EFFECTS OF POLYMERIZATION PROCESS VARIABLES ON THE PROPERTIES OF SUSPENSION POLYMERIZED TONER

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1 Introduction

Polymerized Toners have attracted more attention recently. Because the demand for fine images and high resolution with uniformity in color laser printing has increased rapidly. Toner can be classified into two categories according to its preparation methods. Pulverization method in which charge control agents (CCAs), colorants, and other additives are dispersed in a molten resin matrix, followed by cooling, crushing, pulverization, and classification of the pulverized material to separate toner particles with the intended particle size. Polymerization method which prepares both water phase which contains suspending agent and oil phase which has monomer, CCA, colorants, and other additives, separately at first. And then mixing, polymerization, washing and drying follow step by step. Compared with the pre-developed pulverization process, the polymerized toner process eliminates the crushing and sorting of the pulverized products and their subsequent procedures, thereby lowering manufacturing costs. Fig. 1 compares SEM images of polymerized and pulverized toner particles. The suspension polymerized toner is spherical, whereas the form of the pulverized toner is indefinite. Pre-developed pulverized toner has unresolved problems such as a low toner yield, limitations of the variance in the process of melting and mixing internal additives that caused low printing quality. Accordingly, polymerized toners are being developed to solve the problems of pulverized toner and make high-speed and high-quality color laser printing possible. In this study, styrene-based polymerized toner was prepared using an inorganic suspending system composed of calcium chloride and trisodium phosphate. Syringe with pump was used to control the size of toner particles uniformly. How do quantity of the inorganic suspending agent and rotating speed of the stirrer affect shape of polymerized toner particles were studied. Moreover, the effects of pH of the reacting medium and injection rate of oil phase into water phase on the polymerization of toner particles were studied.

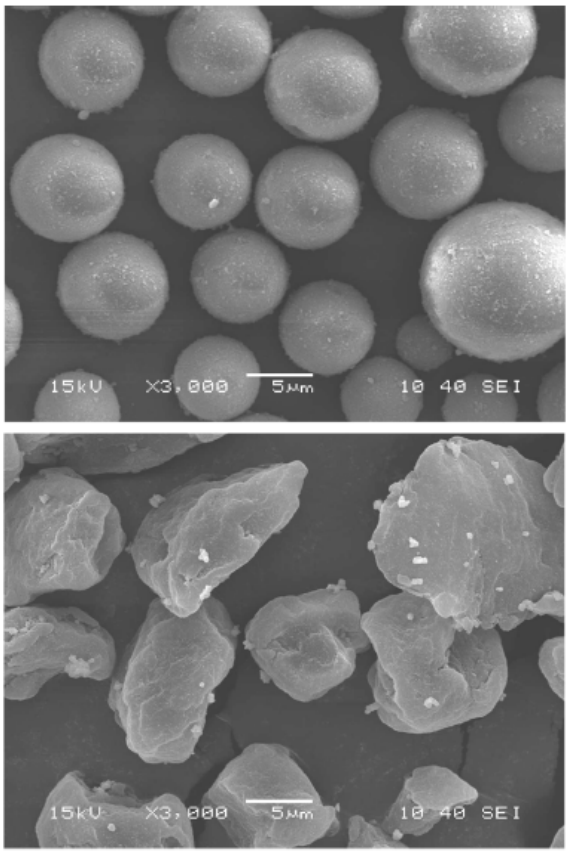

Fig. 1. SEM images of polymerized (top) and pulverized (bottom) toner particles.

2 Experimental

2.1 Materials

Styrene and n-butyl acrylate purchased from Junsei Chemicals (Kyoto, Japan) were used as monomers. ADVN (2,2'-azobis-(2,4-dimethylvaleronitrile), Wako Chemical, Osaka, Japan) and divinylbenzene (DVB, Sigma-Aldrich Chemicals, New York, USA) were used as an initiator and a crosslinking agent, respectively. Calcium chloride (Sigma-Aldrich Chemicals) and sodium phosphate tribasic (DC Chemical) in water were used to make an inorganic suspending system.

2.2 Preparation of water phase

The water phase (suspending medium) was prepared by dissolving calcium chloride and trisodium phosphate in water. Calcium chloride and trisodium was put to have molar ratio of 1:1.5. And then, the solution was stirred at 60°C, 12000rpm for 45min.

2.3 Preparation of oil phase and suspension

The oil phase was prepared by mixing styrene, n-butyl acrylate, colorant, CCA and other additives. The oil phase was injected by a syringe pump in the water phase at a constant rate. Effects of varying rotating speed of the stirrer, injection rate of oil phase were studied.

2.4 Polymerization, washing and drying

After formation of droplets, toner particles were polymerized at 60°C for 12h at 300rpm. After polymerization is complete, is cooled to room temperature. By using 1N HCl in order to remove the inorganic suspending agents adhered to the polymerized toner particles, pH was dropt to 2. Until pH value is neutral. The toner particles were filtered and washed with distilled water each several times, and then dried using a vacuum oven at 40°C for 1day.

2.5 Characterization of toner

The particle sizes and size distribution of toner particles were measured with particle size analyzer (Sysmex FPIA-3000, Malvern, UK). To investigate the thermal behavior of the toner particles, a differential scanning calorimeter (DSC, DSC2910) was used. Flow characteristics of toner particles were analyzed using a flow tester (Flow Tester CFT-500D, Dong-il Shimadzu). A field emission scanning electronic microscope (FE-SEM, LEO-1530FE, Carl Zeiss NTS GmbH, Oberkochen, Germany) was used to investigate not only the shape of the toner particles but also the morphology of the toner particles.

3 Results

3.1 Effects of rotating speed on the physical properties of toner

Both small particle sizes and narrow size distributions are indispensable for fine images and high resolution with uniformity in color laser printing. To evaluate the effects of rotating speed on the physical properties of toner, experiments were conducted at various stirring speeds. Experiments with stirring speed ranging from 2000 to 12000 rpm were conducted, and the results are shown in Fig. 2, in which the particle size and the size distribution of the particles against the rotating speed are plotted. It is inferred that the particle size can be increased by increasing the stirring speed. When the stirring speed is low, the reason why the mean particle size is small is that the fine particles are much generated. On the other hand, the average particle size seems to be enlarged while the re-cohesion of the fine particles occurs at high rotating speed. In case of size distribution, smaller size distribution values indicate a narrow size distribution. As shown in the Fig. 2, to obtain the toner particles that have uniform size, high rotating speed is required.

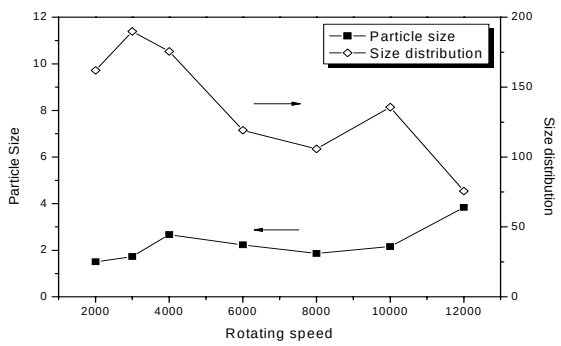

Fig. 2. Particle size(-■-) and size distribution(-◇-) as a function of the rotating speed.

Table 1. The values of diameter, diameter CV, circularity and circularity CV of toner particles prepared at various rotation speeds.

Sample	Rotating speed (rpm)	Diameter (μm)	Diameter CV	Circularity	Circularity CV
Exp#1	2000	1.498	162.03	0.734	22.7
Exp#2	3000	1.724	189.89	0.764	20.13
Exp#3	4000	2.667	175.6	0.828	16.76
Exp#4	6000	2.233	119.2	0.89	11.92
Exp#5	8000	1.865	105.84	0.909	11.03
Exp#6	10000	2.157	135.67	0.954	6.45
Exp#7	12000	3.84	75.62	0.963	5.22
Exp#8	12000	6.141	51.66	0.950	5.99

Table 1 shows the diameter, diameter CV, circularity and circularity CV of toner particles prepared at various rotating speeds. By adding the wax, Exp#8 was manufactured under the same processing condition as Exp#7. If the wax is added, the generation of the unnecessary fine particles is decreased and the narrower particle size distribution can be obtained.

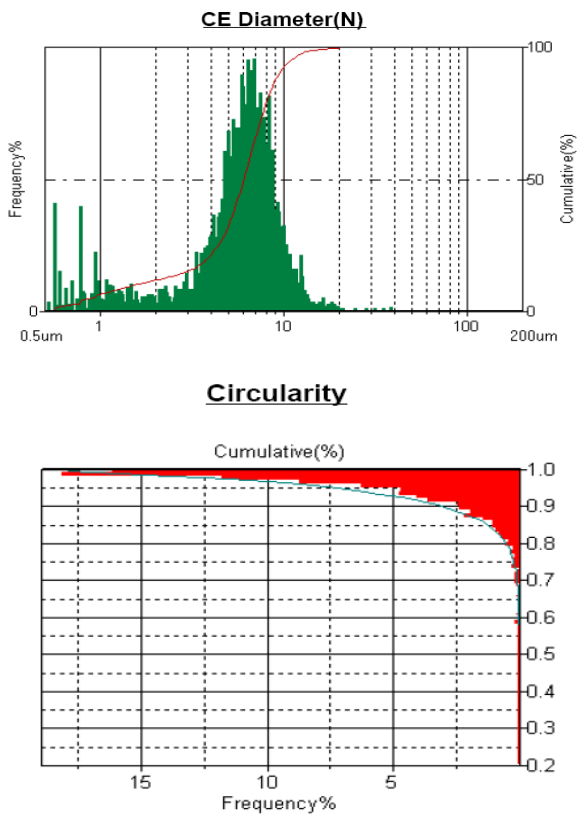

Fig. 3. The particle size distribution (top) and circularity (bottom) of the toner particles.

Fig. 3 shows results of particle size distribution and circularity of the toner particles as the wax is added. The top graph in Fig. 3 showed a sharp peak indicating a narrow size distribution. The fine particles existing a little bit play a role enhancing the fixation property of the toner.

3.2 Thermal properties of toner

The thermal property of toner is one of the most important characteristics. The heat and pressure is required so that the toner can fix in the paper. The glass transition temperature of the toner is the index determining the fusing temperature of the toner. It is cohered in the cartridge if the Tg of the toner is too low. If Tg is too high, the large-scale loss is generated in the energy efficiency. The Tg of the toner obtained in Exp#8 is 65.7°C from DSC data in Fig. 4. And the Tg of the toner for the widely used energy efficient laser printer is 50~70°C.

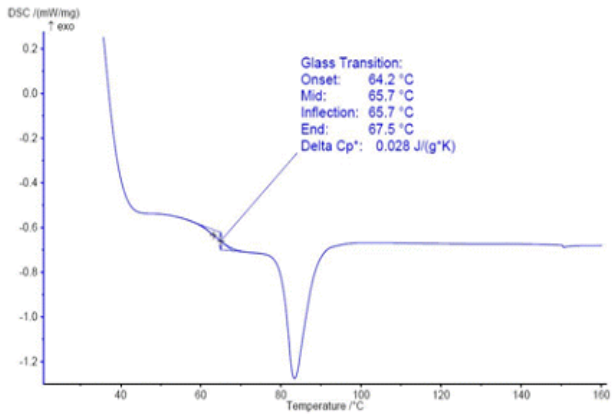

Fig. 4. DSC thermogram of the toner particles.

3.3 Effects of pH on the characteristics of toner

The experiments were carried out in the weak acid, neutral and weak base condition in order to investigate the influence of pH on the preparation of toner. Fig. 5 shows graphs of particle size distribution according to pH change. When the condition is weakly basic, the toner particles having uniform-size was not prepared. The zeta potential of the water phase is the same plus polarity as the surface of oil phase when the condition is weakly basic. It is inferred that repulsive power acts between the oil phase and water phase and it obstructs the formation of toner particles. As shown in the printing sample in Fig. 5, the imaging defects including the printing picture density decrease and etc. were generated when pH was high. When the pH of the water phase was 5.5, polymerized toner with excellence in not only physical properties but also printing image quality could be obtained.

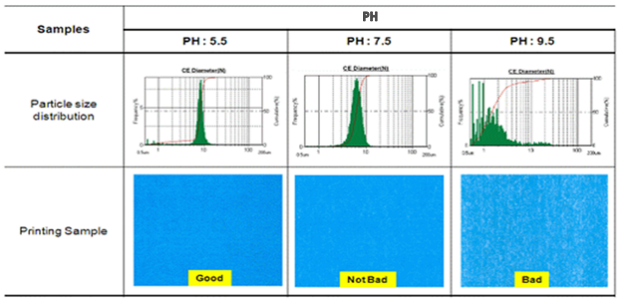

Fig. 5. Effects of pH on the particle size distribution and printing quality of the polymerized toner.

3.4 Effects of injection rate of the oil phase into water phase on the properties of toner

To investigate the effects of the injection rate of the oil phase into the water phase by syringe pump on the characteristics of polymerized toner, the injection speed was changed from 100 ml/h to 200 ml/h. The toner particle size distribution had not changed even though the injection speed was increased. However, as the injection speed was fast, the particle size was increased.

4 Conclusion

By using the inorganic suspending system composed of calcium chloride and trisodium phosphate, suspension polymerized toner for laser printer was prepared and its characteristic was investigated. Rotating speed of the stirrer affected largely the shape of polymerized toner particles. With increasing the rotating speed, the average toner particle size increased. Toner having an ideal particle size and size distribution could be obtained at 12000 rpm. The polymerization of toner particles was considerably affected by pH of the reacting medium. The injection rate of the oil phase into the water phase affected particle size slightly. High-quality polymerized toner could be prepared using the inorganic suspending system using an optimized composition and processing condition.

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