Preparation of Pigment-Containing Polyester Toner by Chemical Milling

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Abstract

We previously reported a novel method of chemically-preparing polyester color toner (CM toner®). The proprietary design of the first generation CM toner® was based on a functional polyester resin, a charge control agent, a wax, and dyestuff.

Here we report an extension of the CM toner® technology to produce a pigment-based polyester color toner. Two innovations were incorporated in the technology. First, to disperse pigment particles finely in the toner particles and also to prevent exudation of pigment during chemical milling, we used a pigment master batch utilizing a polyester binder resin that is chemically similar to the toner resin. Secondly, we also developed a functional polyester resin containing an appropriate amount of a selected ionic functional group in the chain so that increased surface chemical potential of polymer droplets would overcome increased viscoelasticity of droplets containing pigment particles.

Pigment CM toner® particles (pigment content as high as 10 wt. %) with the volumetric mean diameter in the range of 5-10 microns and the 80% span as low as 0.55 were produced. A four-color toner set was developed and it showed excellent imaging quality as well as a good printing page yield in a commercial color laser printer.

Introduction

The ever-increasing amount of digital information being processed and communicated has increased dramatically the need for higher resolution of printing images. One of the popular digital imaging technologies is the electrophotography, which was reported as a technique reaching its technical limit for high resolution image.[1,2] For the innovation of the electrophotographic image quality, it is critically important to raise the imaging capabilities of toner to the level suitable for high quality digital imaging and also to produce the toner with new innovative methods.

There have been many efforts to improve the resolution of the printed image by improving the toner by the practitioners in the toner industry. The chemically produced toner (CPT) based on a polymerization process has been developed as a high resolution toner with a reduced particle size at a relatively similar production cost as that of the melt mixing methods.[3] Even though the polymerized toner has the aforementioned advantage over the melt mixing methods it has several shortcomings.

We previously reported a novel method of chemically-preparing polyester color toner (CM toner®).[4-6] The proprietary design of the first generation CM toner® was based on a functional polyester resin, a charge control agent, a wax, and dyestuff along with a UV stabilizer. The CM toner® demonstrated excellent control of particle size and size distribution, intense color, excellent dispersion of colorant, easy controllability of color gamut, satisfactory photostability and fast oil-free fusing. With a suitable additive package, the CM toner® base can be converted into a color toner composition that can work with many modern mono-component color laser printers, producing excellent print images with exceptionally economic toner consumption and stable printer operation. Further, the toner presented an exceptionally low environmental load for the polyester resin used did not contain a monomer such as bisphenol-A or a heavy metal catalyst residue.

Here we report an extension of the CM toner® technology to produce a pigment-based polyester color toner. Two innovations were incorporated in the technology. First, to disperse pigment particles finely in the toner particles and also to prevent exudation of pigment during chemical milling, we used a pigment master batch utilizing a polyester binder resin that is chemically similar to the toner resin. Secondly, we also developed a functional polyester resin containing selected ionic functional groups in the chain so that increased surface chemical potential of polymer droplets would overcome increased viscoelasticity of droplets containing pigment particles. The particle formation process of the pigment CM toner® is now driven primarily by surface chemical potential rather than mechanical power, resulting in a simple, controllable, reproducible and therefore highly economical process.

Experimental

Preparation of Polyester

An environmentally friendly polyester resin was prepared by a melt condensation process, which contains neither bisphenol A group nor heavy metal residue. Polyester monomers, dimethyl-terephthalate, dimethylisophthalate, sodium salt of dimethyl 5-sulfoisophthalte, propylene glycol were charged in a glass reactor fitted with a paddle stirrer and a fractionating column. Titanium tetra-isopropoxide and IRGANOX 1010 were used as the ester exchange catalyst. The reactants were charged at ambient temperature and purged with high purity nitrogen gas for about 1 hour before heating up to 150°C to form a homogeneous melt. Subsequently, the ester exchange reaction was carried out by heating the reaction mixture from 150°C to 220°C under a flowing nitrogen atmosphere and subsequently maintained at 220°C at reduced pressure until approximately calculated amount of distillate is collected.

The number average molecular weight of produced polyester was 6,000 and the polydispersity index was about 3 ~ 8, and the thermal analysis of the polyester resin gave the glass transition temperature of 65°C.

Preparation of a Colorant Masterbatch

Since we employ pigment as a colorant, it needed to finely disperse the pigment in the polymer resin. The polyester resin was dissolved in a solvent to mix with the pigment in mixing vessel equipped with homogenizer to get the pigment homogeneous dispersed at an elevated temperatures about 70°C. The mixture was subject to the twin-screw extruder at a reduced pressure to eliminate the solvent. The colorant mixture after extruder was crushed for convenient use. The final composition of the pigment in the colorant mixture was about 40 wt%.

Particle Formation by Chemical Milling

The first step of particle formation by the chemical milling is mixing the polymer resin and an evaporable process aid. For example, in a round bottom flask equipped with an impeller type agitator and condenser, the polyester resin, a pigment masterbatch, wax, and a processing aid as an evaporatable plasticizer were charged into a vessel until the mixture formed homogeneous mixture. The mixture was put into a chemical milling vessel where the aqueous medium was heated to 70°C with surfactant and dispersion stabilizer. The mixture was thoroughly agitated under a total reflux condition under a vigorous agitation.

When the particle size of toner was reached a certain range, the evaporable process aid was removed from the agitating vessel. The shearing continued until the vapor of the process aid stopped evaporating and the dispersion was allowed to cool down to the ambient temperature. The toner particles were separated from the aqueous medium using a filtration process and were washed with fresh water to remove the surfactant and dispersion stabilizer. The particles were then dried in a vacuum oven at 45°C.

Characterization

Particle size and distribution were determined using a TAII Coulter device (Coulter Elctronics, Inc). The aperture of the tube in the Coulter analysis was 75 micron in diameter. 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,

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

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 Vertex Image (New Jersey) using blow-off method. The blow-off pressure was 5 psi and the applied time was 15 sec.

Results

Control of the Particle Size

Conventional chemically produced toners are prepared typically by either a suspension or an emulsion polymerization method,[8,9] in which monomers dissolved or dispersed in a liquid medium are converted to polymer particles dispersed in the liquid medium. Our chemical milling process is completely different from the methods in that the melt of a fully developed polymer resin in contact with an organic medium is converted to a dispersion of resin particles in the medium through the interfacial energy of a surfactant used in the process. For a successful chemical milling, several factors are playing important roles such as surfactant, process aid, and homogeneity of resin.

To investigate the effect of polyester structure on the particle formation in chemical milling systems, various amount of ionic contents polyester was prepared to carry out chemical milling. The polyester without ionic groups was found to exhibit very large particles (not shown here) and a very broad size distribution whereas the particles from ionic polyesters showed narrow size distribution. This implies that the ionic structure of the polyesters contributed to the stability of the particle dispersion during communition process. This is in good consistency with our previous reports on the self-emulsification of ionic polyesters.[10] The ionic group of polymer could be the stabilizing sites when the polymer contacts polar medium and the equilibrium size of the particle was affected by the polarity of the medium as well as by the content of the ionic structure of polymer. The ionic contents of the polymer droplet would have close relation with the size distribution of the toner particle. The equilibrium size of toner particle would be determined by the mechanical shear and the ionic contents of the polymer, which represents the surface tension of the droplet of the polymer solutions. When the polymer solutions dispersed in the medium of chemical milling, the droplets of polymer solution would have variation in amount of ionic group to lead the different equilibrium droplet size. To have a uniform distribution of the ionic group in the droplet of the polymer solutions would be needed a certain amount of the ionic group in the polyesters.

For the case of the toner particle from the polyester, the images of the particle taken with microscope were illustrated in Fig. 1. When the colorant masterbatch was incorporated with polyesters, it forms very homogeneous dispersion of the pigment. As the process aid started to evaporate, the particle size was slightly changed, however, it did keep its major distribution with time whereas some chemical toner process experienced dynamic change of the particle formation. It is noticeable that the particle size distribution was shaped at very early stage. The strong dependency of the particle size and its distribution on the polyester design implies that surface chemical potential of polymer droplets would overcome increased viscoelasticity of droplets containing pigment particles. From this result we confirmed that the main principle of the particle formation in chemical milling way is the surface chemical potential of the dispersion droplet of polymer solution rather that mechanical shearing force.

To test the effect of the homogeneity of the polyester, we tried to incorporate commercially available pigment masterbatch comprising of pigment and commercial polyester and masterbatch made of DPI polyester, while the binder resin was the DPI polyester prepared here. The particle size distribution for this example was found to demonstrating that the particle with the

homogeneous polyester system had narrower size distribution. But it is noticeable that the particle size distribution is narrow enough for the application of the toner particle where the commercially available pigment masterbatch was employed.

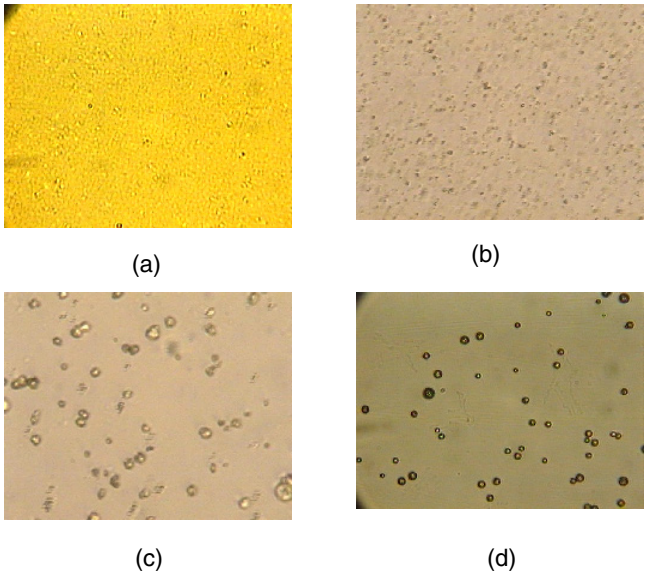

Figure 1. Micrograph taken during chemical milling (a) mixing of masterbatch with polyester resin (b) 1 min after chemical milling (c) 1 hr after chemical milling (d) 4 hrs after chemical milling

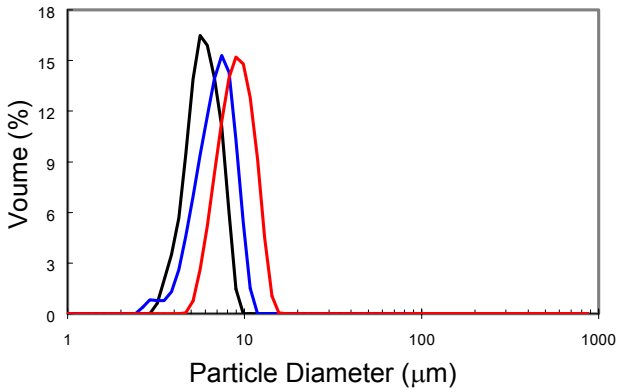

Figure 2. Size controllability of the chemically milled polyester toner of cyan color

The mean diameter of the toner particle was investigated in terms of the amount of the surfactant added with same mechanical shear rate. Figure 2 demonstrates the controllability of the toner particle size. The size distribution of the toner particles was found to be controlled in the range of the 5-10 microns implying that the amount of surfactant quantitatively decide the mean diameter of the particle. This is very easy way to get variation in toner particle size. Another way to adjust the toner particle size is to change in mechanical shear rate under given surfactant amount.

As the resolution of printing image become higher and higher, a smaller sized toner is required to meet high image quality. We tried to make the CM toner more saturated color toner which create larger color gamut than that of currently achievable. Highly saturated color toner would be attained by an incorporation of more amount of pigment masterbatch than that of commercial toners. The difficulty of conventional method restricted from elastic characteristics of the toner caused by pigment amount. The more elastic property with high amount of pigment make it difficult to be small sized toner, however, the chemically milled toner was found to be possible to make small sized toner particle with high amount of pigment because the particle formation in the chemical milling techniques were mainly accounted for the surface chemical potential supplied by the polyester design. This is a capable advantage for color management of chemical milling technique. Figure 3 illustrates the color gamut comparison for a commercially available toner and the chemically milled toner with normal amount of pigment, and with higher amount of pigment by 30%. The chemically milled toner with normal amount of pigment showed comparable color gamut with that of commercial toner while the chemically milled toner with high optical saturation occupied broad area in color coordinate. This result forms a strong basis that the chemically milled toner provide be a suitable design for the next generation toner in terms of color management.

The charging characteristic of the toner is a strong influential factor in machine design. We tested the charging characteristics with blow-off method as a function of amount of CCA incorporated in the toner and it was listed in Fig. 4. It is noticed that the charging level of chemically milled toner was found quantitatively controlled as a function of CCA amount. This will be another advantage that the chemically milled toner can give to machine designers.

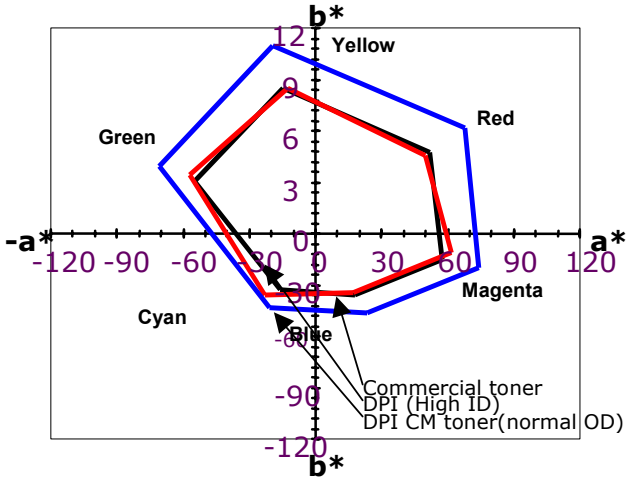

Figure 3. Comparison of color gamut of commercially available chemical toner and CM toner with normal optical density and high optical density

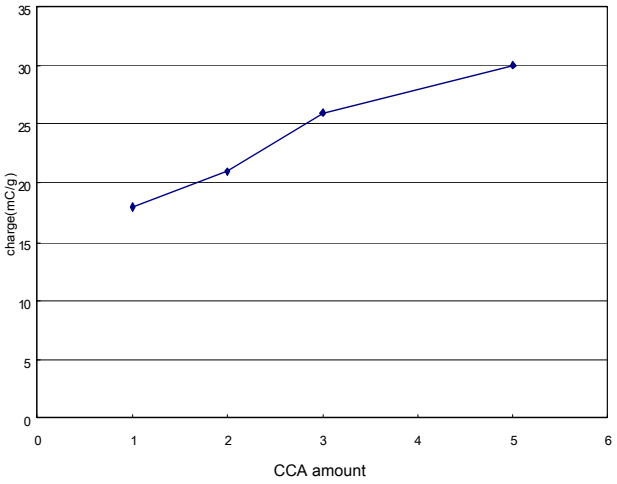

Figure 4. Blow-off charge developed on the toner with different CCA amount

Finally fusing property of CM toner was investigated as a function of temperature. The fusing of the CM toner was excellent in the range of 150 ~ 220°C where most printers currently employed. We expect that the appropriate resin design of polyesters with acceptable rheological frame can shift the fusing latitude to our needs. It is widely accepted that the high speed printers would take advantage of the polyester due to its easy melt flow and the CM toner will meet future requirement of the toner polyester for future design of high speed printings.

Conclusion

We developed a novel chemical milling method for producing small sized toner with narrow size distribution, comprising of polyester, wax, charge controlling agent, and pigment.

By chemical milling method, it was possible to prepare the polymeric particles to have any volume averaged mean value in the range of 3~ 15 μm by application of simple process parameter. The particle had a narrow size distribution with the 80% span as low as 0.5. The CM toner could be designed for the highly saturated optical density leading to a broad color gamut and it was also simply controllable to have any charge level quantitatively as a function of CCA amount. The fusing characteristic of the CM toner was matched with the currently used printing machines. The capability of the CM toner proved in this study could supply several advantages for the future toner requirements.

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