Study on the Factor for the Morphological Control of the Chemically Prepared Toner

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Abstract

The morphology of the dry toner particle for laser printer plays a very important role in the electrophotography (EP) process. For example, spherical shape of the toner particle provides good development efficiency, whereas irregular shape of the toner particle gives good blade cleanability. Thus, controlling the morphology of toner particle is a key technology to satisfy both preferences. Chemically Prepared Toner (CPT) has many advantages in that way.

In this study, the factor to control the morphology of the emulsion/aggregation toner is discussed. Since emulsion/ aggregation toner is prepared by thermally coalescing aggregates of toner components, the morphology of the coalesced toner particle depends on the thermal process and the thermal properties of the aggregates. Thermal property such as Tg has close relationship with the property of the toner components such as molecular weight of the binder emulsion. Thus, we demonstrate that how the control of the properties of the emulsion would impact on the morphology of the toner particle. It was found that the molecular weight of the emulsion plays a role in forming the toner shape and the surface morphology.

Introduction

The use of the chemically prepared toner (or polymerized toner) has been raised recently as the demand of the high performance color laser printer in consumer market increases. In contrast to pulverized toner, the chemically prepared toner is mainly prepared and categorized by two different processes. One is suspension polymerization process and the other is emulsion/aggregation (E/A) process. One of advantages of the chemical toner is its spherical shape over conventional toner. Usually spherical toner provides ideally good development efficiency in the electrophotographic process due to its uniform chargeability. However, there is also disadvantage, which is to provide less cleanability of the toner from the development roller in the process. Thus, somewhat deformed spherical shape toner is more realistic, providing good development efficiency as well as good cleanability.[1] In that perspective, the chemical toner prepared by suspension process is ideally spherical, but it is very difficult to control or deform the shape of the toner due to the nature of its process. The chemical toner, prepared by emulsion/aggregation process is relatively free from that limitation. Our study for the chemical toner has focused on the process to control the shape of the chemically prepared toner using emulsion/aggregation process. In this paper we present the results of the effects of molecular weight on the morphology of the chemical toner. Four distinct variations in molecular weight were used to investigate the differences in morphology of the toner shape. The molecular weight of the toner was varied using the chain transfer agent in the polymerization process.

Experimental

Preparation of Latex Emulsion and Pigment Dispersion

The latex as a binder resin was prepared by emulsion polymerization. In addition, a monomer soluble wax was incorporated in the monomer phase as a release agent. Styrene, butyl acrylate, and methacrylic acid were used as monomer reagent. The chain transfer agent such as dodecanethiol was added to the monomer mixture varying concentration of 0, 2, 4, and 7 weight percent out of total monomer weight. No charge control agent was added. Potassium persulfate was used as a water soluble initiator. The polymerization was performed at 80°C for 6 hours under nitrogen environment.

Pigment dispersion was prepared by glass bead milling process using carbon black pigment and de-ionized water with surfactant. The milling process time was 2 hours.

Aggregation and Coalescence

The latex emulsion and pigment dispersion were mixed in the reaction vessel. Aggregation was started by dropping a coagulant slowly while stirring. The mixture was heated with a heating rate ~1°C /min to 95°C. And then the temperature of the mixture was isothermally maintained at 95°C until the end of the process. Series of the sample of the mixture were taken at the specified temperature And Time Interval. Finally The Product Was Washed And Filtered.

Sample Analysis

The molecular weights were determined using the laser light scattering gel permeation chromatography, DAWN-EOS manufactured by Wyatt technology. The volume average particle size (D_v) and the number average particle size (D_n) with their size distributions were measured using the laser light scattering particle size analyzer, LA-910 manufactured by Horiba Co., LTD. Differential scanning calorimetry (DSC) was performed to determine the glass transition temperature of the latex. The micrographs of the Scanning Electron Microscopy (SEM) image were taken using the Hitachi S-3500N. The SEM images were taken at the magnification of 30,000X. The intensity of the electron beam was 20kV.

The Tg of copolymer can be estimated or designed approximately using the famous Fox equation.[2]

$$1/Tg_{12} = w_1/Tg_1 + w_2/Tg_2 + \ldots \qquad (1)$$

Where Tg_{12} is the glass transition temperature of blend or random copolymer and Tg_1 is the glass transition temperature of polymer 1. w_1 is the weight fraction of the polymer 1 in the system.

In addition, molecular weight is another factor to control Tg of the binder resin. When monomer ratio is fixed, the Tg of the resin is a function of molecular weight described by following equation.[3]

$$Tg = Tg^{\infty} - k/M_n \qquad (2)$$

Equation (2) is the Fox-Flory equation, where Tg^{∞} is the glass transition temperature of a linear chain of infinite molar mass. M_n is a number average molecular weight. k is $2\rho N_a\theta / \alpha_f$, in which ρ is the density of the polymer, Na is the Avogadro number, θ is contribution of one chain end to the free volume, and α_f is the thermal expansion coefficient of the free volume.

Results and Discussion

Particle Aggregation and Coalescence: Formation of Chemical Toner

First, we discuss how the submicron particles are transformed to micron-sized toner particle. The latex having M_w of 42,781 was used for this experiment. The volume average particle size of the latex was 160 nm. At the beginning of the aggregation process, the particle dispersion started to aggregate by adding a coagulant. In Figure 1 it is shown that the initial particle size distribution of the aggregates at 40°C is very broad, ranging from submicron to micron size. As temperature increases, the size distribution is shifted to the right with increase of the mean particle size. At one hour isothermal heating (95°C), it is seen that the broad particle size distribution becomes significantly narrower. The mean particle size of the particles continuously grows with keeping the size distribution narrow. The volume average particle size at the end of the process was 7.6 μm.

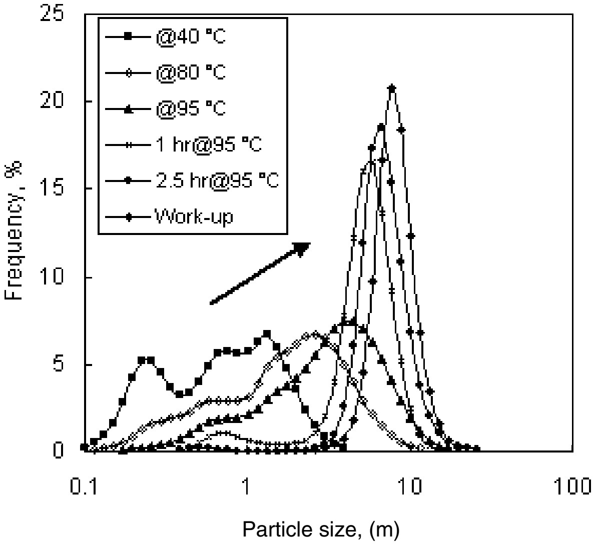
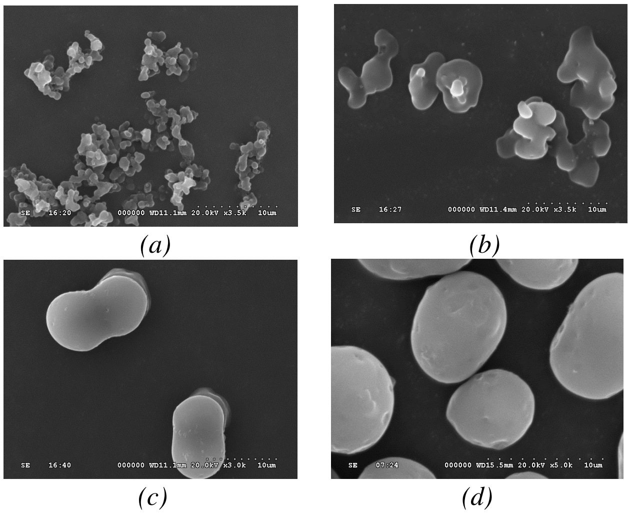


Figure 1. Evolution of the particle size distribution

Series of the particle images in Figure 2 exhibit formation of the particle as elapse of process time. In Figure 2-(a) it is seen that the aggregates composed of a plurality of the submicron particle cluster which is partially coalesced, showing an irregular shape. Figure 2-(b) shows the partially coalesced particles formed smoother surface and the image of (c)(d) approaches to more toner-like shape. When one particle approaches near to other particle in the process, those particles have possibility to aggregate by ionic strength or to collide by stirring, producing a bigger coalesced particle. Thermodynamically, when the processing temperature exceeds over the Tg of the latex, the polymer chain in the particle has tendency to move freely as increase of the Gibbs free energy, so that viscous mobility of the molecular chain occurs in the particle. Thus, the aggregated clusters have freedom to be coalesced together. As a consequence, the coalesced clusters of the aggregates result in smoother and more uniform shape under the given temperature condition. Thus, in our experiment it can be said that the toner particles are formed by simultaneous process of aggregation and coalescence.



(a) *(b)*

(c) *(d)*

Figure 2. SEM micrograph of particle formation in series of time elapse (30,000x) (a) at 95℃ (b)1 hr elapsed at 95℃ (c) 2.5 hr elapsed at 95℃ (d) work-up (3.5 hr)

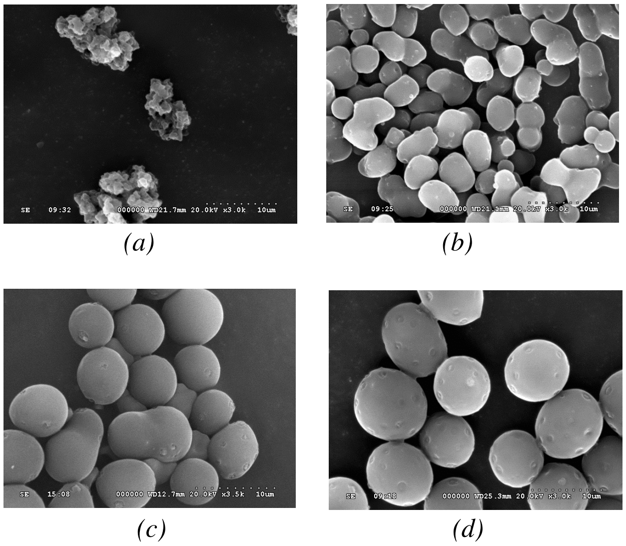
Shape Difference of the Chemical Toner in Variation of the Molecular Weight

Utilizing the result described in the previous section, four chemical toners with different molecular weight were prepared to study the relationship of the toner shape with the molecular weight of the latex. All experimental parameters were fixed except the concentration of the chain transfer agent added in the monomer. Table 1 represents the molecular weight of the latex in series of variation of the chain transfer agent. It is seen that the M_w and M_n decrease as the concentration of the chain transfer agent increases.

Table 1: The molecular Weight of the Latex Binder

CTA %	**0**	**2**	**4**	**7**
Mw	337,153	107,005	42,781	29,965
Mn	43,999	8,296	4,920	2,736

It is illustrated in Figure 3 that the SEM images of the toner particles respectively prepared using the latex with four distinct variations in molecular weight. It is seen that there is evident shape difference of each toner image. In the Figure 3-(a), it is shown that the smooth particle shape was not formed. Figure 3-(a) represents the particles in which no chain transfer agent was used. The reason why this particle was not coalesced completely is due to the high molecular weight of the latex which cannot be processed under our experimental condition. In Figure 3-(b) aggregates are completely fused, so as to form micron-sized toner particles. As the molecular weight decreased below 42,000 (M_w) shown in Figure 3-(c) and (d), the shape of the particles approaches to more uniform and spherical shape. In Figure 3-(d) the toner particle shows the most spherical shape among all images in Figure 3. It is considered that these all morphological differences are due to the degree of interaction between interfacial tension on the particle and the viscous chain mobility of the toner depending on the molecular weight when fixing all other parameters.



(a) *(b)*

(c) *(d)*

Figure 3. SEM micrograph of toner particle (30,000x) (a) 0% CTA (b) 2% CTA (c) 4% CTA (d) 7% CTA

It has been reported that shape of chemical toner prepared by emulsion/aggregation process can be controlled by manipulating temperature and process time. In this paper we have demonstrated that the molecular weight of latex resin is another factor to influence on the chemical toner morphology. Thus, control of the molecular weight of the toner can be utilized in the shape control of the toner as long as its molecular weight is within the range satisfying toner durability and fusibility in electrophotographic process.

Conclusion

We demonstrated that the formation of the chemical toner visually and its morphological change when the molecular weight is varied. The particle size gradually grew in both aggregation and coalescence process. At the isothermal heating, shape of the size distribution significantly became narrow and plurality of the aggregates formed more uniform and toner-like particle shape. Variations in molecular weight of latex binder resin were applied in the process. It is clear that molecular weight of the latex emulsion contributes to morphological difference in the process. It was found that latex emulsion with high molecular weight is difficult to form completely coalesced particle. It is considered that there is a process range of the molecular weight of the latex to produce the various shape of the toner. The particles below M_w of 100,000 showed that the aggregates were coalesced, exhibiting variations of particle shape. As the molecular weight of the latex decreases, the shape of the toner was formed close to spherical shape. Thus, the shape of the chemical toner can be tailored by varying a parameter such as molecular weight of the resin, providing full advantage of the chemical toner.

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Author Biography

Jun Young Lee received his BS/BA in Chemical Engineering/Chemistry in the University of Massachusetts at Amherst (1997) and his dual MS in Chemical Engineering/Electrical Engineering in Tufts University (2002). Since then he has worked in the Digital Printing Division at Samsung Electronics in Suwon, Korea. His work has focused on the research and development of imaging materials.