

# Preparation of Toner Particles with Micro-serrated Texture by Chemical Milling

*Chul-Hwan Kim, Eui-Jun Choi, Seung-Wook Lim, Suk-Jin Kim and Hyun-Nam Yoon*  
*R&D Center of DPI Solutions, Inc.*  
*Daejeon, Korea*

## Abstract

Recently various dispersion polymerization methods have emerged as an economical alternative for producing small sized toners and thus improving the resolution of electrophotography (EP) images. The polymerized toners generally have a small particle size, a narrow size distribution and a spherical shape with a smooth surface. However, the methods present several difficulties such as process and equipment complexity, potential for solvent contamination of toner particles, inflexibility of formulation variation and slow charging characteristics.

We developed a novel chemical milling method of producing small toner particles, which has the advantages of the polymerization methods but are free of the above-mentioned disadvantages. The spherical toner particles produced by the chemical milling method may have the mean diameter any value in the range of 3-15  $\mu\text{m}$  with a simple adjustment of the process parameters. The particles generally have a narrow size distribution with the span ( $= (d_{90}-d_{10})/d_{50}$ ) as low as 0.6. Furthermore, the particle surface morphology may be controlled to have a rough texture, which significantly improves the charging characteristics of the particles. The process is applicable for a wide range of binder resins, including commercial styrene/acrylic and polyester resins. Physical properties of the chemically milled toners as well as their EP performance are presented.

## 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.<sup>1,2</sup> 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.<sup>3</sup> Even though the polymerized toner has the aforementioned advantage over the melt mixing methods it has several shortcomings. Since the aqueous medium is generally used in the polymerization reaction, difficulty arises in filtering process to separate water from slurry as well as in drying process to develop the finished toner from the prepared particles. The aqueous suspension polymerization limits the types of monomer components for the base resin. The shape of the polymerized toner particles is generally spherical and the particle surface morphology is smooth. Therefore, charging property of the toner particles is inferior in terms of the properties such as charging speed and level.

Here we introduce a new method for producing toner particles in a non-aqueous medium without any chemical reaction, of which image resolution power is comparable if not superior to that of the polymerized toners. Also is reported a method which allows us to modify the particle surface morphology varying in a wide range from smooth to deeply serrated structure. The surface modification further has a beneficial effect of changing the charging characteristics of the toner particles. The DPI toner production method, which we call the chemical milling method, consists of mixing and dispersion steps followed by filtering and drying. The method can be easily scaled-up for commercial production.

## Experimental

### Preparation of the Polyester as a Base Resin of the Toner

A cationically dyeable polyester was prepared by a melt condensation process. Polyester monomers, dimethylterephthalate, dimethylisophthalate, sodium salt of dimethyl 5-sulfoisophthalate, propylene glycol in the molar ratio of 0.50/0.47/0.03/1.00 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 200°C under a flowing argon atmosphere

over 4 hours and subsequently maintained at 200 °C until approximately calculated amount of distillate is collected.

The reaction mixture was then further polymerized by further heating to 210°C in about 30 minutes and then maintaining at the temperature for one hour while under agitation of 50 rpm. The agitator speed was then lowered to 30 rpm and the reactor put under a vacuum 0.5 torr for half an hour. Polymer was recovered by releasing the vacuum, the reactant cooled down to about 150°C, the reactor content poured onto a glass plate and allowed to cool down to an ambient temperature. The number average molecular weight of produced polymer was 6,000 and the thermal analysis of the polyester resin gave the glass transition temperature of 65°C.

### Particle Formation by Chemical Milling

The first step of particle formation by the chemical milling is mixing the polymer resin and an evaporatable plasticizer. For example, in a round bottom flask equipped with an impeller type agitator and condenser, the polyester resin and a processing aid as an evaporatable plasticizer were charged in a weight ratio of about 100:20 parts. The mixture was thoroughly mixed and molten by heating to about 150°C under a total reflux condition under a vigorous agitation. The mixture became transparent indicating that the additive was finely dispersed in the resin melt.

About 100 parts of a mixture of Isopar L:V(1/1) and 12 parts of a surfactant were charged into the flask which contained the resin mixture under agitation at 150 °C. The Isopar mixture was the dispersion medium and the surfactant is a block copolymer of vinyl-pyrrolidinone and alkyl. After the charging, the mixture was further maintained at the temperature while the agitator speed was increased to the specified value of the process. The shearing continued until the vapor of the plasticizer stopped evaporating and the dispersion was allowed to cool down to the ambient temperature. The toner particles were separated from the organic medium using a filtration process. The organic medium entrained in the filter cake was washed off by washing with iso-hexane. The particles were then dried in a vacuum oven at 45 °C.

### Characterization

Particle size and distribution were determined using a TAAI Coulter device (Coulter Electronics, 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,<sup>4,5</sup> 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 an organic medium is converted to a dispersion of resin particles in the medium with the help of the surface chemical forces of a surfactant. A successful chemical milling depends on several factors. One example is shown in Fig. 1 in which the size distributions of the polymer particles produced by chemical milling runs with and without an evaporatable plasticizer are shown. It is apparent that the plasticizer allows easy formation of polymer dispersion with a small average particle diameter and a narrower size distribution. It is believed to be a result of that the incorporation of a plasticizer in the polymer melt brings about a substantial reduction of the melt viscosity so that the relative ratio of the melt viscosities of the melt and the medium becomes smaller. The viscosities of the dispersion-forming melt and the dispersion medium at different temperatures are plotted in Fig. 2. It is well known fact that breakage of polymeric melt droplets was mainly caused by transmission of a shearing force between two immiscible liquids with similar viscosity values. Fig. 2 confirms that the polymer viscosity significantly decreases and therefore becomes closer to that of the dispersing medium in the presence of the processing aid.

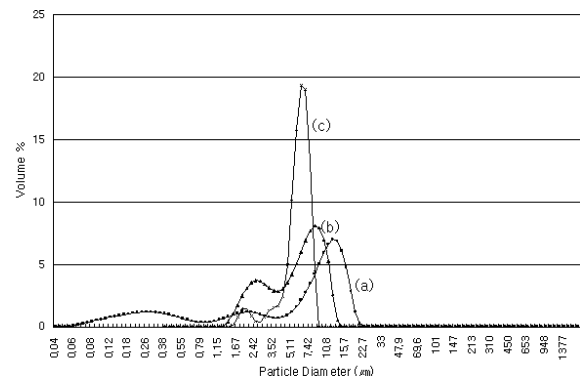


Figure 1. Particle size distribution of the polymer dispersions produced by chemical milling where the amount of the processing aid was (a) 0 wt.%, (b) 10 wt.%, and (c) 20 wt.%.

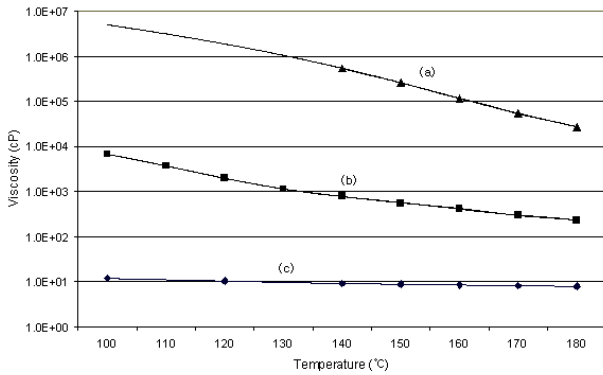


Figure 2. Viscosities of dispersed polymer samples and the dispersion medium at different temperatures: (a) Polyester sample of this study, (b) a polyester mixture with 20 phr plasticizer, and (c) the dispersion medium, Isopar V.

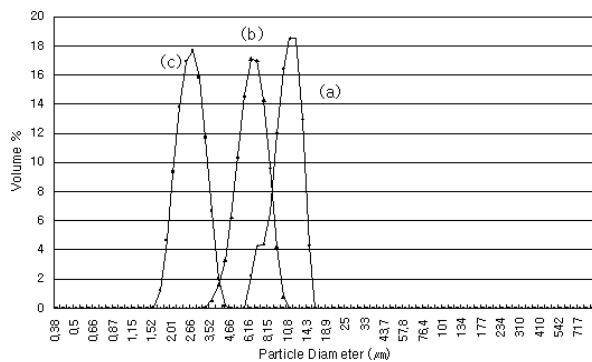


Figure 3. The particle size distribution of the polymer dispersions prepared by chemical milling at different shearing

Control of the particle size in the chemical milling is achieved either by varying the amount of surfactant or by varying the shearing rate. The particle distributions produced at different shearing rates are shown in Fig. 3. A sharp dependence of the particle size on the shearing rate is apparent. Variation of the particle size with different amounts of surfactant at a relatively mild shearing rate was determined. A modest dependence of the particle size was observed. This may be interpreted as that there exists a critical shearing rate for each surfactant amount level and, below the rate, only a fraction of the added surfactant participates in stabilizing the polymer droplets formed.

The mechanism of formation of polymer droplets may be formulated based on the observed particle images in the course of the chemical milling process. The microscopic data clearly demonstrate that small polymer droplets are formed by the sequence of shear deformation, break-up and particle stabilization. Fig 4 shows the microscopic image of the intermediately deformed particle. As the shear rate increases, the large droplet deforms to a slender structure and it breaks up to a form fine droplet. Since the interfacial

tension is inversely proportional to the square of radius, it is the stretched region where there is no strong interfacial tension to counter the shearing stress to break and, as a result, two smaller droplets form from a droplet.

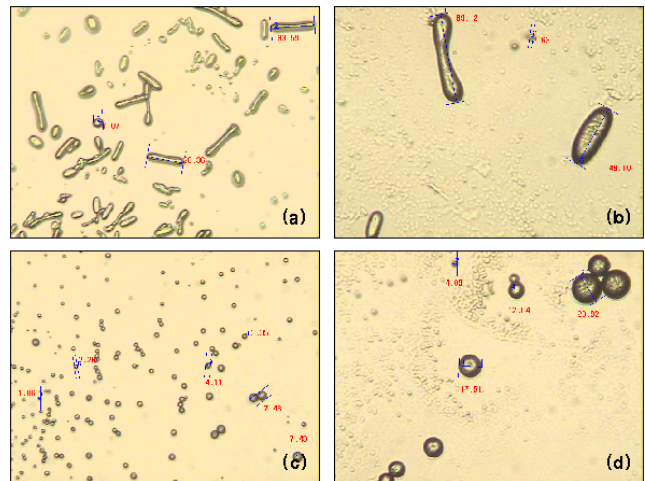


Figure 4. Optical micrographs of the polymer particles in the dispersions produced under different chemical milling conditions; (a) An intermediate stage at 400 rpm agitation, (b) Final stage at 400 rpm, (c) An intermediate stage at 100 rpm, and (d) Final image at 100 rpm.

### Effect of Initial Condition

It is anticipated that the initial condition of the state of the polymer melt phase may affect the particle size distribution. The surfactant should be uniformly distributed throughout the polymer phase so that the surfactant activity may be in effect throughout the system and thus form a more uniform dispersion. When the size of the polymer droplets was initially uniform prior to the surfactant addition, the surfactant may cover the surface of polymeric droplets evenly to produce uniform droplet size after milling. Theoretically, in a many body problem wherein formation of a particle is closely correlated with generation of other particles in the system, the particle size distribution is strongly dependent on the initial condition.<sup>6</sup>

### Effect of Surfactants and Plasticizer Evaporation on Particle Surface Morphology

In a surface chemically driven process such as the chemical milling, the particle surface morphology would be smooth as the particle shape is spherical. However, we developed a way of producing spherical resin particles with rough surface texture by a careful selection of surfactants and the plasticizer we used in the process. In the last phase of our process, the surface of polymer droplets is distorted by rapid evaporation of the plasticizer. In addition, the melt viscosity of polymer in the droplet increases sharply with the loss of plasticizer. Under the dynamic condition, we found that the particles produced with the help of a

polymeric surfactant develop a rough surface texture. In fact, a wide variety of particle surface texture can be produced by a judicious choice of surfactants. A polymeric surfactant we use extensively is a Ganex surfactant that is a graft copolymer of vinyl pyrrolidone and alkyl chains. Another is a Genapol surfactant that is a more traditional non-ionic surfactant based on ethylene oxide moieties. The two surfactants have different molecular weights and HLB numbers hence physicochemical natures are clearly distinct.<sup>7</sup> Fig 5 shows different surface morphologies of the polyester resin particles prepared with the Ganex alone and a mixture of he mixture of Ganex and Genapol. The surface texture of the particles produced with the mixed surfactants shows a smoother surface than the particles made with Ganex alone. This may be explained by the fact that smaller Genapol surfactant has more mobility in the process condition and more readily responds to the higher surface tension associated with the rough surface texture created by departure of the plasticizer from the droplets.

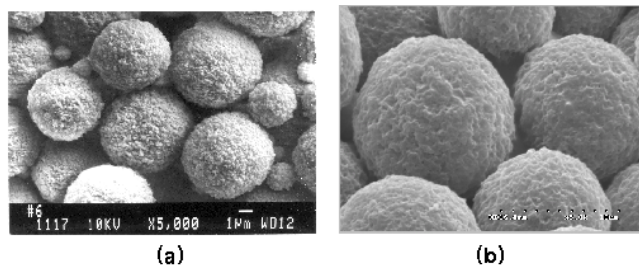


Figure 5. SEM micrographs of resin particles produced by chemical milling with (a) Ganex alone and (b) Mixed Ganex and Genapol.

The surface morphology also depends on the types of plasticizer we use in the process. We examined the effects of the polarity of solvents on the particle surface texture. Two organic solvents and a mixture of the solvents were used as plasticizers in chemical milling to produce polyester particles. The particle formed with a pure solvent with the low polarity displayed the least rough surface and the particles made with a pure solvent with the high polarity showed the most rough surface while the mixture produced the particle surface texture intermediate between the two extremes. This might be caused from the different interaction of the surfactant used in the milling with the solvents. The less polar solvent is soluble in the surfactant while the polar solvent was observed to minimally soluble in the Ganex surfactant. The solvated Ganex molecules that were originally located on the droplet surface made the polymer melt near the surface be directly subject to the interfacial tension without stabilizing the micro-serrated surface and therefore the particles end up with a smoothed surface texture.

### Charging Behavior

DPI's chemical-milled toner particles generally have unusual surface morphology. The rough surface texture affects the triboelectric charging characteristics of the toner particles, especially the charging level and the speed. To see the effects more quantitatively, we prepared four toner samples with different roughness level. The SEM micrographs of the samples are shown in Fig. 6 (a) – (d). To quantify the roughness, we defined the roughness index as the ratio of surface areas of the particles and of the particles with the same diameter but with a perfectly smooth surface. The surface area of particles with a rough surface texture was determined by the BET isotherm. The roughness index was defined as following equation.

$$\text{Roughness index} = (1/6) \rho * d * A_{\text{exp}}$$

where  $\rho$  is the density of the polymer,  $d$  is the diameter of the particle and  $A_{\text{exp}}$  is a surface area of particles obtained from the BET isotherm experiment.

The roughness index of the particles shown in Fig 6(a)-(d) was 1.0, 1.6, 1.8, and 2.1, respectively. In Fig 7, the charging behavior of the particles with the mixing time is plotted. The particles with the increased value of the roughness index clearly displayed a faster charging behavior while the equilibrium charging levels of the different particles approached to the similar level. Here these particles comprised only of the polyester. Therefore, the observed difference in charging behavior may be interpreted to be originating only from the morphological variation of the particle surfaces. Since the electrical charges inherently accumulate on sharp edges, the micro-serrated morphology is thought to be superior to the smooth morphology in charge accumulation on the particle. The surface morphology of the particles mainly determines the charging speed.

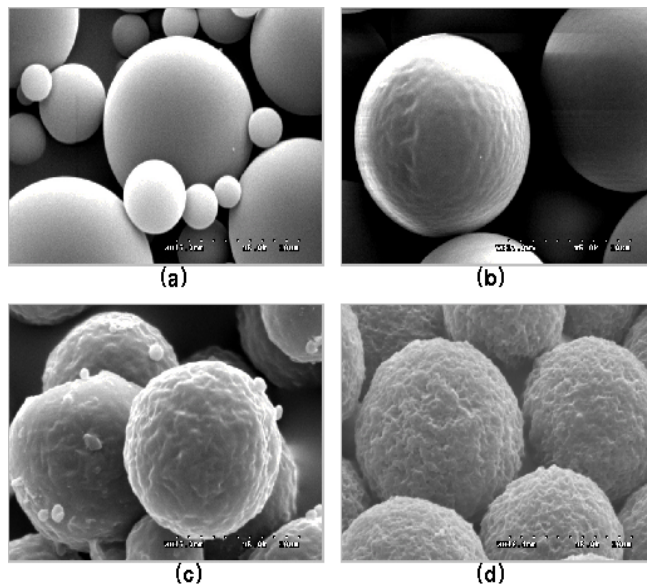


Figure 6. SEM micrographs of resin particle with a different roughness index values; (a) 1.0, (b) 1.6, (c) 1.8, and (d) 2.1.

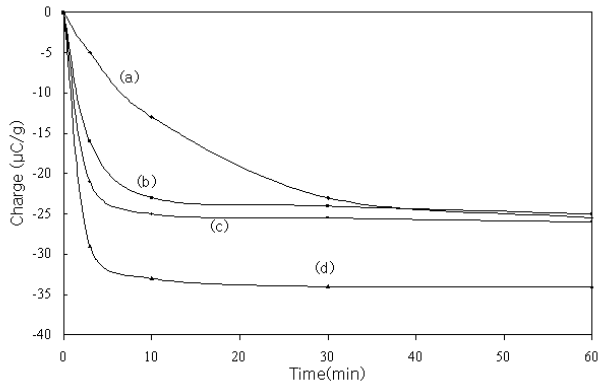


Figure 7. Charging behavior of polyester particles with a different roughness index values; (a) 1.0, (b) 1.6, (c) 1.8, and (d) 2.1

## Conclusion

We established a novel chemical milling method as a method of producing high-resolution toner particles with an exceptionally narrow size distribution and, at the same time, free from disadvantages of the so-called polymerization methods. We were able to prepare polyester toner particles with the average diameter in the range of 3 ~ 15  $\mu\text{m}$  and established the process parameters to control the diameter. Furthermore, the particles had an exceptionally narrow size distribution with the span as low as 0.6 in some cases. The surface morphology of the chemically-milled toner may be controlled to have an extensive micro-serrated texture and the particles demonstrated significantly accelerated charging behavior.

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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.