Preparation of Polyester Toner Particles with a Self-Emulsified Chemical Milling Method

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Abstract

Various dispersion polymerization methods have emerged as an economical means of producing small sized toner particles thus to enhance the resolution of electrophotography (EP) images to a higher level. The so-called polymerized toners generally have a small average particle size, a narrow size distribution and a round particle shape with a smooth surface. However, the polymerization methods present several difficulties such as complexity of process and production facility, potential for solvent or monomer contamination of the toner particles, inflexibility of formulation variation and slow charging characteristics. Recently we developed and reported the novel chemical milling (CM) method of producing small polyester toner particles, which has the advantages of the polymerization methods but, at the same time, are free of the above-mentioned disadvantages.[1]

Here we present a self-emulsified CM method, a modification of the chemical milling method as well as the physical properties and EP performance of toners prepared by the method. The method takes advantages of the physical and surface chemical properties of novel polyester toner resins and thus does not require use of a process aid or a surfactant in the toner particle formation. Much like the traditional CM method, the method exhibits excellent controllability and economy in the production of spherical polyester toner particles with a small diameter and a narrow size distribution. We demonstrate toner particles with the volumetric mean diameter of about 6 μm and the 80% span of 0.6.

Introduction

The ever-increasing amount of digital information being processed and communicated has increased dramatically the need for higher resolution printed images. A popular digital imaging technology is electrophotography, which often been described as a technology reaching its technical limit in the image resolution.[2,3] For continuing enhancement of the quality of electrophotographic image, it is critically important to raise the imaging performance of toner to the level required for high quality digital imaging (e. g., high resolution beyond current 600 dpi) and also to continuously develop innovative methods of producing such toners.

There have been many efforts to develop high-resolution toner by a chemical method of preparation. As a result, several chemically-produced toners (CPT), based on a form of dispersion polymerization process, that have a reduced particle size and a narrow size distribution with a comparable production cost as that of a melt mixing method[4,5] have been introduced commercially. A main principle governing of the polymerized toner is use of surface chemical force that stabilizes the interface between two immiscible liquid phases, usually that of a monomer and a dispersion medium, by a surfactant. However, the inclusion of surfactant in the particle formation process brought about process complexity for an industrial process. We circumvented the problem by an innovative design of the molecular structure of polyester resin and developed a CPT process that does not require use of a surfactant and therefore is significantly simpler than a conventional CPT process. We termed this process a self-emulsified CM process.

In this report, we introduce the self-emulsification CM process for high-resolution toner and the physical properties of the toner. As will be seen below, the process is carried out in a non-aqueous medium without any surfactant. The principle underlying the process may be understood on the basis of molecular design of the binder polymer and the physicochemical interaction between medium and polymer dispersant.

Experimental

A cationically dyeable polyester containing ionic groups in the chain was prepared by a melt condensation process. The details of the polymer preparation method was described in our previous reports.[1] In some cases, we varied the ion content of polyester from 0 to 10 mol. %, which was one of the key variables of the study. The number average molecular weight of the polymer was about 6,000 and the thermal analysis of the polyester resin gave the glass transition temperature of 65°C.

The first step of particle formation by the self-emulsified CM method was mixing of the polymer resin and a paraffin wax with a melt blender. Then the mixture was mechanically crushed into about 1-mm size particles. For example, in a mixing head of extruder, the polyester resin and paraffin wax and a dye stuff were charged in the weight

ratio of about 100:5:2 parts. The mixture was molten by heating it to about 150°C and thoroughly blended to form a fine dispersion. During the dispersion mixing step, the dye reacted with the functional group of polymer resin to bind to the extent that the final resin mixture showed water fastness.

About 200 gr of a highly polar organic medium was charged into a flask and heated to about 140°C. Then about 100 gr of the resin mixture was put into the flask. The mixture was maintained at the temperature while the agitator speed was increased to a specified value. The shearing continued until the particle size stopped decreasing. The dispersion was allowed to cool down to ambient temperature and the toner particles were separated from the dispersion medium by filtration. The medium entrained in the filter cake was washed off with water. The particles were then dried in a convection oven for 20 hours at 50°C and a vacuum oven for 12 hrs at 45°C (These temperatures sound a little too high.)

Particle size and distribution were determined using a TAII Coulter device (Coulter Electronics, Inc). The size distribution of the toner particle was represented by the 80% span value. More specifically, the span was calculated from the Coulter analysis data using the formula,

$$Span=(d_{90}-d_{10})/d_{50}.$$

Here d_{10} is the diameter value at which the volume fraction is 10 percent by the volume in the cumulative volumetric diameter distribution diagram, d_{90} the diameter value at which the volume fraction is 90 percent and d_{50} the diameter value at which the volume fraction is 50 percent. Electron microscopic analysis was performed using a JEOL JSM-T22a scanning electron microscope.

The charge of the toner particles was measured with a Faraday cage produced by Vertex Image using the blow-off method. The blow-off pressure was 5 psi and the applied time was 15 sec.

Results

Control of the Particle Size

Conventional CPT's typically are prepared by a suspension or an emulsion polymerization method,[5-7] in which a monomer dissolved or dispersed in a liquid medium is converted to polymer particles dispersed in the medium. The self-emulsified CM process is completely different from the polymerization methods in that a molten polymer resin is converted to a fine dispersion of resin particles in a liquid dispersion medium by the surface chemical property of the polymer resin. We designed the polyester resin to contain ionic groups in the chain. The ionic groups induce formation of the polymer dispersion and also stabilize dispersed particles in the medium. The use of a highly polar medium was to induce the ionic groups in the interfacial region between the polymer particle and the medium thus to stabilize the polyester particles through the attractive interaction between the ionic groups and strong dipoles of the medium. We used a series of alcohols and their mixtures with a boiling temperature higher than 150°C such as ethylene glycol, propylene glycol, glycerol, butane diol etc.

Success of the self-emulsified CM process depends on several factors. One example is shown in Fig. 1 in which the man size of polymer particles produced by the process is plotted as a function of difference of the solubility parameters of the medium and the polymer. Here α, σ, r mean solubility parameter of polyester, solubility parameter of medium and resulting diameter of polyester particle. Since the process requires a balance of the chemical potentials of the two phases, the chemical nature of the medium strongly affects the resulting size and size distribution. Figure 1 demonstrates that the toner particle size increases with decrease of solubility parameter difference, implying that the mean size of particles obtained by the self-emulsified CM method may follow the well-known Young-Laplace Equation. Another important role of the highly polar medium is to incorporating the wax in the polymer particles. The medium makes the exposed wax unstable and thus forces it to remain inside the particles. Figure 2 shows location of the wax in the particle. Figure 2(a) is a microscope image of toner particles and Fig. 2(b) was taken after removing polyester resin of the same particles with a solvent. Polyester particles apparently entrapped the wax at a rate of 2-3 wax particles per toner particle.

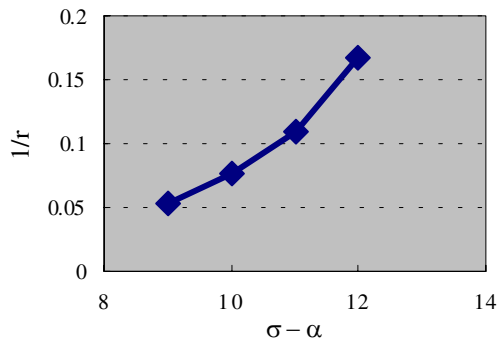

Figure 1. Plot of volumetric mean size of particle in various polar mediums.

It is noteworthy that the process offers a very fast means to attain the equilibrium particle size distribution, as depicted in Fig. 3. The mode value reached an asymptotic value within 30 minutes and was nearly invariant afterward. It is well known that breakages of polymer melt droplets was mainly caused by transmission of a shearing force between two immiscible liquids with similar viscosity values. However, the self-emulsified CM process seems to proceed surprisingly fast. Even when a very low shear was applied, the polyester was converted into small particles in a very short time period. The fast breakage might be driven not just by the mechanical shear but also by a change in the conformation of polymer chain. We hypothesize a mechanism of the particle formation in which a polyester containing ionic groups self-assemble into a particulate form. The ionic groups that contact the medium when it was

provided sufficient thermal energy to translate out to the outer region of the particles. Also, molecules of the meiumd also may diffuse into the polyester resin. The interface at which the medium molecules meet the polyester is anticipated to generate the particle shape. Once the genesis of particle occurs, even a small shear rate could induce the breakage and transform the geometry into a spherical shape. Figure 4 illustrates the particle geometry observed by SEM.

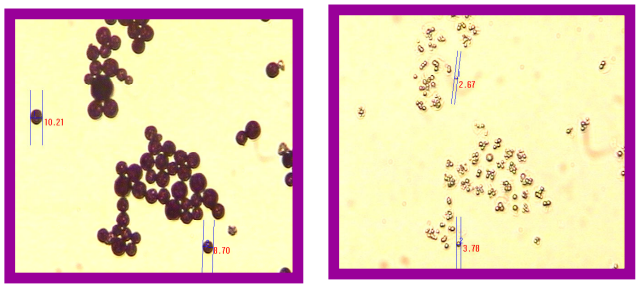

Figure 2. Optical micrographs of the polymer particles(left) and after revomal of polyester(right)

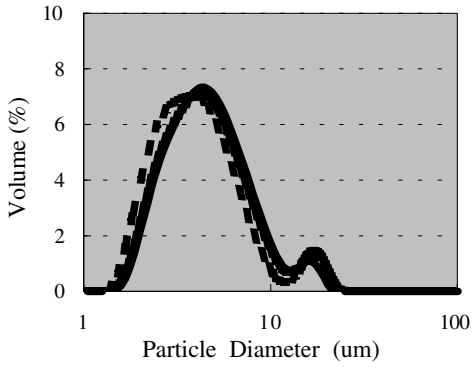

Figure 3. The particle size distribution of the polymer dispersions prepared by chemical milling at different time at 0.5 hr(dotted line) and 3hr(line).

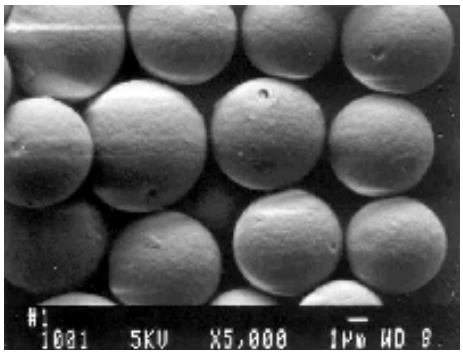

Figure 4. SEM micrographs of resin particle prepared by self emulsified chemical milling

A narrow size distribution is important for toner application. A particle size distribution may be represented by D90 and D10 of the distribution curve. Given a chemical condition of the process, the shear rate controls the particle size distribution, as shown in Fig. 5.

Dependence of D90 and D10 on the mean diameter value is plotted in Fig. 5. The D10 changes little with the mean particle size while the D90 abruptly increases. This means that the D10 value is related essentially to the chemical condition and the D90 value, however, seems to depend on the kinetic factor. An way to have uniform momentum transfer was use of a process aid to substantially reduce the melt viscosity of dispersed polymer.[1] It is therefore expected that use of a process aid would shift D90 to a smaller value. We employed ethylacetate as the process aid checked whether a narrower size distribution would be produced. Figure 6 confirms that the process aid allows formation of polyester particles with a small average particle diameter and a narrow size distribution. It has span value 0.6.

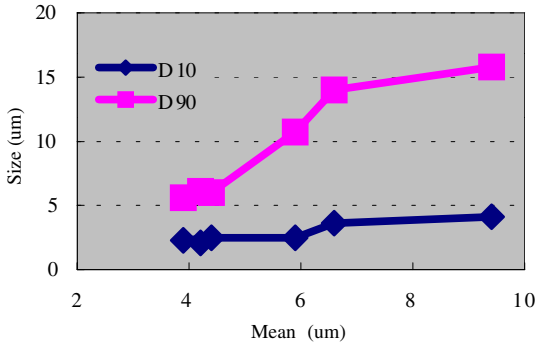

Figure 5. Dependence of D90 and D10 on the mean diameter value

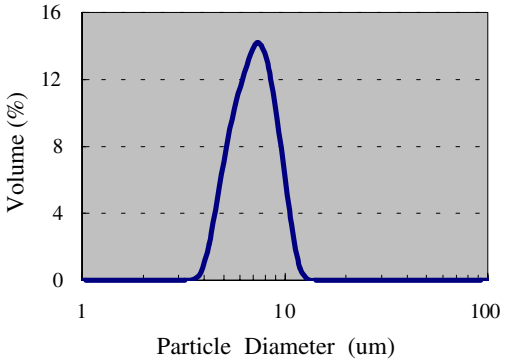

Figure 6. The particle size distribution of the polymer dispersions prepared by chemical milling in the presence of process aid

The toner particles prepared by the self-emulsified CM method was further treated with additives such as silica and used as a monocomponent developer. The chemically milled toner formed a good printed image without causing operational problems in a HP-4500 printer. The toner

prepared in this study was found to meet the requirements of a toner for a color laser printer with a oil-fee fusing system.

Conclusion

We developed a self-emeulsified CM method as a novel and productive means of producing high-resolution toner particles with a narrow size distribution for a printer with an oil-free fusing system. Innovative molecular design of resin makes it possible to form polyester toner particles without using any surfactant. Furthermore, the particles had an exceptionally narrow size distribution with the span value as low as 0.6. The toner showed a good printing performance.

References

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Biography

Dr. Chul-Hwan Kim is R&D Team Leader in DPI Solutions, Inc., a materials technology development in Korea. He received MS and Ph.D (1996) from Korea Advanced Institute of Science and Technology in polymer science with a dissertation on lithium ionomer electrolytes. His research interests are functional polymers and polymer processing, especially in the area of imaging materials such as EP toners, inkjet receiving layers and dye diffusion thermal transfer media. Recently he expanded his research interests into polymeric materials for electronic displays such as organic EL, LCD and electrophoretic displays.