner particles of desired size.

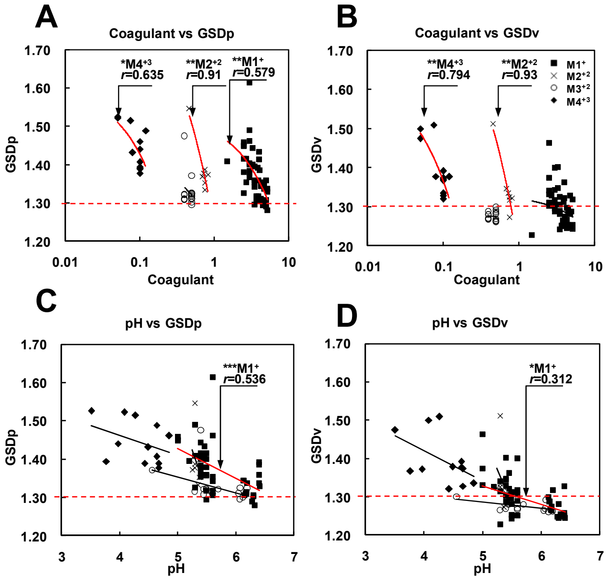

Figure 1. *Aggregation behavior of polyester colloidal particles by the various metallic coagulants. A and B represent the dose dependencies of each metallic coagulant on the GSDp and GSDv of the aggregated particle distributions. C and D represent the pH dependencies of each coagulating condition on the GSDp and GSDv of the aggregated particle distribution. Pearson correlation coefficient with clear correlation ($r>0.3$) was presented on each coagulant data. * $P<0.05$, ** $P<0.01$, and *** $P<0.001$ represent the results of reliabilities on correlation analysis.*

Polyester-based CPT with uniform and narrow size distribution has been introduced by Samsung Fine Chemicals (SFC) [3]. This toner offers superior print qulity and environmental stability with the combined characteristics of polyester resin and CPTs. To control and optimize the aggregation of polyester, wax, and pigment dispersion, we need to understand the various matrix environment based on Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and the ionic effects between polyester colloids and the various metallic coagulants. In this paper, we would like to present the aggregation behavior of polyester colloids that enables us to manufacture high performances polyester based CPT.

Experimentals & Results

The polyester resin, which has a proprietary composition, is dispersed through a neutralization emulsification method. After completely removing the organic solvent, the sub-micrometer resin particles are stabilized in water-based medium. The pigment and wax are individually dispersed in water-based systems using a high pressure homogenizer. The polyester resin, pigment and wax dispersions are mixed together to produce toner particles through a size and shape control process. The equipment selection and control of the process parameters allow the individual sub-micron particles to form a core toner particle with a targeted diameter, size distribution, shape, and surface morphology as described in Kim, et al. [4].

SFC-CPT toner offers a narrow particle size distribution (GSD_p and GSD_v represents geometric size distribution of number and volume data where $GSD_p = (D84,n/D16,n)^{1/2}$, $GSD_v = (D84,v/D16,v)^{1/2}$) and a uniform shape (Circularity over 0.985 using Sysmex FPIA-3000). The spherical toner particles have a mean diameter of about 5.9~6.5 µm. (Size distribution measured using Multisizer IV®: Beckman Coulter, Inc. Brea, CA).

Minitab13 statistical analyses software package (Minitab Inc. USA) performed a Pearson correlation analysis to measure the degree of linear relationship (presented as Pearson correlation coefficient: *r*) between two variables. A *r*-value higher than 0.3 signifies a clear quantitative correlation.

Aggregation of polyester colloidal particles using various metallic coagulants: Size Distribution

Polyester colloidal particles are lyophobic colloids that are distinguished from lyophilic colloids in part by the sensitivity of the dispersion to electrolytes and the use of surfactants or dispersants to stabilize the dispersion. The stability of polyester colloidal particles in solution is controlled by a combination of electrostatic repulsion and London-van der Waals attraction forces, as described by DLVO theory of colloidal stability [2, 5]. Fig. 1 shows the aggregation of polyester, wax, and pigment dispersions with the addition of metallic coagulants. In Fig. 1, the characteristics and amounts of metallic coagulants are depicted by arbitrary coagulant numbers and concentration units except for the valence of the metal ions. For example, $M3^{+2}$ represents metallic coagulant #3 with a divalent ion.

As shown in Fig. 1A and 1B, quite different quantities of coagulants were required to form the aggregated particles. A different working concentration for each metal coagulant was required to make the narrow particle size distribution. The distinctive quantity of each metal coagulant was highly dependent on the valence number of the metallic coagulant ion. This observation agrees well with the empirical Schulze-Hardy rule [6] stating that hydrophobic colloids flocculate most efficiently by ions with high charge number. Small quantities of metal coagulants with a higher ion valence number ($M4^{+3}$) increased the viscosity of the reactant by severe colloid aggregation as compared to metal coagulants with a lower ion valence number ($M1^{+}$).

In addition, the quantity of the each metallic coagulant required to achieve a narrow particle size distribution at the target mean aggregate size reached an optimum operation limit that, when exceeded produced a viscous, inoperative, sludge in the reactor as show in Fig. 1A and 1B. The quantitative dependencies of $M1^{+}$ (only GSDp), $M2^{+2}$, and $M4^{+3}$ on particle size distribution were statistically evident.

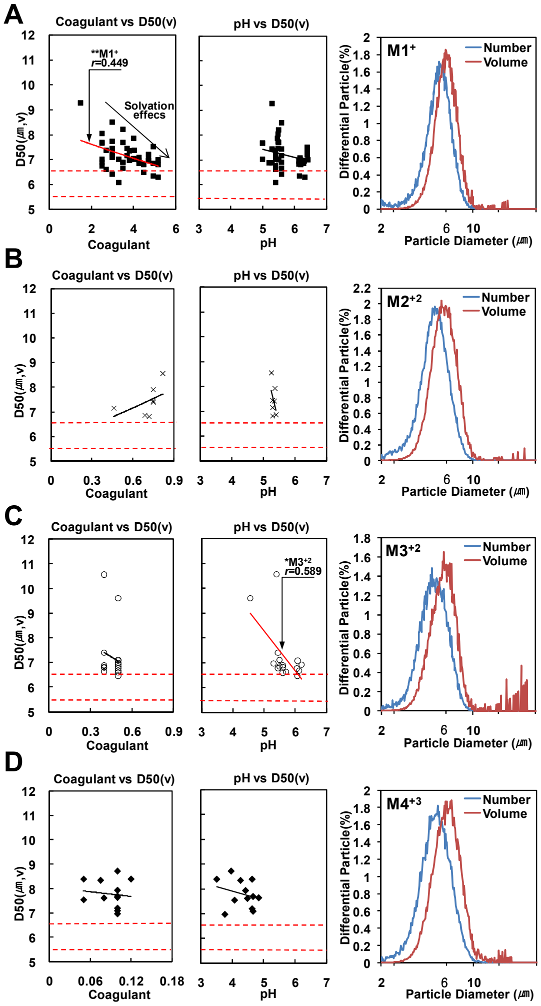

***Figure 2**. Manipulation of particle size for each aggregation system by the various metallic coagulants. Left and middle charts represent the dosage dependence of each metallic coagulant and pH dependence of each coagulating condition on the particle size of the colloidal aggregates. Right chart is a representative particle distribution of each coagulation system. A, B, C, and D represent the charts of $M1^{+}$, $M2^{+2}$, $M3^{+2}$,and $M4^{+3}$ coagulant, respectively. Pearson correlation coefficient with clear correlation ($r>0.3$) was presented on each coagulant data. * $P<0.05$ and ** $P<0.01$ represent the results of reliabilities on correlation analysis.*

Fig. 1C and 1D show that the particles aggregated over a broad pH range and varied with the type of metallic coagulant. Moreover, the dependence of the aggregated particle distributions on pH overlapped and converged at pH 5.5 ~ 6.5 for all of the coagulants. In general, the cationic charge of high valent metallic coagulants decreases with increasing pH so that their coagulation power can be controlled by pH. For example, ferric ions (Fe^{3+}) form hydroxyl ferric complex ions as the pH increase, that is, $Fe(OH)^{2+} + 3(OH)^{-1} \leftrightarrows Fe(OH)_2^{+1} + 2(OH)^{-1} \leftrightarrows Fe(OH)_3 + (OH)^{-1} \leftrightarrows Fe(OH)_4^{-1}$ [7]. Aluminum ions (Al^{3+}) also form hydroxyl aluminum complex ions as the pH increases: $Al_8(OH)_{20}^{4+}$, Al^{3+},

$Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4^-$ [8]. Even though it is generally more favorable to aggregate the particles using multivalent metallic coagulants under acidic conditions (pH less than 5.0 in Fig. 1C and 1D), aggregation is more controllable at a pH of about 6.0. Therefore, it was the pH condition, more so than the coagulation strength of the metallic coagulant that was more critical to produce a narrow volumetric size distribution of aggregated polyester colloidal particles. Based on a solution chart for Fe^{+3} and Al^{+3} ions [7, 8], only the monovalent form of these metallic hydroxide ions (such as $Fe(OH)_2^+$ and $Al(OH)_2^+$) is mostly available at a pH of about 6.0. This ionic form does not seem suitable to produce aggregated colloidal particles with a narrow size distribution. Similar behaviors for divalent metallic ions are also reported [9].

Amongst all the properties of polyester colloidal dispersions, the acid value is the most critical factor as it relates the pH dependence on aggregate particle formation. We observed that as the pH of the dispersion solution increased, the carboxylic acids exposed on the surface of polyester dispersions was ionized to carboxylates, and the stability and viscosity of the polyester dispersions increased. Due to the increased electrostatic interaction between the carboxylated functional groups on the polyester colloid surface and the metallic coagulant ions, colloidal aggregation seemed to be favorable to make aggregates with narrow particle distribution.

Aggregation of polyester colloidal particles using various metallic coagulants: Size Targeting

Fig. 2 illustrates the particle size dependence based on the concentration of each coagulant and the pH of the solution. Fig 2A shows that as the concentration of the $M1^+$ coagulant increased at a pH ~6.0, the toner particles converged to small particle size. However, the colloid particle size could not be manipulated during the aggregation process to achieve the target size range using $M2^{+2}$ and $M4^{+3}$ coagulants (Fig. 2B and 2D). During this aggregation stage, neither the coagulant concentration nor pH had any effect on reducing the particle size down to an acceptable level. Low solution viscosities near a neutral pH also indicated that aggregation failed to occur (aggregation failure data was excluded from Fig. 2B and 2D). As discussed earlier, the valence number of metallic coagulants decreases near neutral pH so a particle with a mean size below 6.5 µm and narrow size distribution was not obtainable. With respect to $M3^{+2}$ (Fig. 2C), a metallic hydroxyl ion does not form at a pH less than 7 (i.e., in acidic or neutral conditions), so a small particle size with a narrow size distribution could be obtained by the selection of the proper coagulant concentration near a neutral pH condition (in-house titration properties of $M3^{+2}$ coagulant agreed well with published results) [9]. The $M3^{+2}$ coagulant was another good candidate for colloidal polyester aggregation but this system needs to resolve the issue with the elevated quantity of large aggregated particles before this option becomes viable (data not shown). When the $M2^{+2}$ and $M4^{+3}$ aggregated samples were treated with a sodium hydroxide solution to prevent additional aggregation (freezing), the larger particles decreased in size, 7.4um → 5.9 µm, 7.2 um → 6.2 µm respectively, due to the mechanical sheering force of the agitation process. In addition, the freezing step for divalent metallic coagulants required a chelator to prevent particle adhesion during coalescence step. The residual chelator-metal salt complex may contribute to some electrostatic related quality problems.

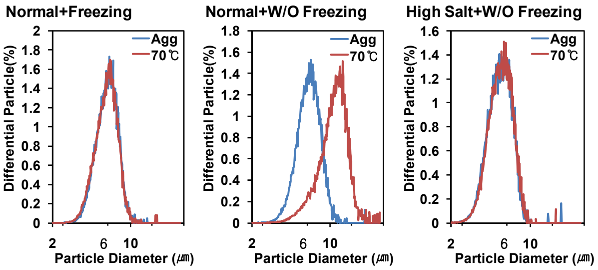

Figure 3. Effect of excessive $M1^+$ coagulant on the aggregation behavior of polyester colloidal particles. Each chart represents the particle distribution at the aggregation stage (Agg) and the pre-coalescence stage (70 ℃) either with or without (W/O) freezing step. Normal is representative condition of $M1^+$ coagulant and High Salt is the modified condition with the increase of $M1^+$ coagulant by 20%.

Effect of solvation or hydration forces on $M1^+$ coagulation system

The aggregation behavior of the $M1^+$ coagulant system produced a more stable and reproducible aggregated particle than any other coagulation systems that was investigated (as shown in Fig. 1 and 2). In addition to coagulant mediated particle aggregation, repulsive forces between the $M1^+$ coagulant and aggregated particles were observed. When an excess amount of $M1^+$ coagulant was added to the system, particle growth was suppressed in spite of a change in the pH value. This phenomenon is depicted in Fig. 2A (marked in additional arrow line) and is referred to as the solvation effect or hydration force [2]. This is the interactive force that occurs between two charged surfaces when they approach closer than a few nanometers. At such a close distance, their interactions in an aqueous solution fail to be explained by the DLVO theory [10].

Fig. 3 presents additional test results regarding the aggregation behavior of the $M1^+$ coagulant. Under an optimized $M1^+$ coagulant condition, we observed small particle size and a narrow toner particle distribution during the Normal+Freezing stage of the preparation process. Without the sodium hydroxide treatment, additional aggregation of the toner particles would occur when the process temperature is increased (Normal+W/O_Freezing). During agitation, colloidal particles may penetrate through the interfacial electrical double layer and coalesce but only if the collision has sufficient energy to disrupt the charged surface layers. This disruption is more likely to occur at higher temperatures and is one reason why toner particles without the freezing process begin to aggregate at the elevated temperature [11]. However, the growth of toner particles without freezing (i.e., without sodium hydroxide treatment) was suppressed with an excess amount of $M1^+$ coagulant (High Salt+W/O Freezing). Under these conditions, the excess $M1^+$ ions produced a repulsive force at the surface that prevented any additional aggregation of the particles. The aggregation conditions for the $M1^+$ coagulant were optimized for particle size and particle size distribution through a set of Design of Experiments (DOE), which are being

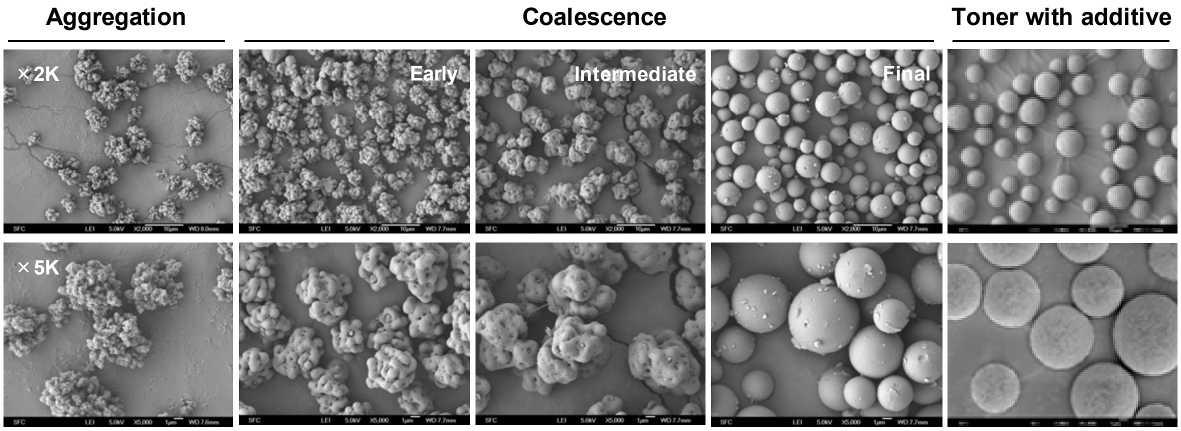

Figure 4. *Toner particle morphology for each process stage. Each SEM image represents the particle morphology at the aggregation, early coalescence, intermediate coalescence, and final coalescence stages. Additional image of final toner product (toner with additive) is presented.*

used to develop our manufacturing processes for polyester-based chemically prepared toner (DOE data not shown).

Morphological changes after aggregation

In addition to the narrow particle distribution, the SFC polyester-based CPT (SFC-CPT) has additional advantageous characteristics, including a uniform particle shape, uniform composite dispersion, controlled surface morphology, and core-shell structure. Fig. 4 depicts the morphological changes that occur to SFC toners after aggregation step in the manufacturing process. Aggregates of polyester colloidal particles (aggregation) began to fuse with adjacent particles (early coalescence), fill the crevasse between aggregates (intermediate coalescence), and coalesce into spherical shapes with a circularity value great than 0.985 (final coalescence). The surface of the particles is very smooth and the roughness variation is controlled to within 22% (based on BET surface area) [3]. These core-toner particles are then treated with external additives to produce a final toner particle with the desired electrostatic charging, transfer efficiency, powder cohesion, and print image quality.

Concluding remarks

Digital printing technologies have matured to complement and personalize industrial printing technologies such as offset and gravure methods. As the usage of office color laser printers and high speed multi-functional printers increases, the demands for high quality images and a smaller environmental footprint are driving most toner manufactures to develop eco-friendly polyester-based CPT [1, 12].

With our ability to accurately control the aggregation behavior of polyester-based colloidal particles in an aqueous system and to produce a uniform circular toner with a narrow particle size distribution, we have developed SFC-CPT compatible to OEM printer engine (data not shown). Considering the overall performance of SFC-CPT, we believe that our toner technology could be excellent candidate for eco friendly polyester based CPT.

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Author Biography

Dr. Sung Yul Kim received his B. S., M. S., and Ph. D. in chemistry from Seoul National University. After three years of post-docotral period in Korea University, he joined Samsung Fine Chemicals. He is currently working at Advanced Material R&D Center of Samsung Fine Chemicals as a principal researcher and his work has focused on the process development for a polyester-based chemical toner preparation.