

Particle Size Distribution and Morphology of Suspension Polymerized Mono-component Magnetic Toner

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Abstract

In this paper, we prepared mono-component magnetic toner by suspension polymerization method. Detailed investigation focused on the particle size distribution and morphology of final product. Theoretical research and experimental result show that particle size distribution (PSD) of polymerized toner is mainly controlled by surfactants and inorganic stabilizer. Deliberated selected surfactants can decrease the surface tension significantly and without emulsion formation. Added fine inorganic magnetic pigment forms a strong film, which prohibited the coagulation of dispersed monomer's droplet. After carefully selection of operation conditions, final polymerized toner with average diameter of around 10 microns and span of 1.5 to 2.0 can be acquired. The added hydrophilic fine pigment particles have a strong tendency to enrich on the interface which can be seen clearly from SEM and TEM photo of the polymerized toner. Theoretical analysis indicates that surface modification of magnetic particles can increase the affinity between monomer and pigments, so to minimize surface accumulation. Related experiment results showed that selected silane coupling agent and titanate coupling agent are not as so effectively as expected. In the end, mono-component magnetic toner with spherical shape and rough surface was obtained by suspension polymerization method.

Introduction

Toner is a developer widely used by copiers and laser printers. These automatic office machines are all based on electrophotographic process (or Xerography) invented by C.F. Carlson in 1938^[1]. The process follows as this: electronic latent image are formed on a photoconductor by corona (or other means), and subsequently developed by colored toner to form a toned image, and the toned image is optionally transferred onto a transfer materials such as paper, and then fixed by heating, pressurization, heating and pressurization to obtain copied products or prints. Colored toner used for development is either composed by toner and carrier as a dual-component

developer or just composed by magnetic toner only as a mono-component. Although dual-component toner has successfully used by Xerox machine, mono-component toner has also been well developed for Canon copier and HP laser printer for its small development space and easy developer replacement.

Commercial toners used in the process mentioned above have always been manufactured by melt-mixing method. It follows as this: colorants such as magnetic materials dispersed into thermoplastic resin uniformly first, then followed by extruding, cooling, pulverization and classification into desired particle size distribution. This pulverization process is capable of producing considerably excellent toners but accompanied with potential problems, for example, the selection of resin material is rather limited. For the special properties (such as softening temperature, melt index and molecular weight distribution) required for toner resin, it is always hard to find a commercial product meet for these requirement and you may have no room for adjustment if one resin is specified. Another disadvantage for this processing is for pulverization and classification which both high energy cost and low efficiency. This became even worse for the fine toner is becoming popular in order to get a higher resolution image. Meanwhile, because the resin composition is fragile, particles having a wide range of particle sizes are easily produced when the resin composition is micro-pulverized at high speed under lower temperature. A large amount of excessively pulverized fine particles not only decrease the efficiency of production but also increase the fog of copy. Furthermore, it is extremely difficult to uniformly dispersed solid fine particles in a resin. Therefore, in order to overcome the problems of melt-mixing process, it has been propose to produce a toner through suspension polymerization routes.

As for the size of suspension polymerized particle is mostly bigger than 50 microns and the distribution is wide, special treatment should be applied to obtain a product with an average size of 10-20 microns and with a narrow size distribution to satisfy the requirement of toner. According to the model proposed by Winslow and Matreyek for bead suspension polymerization, particle size are mainly decided by the size of dispersed monomer's droplet and the stability

of monomer/polymer's droplet during polymerization. If the coalescence of monomer/polymer's droplets during polymerization can be neglected, which can be realized by using suspension stabilizer, PSD of final product will similar with monomer's droplet. In this case, PSD of toner can be analyzed by Heinz's theory about dynamic balance between breakage and coalescence of dispersed droplet. If droplet coalescence can also be neglected by using stabilizer, maximum particle size of suspended droplet in a turbulent reactor can be estimated by the following equation, which base on microscale theory of Kolmogoroff^[21].

$$d_{p\max} = K \left(\frac{\sigma}{\rho_c} \right)^{3/5} \varepsilon^{-2/5}$$

Here, $d_{p\max}$ is the maximum particle size than can exist in the suspension; K is a constant; σ is the interface tension between monomer droplet and water phase; ρ_c is the density of continuous phase; ε is energy density which rely on agitation speed. This equation illustrate that agitation speed, interface tension and viscosity of continuous phase are the predominated parameters to determine the PSD of monomer's droplets. Although this equation is only suitable for the system with low volume hold-up, without surfactant and inorganic powders, it is still useful to estimate PSD of droplet for suspension systems. Generally speaking, $d_{p\max}$ in a stirred tank is over than 20 microns. So, decreasing interface tension and increasing agitation speed will result in particle size reduction. As for PSD, the only way is to use stabilizer to inhibit coalescence. After pre-selection of stabilizer and other parameters, polymerization reaction for toner was conducted as follows.

2. Experiment

2.1 Materials

Iron Black pigments (IB), industrial grade, with cubic shape and average particle size of 0.2 to 0.3 micron was used as colorant reagent as received (SEM photo shown in Figure 1). Both Styrene and n-Butyl Acrylate are analytical reagents, used as comonomers were distilled at reduced temperature. 2,2'-azoisobutylnitride (AIBN) used as initiator was dissolved in absolute alcohol and recrystallized at lower temperature. Bonston E81, commercial product, was selected as Charge Control Agent (CCA); Polyvinyl Alcohol (PVA1788), with 1700 degree of polymerization and 88% degree of hydrolysis was chosen as stabilizer; lab synthesized poly(ethylene oxide)-co-poly(propylene oxide) (SUR) and PDA were used as co-stabilizer to control particle size distribution of polymerized product. Other additives like KCl etc were also added to facilitate polymerization reaction. Deioned water was used as polymerized medium.

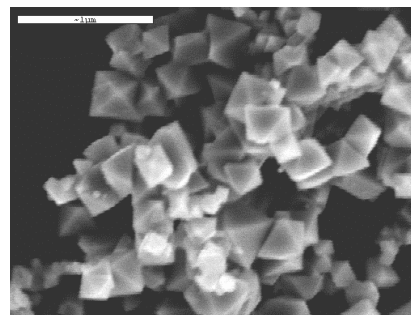


Figure 1. SEM image of IB

2.2 Preparation

Polymerization was carried out in the water phase at a selected temperature between 65-85°C and last for more than 4 hours. Purified styrene and n-butyl acrylate monomers were added to a 600ml sealed glass reactor. The ratio of styrene to n-butyl acrylate was typically selected to be 5 to 1 by volume at room temperature. Premixed monomers and pigments were added to the reactor and polymerization started. AIBN was dissolved in the monomers completely before pigment and CCA added. PVA1788 and SUR were added to the water and used as complex stabilizer; a small amount of KCl was also added to the solution to reduce monomer's water-solubility. Washing with nonionic water for several times to get a clear solution for the final product, filtering with vacuum, drying at reduced pressure were all applied to the final product to get polymerized toner.

2.3 Characterization

PSD of polymerized toner was measured by Malvern particle size analyzer with a range from 0.05 to 555 microns. Morphology was investigated by Scanning Electron Microscope (JEOL JSM 6301F). Transition Electron Microscope (Hitachi 800) was used to observe the inner structure.

3. Results and Discussion

3.1 Particle Size Distribution

Experiment results are shown in Table 1.

Table 1. Experimental Conditions and Results

Sample	D_{50} (μm)	Span*	Surfactant	IB
1	14.03	1.927	SUR	Yes
2	14.43	1.602	SUR	Yes
3	12.91	2.104	SUR	Yes
4	14.34	1.765	SUR	Yes
5	6.98	2.382	PDA	Yes
6	13.94	2.963	PDA	Yes
7	13.40	2.991	PDA	Yes
8	14.41	3.195	PDA	Yes
9	53.34	2.079	PDA	No

$$*\text{Span} = \frac{D_{90} - D_{10}}{D_{50}}$$

From this table, it can be seen that the PSD of polymerized toner has close relations with selected surfactants. Particle size of polymerized toner with SUR as a co-stabilizer localized around 14 microns and with a span less than 2.0. Particle size of polymerized toner with PDA as co-stabilizer is also about 13 microns but with a large span. It means that SUR is better than PDA as a co-stabilizer. This was caused by the different molecular structure of surfactants. As we know, SUR has a hydrophobic group (PPO) anchored into the droplet and a hydrophilic group (PEO) extended into water phase. Stability of adsorbed SUR dispersant comes from extending PEO chain repelled each other when two droplets closed. Meanwhile, PPO group tightly attached to the surface of monomer. For there is no ion charge for the dispersant of SUR, it is easier to obtain a stable film to prevent coalescence without the effect of added ionic reagent. In addition, added IB powders are also act as an inorganic dispersant to facilitate forming stable suspension, which can be resulted from the difference of sample 8 and 9 in table 1. The mechanism of this pickering emulsion is always been explained by mechanical separation. Despite the fact that filled pigments dispersing into the monomer phase first, they can still act as co-stabilizer. Following the conditions mentioned above, the PSD of polymerized toner were successfully controlled into qualified region with average particle size around 14 microns and span of 1.5 to 2.0. Typically PSD of polymerized toner are shown in Figure 2.

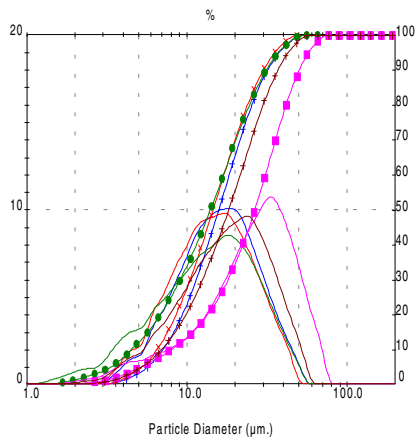


Figure 2 PSD of polymerized toner

3.2 Morphology

Suspension polymerized toner with spherical shape can be seen clearly in Figure 3. That means added IB powders did not alter the solubility of ST-co-BA polymer into comonomers and follows the principle of bead polymerization. Local magnification image shows that added cubic shaped hydrophilic magnetic powders enriched on the surface (as shown in C). Some particles embedded into the resin and some just sit on the surface. This was caused by IB which can be use as pickering emulsifier with surfactants.³

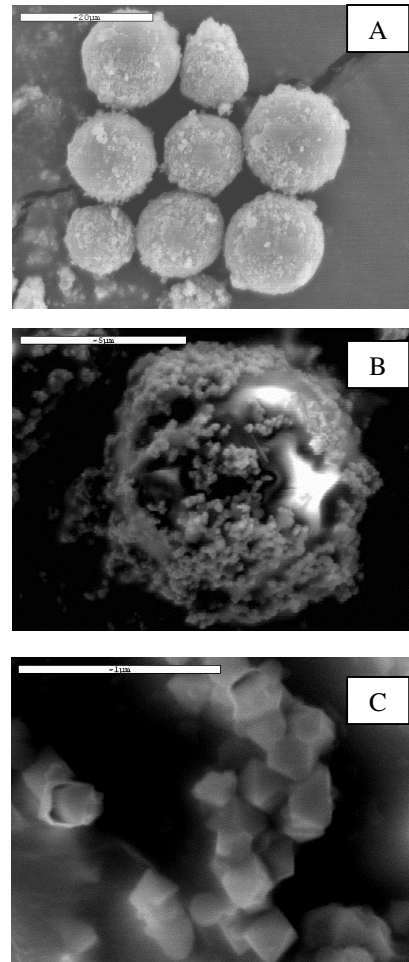


Figure 3. SEM image of polymerized toner. A: Multiple particles; B: Individual particles; C: Local magnification.

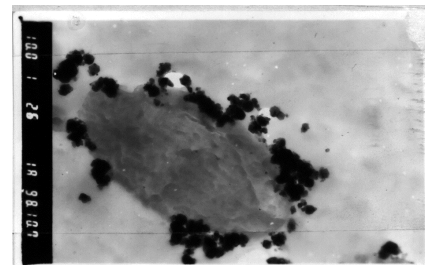


Figure 4 TEM image of polymerized toner

Although IB particles dispersed into monomer droplet at first, they will localize on the surface as violent shear force applied to break big droplet into small droplet when new surface formed. In that case, IB particles can adsorb surfactants and serve as pickering emulsifier. It means every particle enter into the interface area will be localized. So, concentration gradient of fine IB particles resulted between outer layer and inner layer of the droplet, which enhance the Brownian movement of fine IB particles from inner phase

to surface. Thus, mostly IB particles are enriched on the surface and only small amount of IB particles stay in the polymerized toner, which is shown clearly from the TEM photo. (Figure 4). Although couple agent such as silane coupling agent and titanate coupling agent were chosen to improve the affinity between pigments and comonomers, experiment results illustrated that their effect is not as much as expected. As shown in figure 5 and 6, a large amount of IB particles still attached to the surface. Same result came with the issue when pre-polymerization surface modification conducted. This is different with the statement of M.F.Cunningham.⁴ The difference may be caused by the co-stabilizer, which has never been used in their system. This may be caused by the adsorption of added co-stabilizer on the surface of droplet and IB particles will occur in advance, which result in pickering emulsifier formation. Thus, surface modification of IB particles can reduce the tendency of surface enrichment to some extent but have no way to avoid it. In extremely case, hydrophobic IB surface attached to SUR molecular with PPO group and then hydrophilic PEO group extended into water, which also resulted IB surface enrichment.

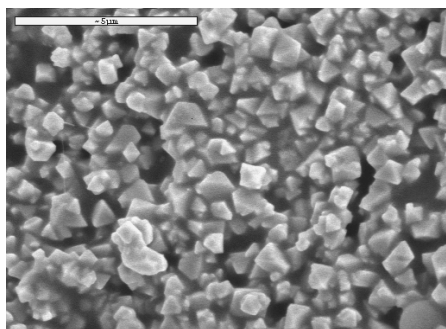


Figure 5. SEM image of Silane modified IB polymerized toner

4. Conclusions

The PSD of suspension polymerization toner is highly dependent on stabilizer. Selected nonionic surfactant SUR with PVA1788 and IB pigment is an effective stabilizer to depress droplet coalescence and to obtain satisfied particles for using as toner. Toner with spherical shape and pigment

enrichment surface also observed and clarified. Experiment results also show surface modification of IB particles is not an effective way to avoid surface enrichment in experiment system.

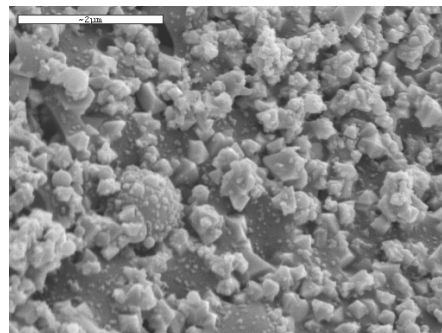


Figure 6 SEM image of Titane modified IB polymerized toner

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Biography

Jun YANG, Male, 1971-, graduated as a Ph.D. from University of Science and Technology Beijing in 1999 and major in toner preparation and characterization. From Jan 1999 to Dec 2000, as a postdoctoral research fellow in Tsinghua University and major in powder technology. Currently as a postdoctoral research fellow of New Jersey Center of Engineered Particulates at NJIT and major in engineered particulate formation and characterization.