Development of Chemically Prepared Toner Using Macromonomer

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Abstract

In this study, the copolymerization of a novel macromonomer, styrene and n-butyl acrylate was investigated to produce toner latexes that are very stable, and their particles are uniform and monodisperse without using any stabilizers or surfactants. Macromonomers are a relatively new category of functionalized polymer materials having one or more polymerizable end groups, thus the use of macromonomers provides an alternative route to stabilize polymer colloids in replacement of surfactants or steric stabilizers in radical polymerizations. Macromonomers acts not only as a stabilizer but also as a comonomer during the polymerization. This toner process is a simple, economical and environmentally friendly process by reducing the amount of wasting water in the washing step due to the surfactant-free process. The size and shape of the toner can be controlled through a selection of the process temperature and the heating time or through a control of the glass transition temperature and the molecular weight of the latexes. The properties of the chemically prepared toner and the results of the printing test are appeared in the presentation.

1. Introduction

Toners for developing electrostatic images are conventionally produced by melt kneading of a colorant, wax, resin and other toner ingredients, followed by pulverization and classification. However, broad geometric size distribution and low toner yields after classification may be obtained in the conventional process. Recently attention has been focused on chemical routes for preparing toners, where a suitable particle size is attained without a classification step. By avoiding the classification step, higher yields can be attained, especially as the target particle size is reduced. Smaller particle size toners are of considerable interest for a number of reasons, including better print resolution, lower pile height, greater yield from a toner cartridge, and faster or lower temperature fusing. A demand to the method to raise the image quality is strong and a further improvement in the image quality is required. The chemically prepared toner (CPT) is preferable to form a high quality image since the toner having a small particle size and a narrow size distribution can be easily obtained by the chemical method.

Several routes to CPT have been introduced. These include suspension polymerization, emulsion-aggregation and solution-dispersion processes. Among them, emulsion-aggregation process offers several advantages including the generation of narrow particle size distributions and the ability to make toners of different shape. The toner shape is particularly important in toner transfer from the organic photoconductor (OPC) to the substrate and in cleaning of the OPC by a blade cleaner. In known emulsion polymerization processes, a surfactant is used to stabilize the emulsion latexes. Also, several aggregation processes have been reported. Numerous patents describe an aggregation process where particles stabilized by ionic surfactants followed by coagulation. However, the surfactant that contributes advantage in the emulsion polymerization and aggregation process can be detrimental to the quality or processing of the final toners. Current emulsion-aggregation processes have a disadvantage in that tribo charge depends on environmental changes to a large extent. Another disadvantage is that the adhesive properties between the toner particles and the substrate are poor at high relative humidity owing to the presence of surfactants on the particles. As a result, the surfactant used in emulsion-aggregation processes should be removed from the toner particles by washing to obtain useful tribo electric properties and good adhesive properties. However, the removal of these surfactants from the emulsion-aggregation particles is very tedious and resource consuming, since surfactant removal is an equilibrium process and requires acceleration in order to be cost-effective. Toner processes that eliminate or at least minimize the need for surfactants are therefore desired.

Macromonomers have attracted considerable interest due to their amphiphilic nature, acting as a stabilizer in aqueous media. Macromonomers are a relatively new category of functionalized polymer (or oligomer) materials having one or more polymerizable end groups, thus the use of macromonomers provides an alternative route to stabilize polymer colloids in replacement of surfactants or steric stabilizers in emulsion polymerizations [1]. Macromonomers acts not only as a stabilizer but also as a comonomer. Macromonomers can form micelles in aqueous media. The micelles generated by the aggregation of the macromonomers serve as the polymerization loci in emulsion polymerization, and the macromonomers participate in the polymerization by reacting with principal monomers [2].

In this study, the emulsion copolymerizaion of styrene, n-butyl acrylate and a macromonomer is investigated to produce toner latexes that are very stable, and their particles in sub-micron sizes are uniform and monodisperse. The toner latexes contain a polymerized resin, a colorant and a wax by using a novel process. Also, the ionic strength of aqueous aggregation medium is adjusted by pH and the concentration of electrolytes (or inorganic salts) without the addition of surfactants. The aggregation step was carried out above the Tg of the resin and heated for coalescence. The size and shape of the toner can be controlled through selection of the temperature and the heating time or through control of the Tg and the molecular weight of the resin. This toner process is a simple, economical and environmentally friendly process by reducing the amount of wasting water in the washing step due to surfactant-free process. This study is the first attempt for developing a dry chemical toner using macromonomers in the toner preparing process.

2. Experimental

2.1. Preparation of toner latex

The toner latex was prepared by emulsion polymerization. Emulsion polymerization was carried out in a 1-L reactor with stirring under nitrogen atmosphere. Styrene (Sigma-aldrich) and butyl acrylate (Junsei) were used as monomer reagent. Macromonomer was purchased from Aldrich and used as received. In addition, a monomer soluble wax was incorporated in the monomer phase as a release agent. Dodecanethiol (Aldrich) was added to the monomer mixture to control the molecular weight. Potassium persulfate (Acros organics) was used as a water-soluble initiator. The polymerization was performed for 6 hours under nitrogen environment. Deionized water was used in all the polymerization. During the polymerization, aliquots of sample were periodically taken from the reaction vessel for characterization.

2.2. Aggregation process

The latex emulsion and water were mixed in the reaction vessel. Pigment dispersion (Yellow, Magenta, Cyan and Black) was prepared by glass bead milling process using de-ionized water with macromonomer. The pigment dispersion was added to the reaction vessel and the pH of the mixture was adjusted. Aggregation was started slowly by coagulant dropping during stirring. The mixture was heated. And then, the temperature of the mixture was isothermally maintained until the end of the process. Series of the sample of the mixture were taken at the specified temperature and time interval to control the toner size. Finally the product was washed and filtered.

2.3. Characterization

The polymerization kinetics was determined by gravimetry. The molecular weights of the latexes were determined using a gel permeation chromatography (GPC, DAWN-EOS, Wyatt technology). THF was used as the mobile phase and was delivered at 1.0 mL/min. The dn/dc value of the resin was measured by a batch method.

The volume average particle size (D_v) and the number average particle size (D_n) were measured using a laser light scattering particle size analyzer (LA-910, Horiba Co., LTD).

Differential scanning calorimetry (DSC) was performed to determine the glass transition temperature (Tg) of the latex. Also, the Tg of copolymer can be estimated approximately using the famous Fox equation [3]. In addition, molecular weight is another factor to control Tg of the latex. When monomer ratio is fixed, the Tg of the resin is a function of molecular weight described by following equation [4].

$$T_g = T_{g\infty} - \frac{k}{M_n} \qquad (1)$$

Equation (1) is the Fox-Flory equation, where Tg^{∞} is the glass transition temperature of a linear chain of infinite molar mass. M_n is a number average molecular weight. k is $2\rho N_a\theta / \alpha_f$, in which ρ is the density of the polymer, Na is the Avogadro number, θ is contribution of one chain end to the free volume, and α_f is the thermal expansion coefficient of the free volume. The micrographs of the Scanning Electron Microscopy (SEM) image were taken using the Hitachi S-3500N.

3. Results and Discussion

Figure 1 shows the polymerization conversion curves versus reaction time at various temperatures. The rates of polymerization increased with the reaction temperatures due to the high rate of initiator decomposition or propagation. Free radicals from the initiators are formed in the aqueous phase and proceeded polymerization by reacting with monomers dispersed in water at the beginning of the reaction. As the reaction was progressed, the latex particles became monodisperse and their sizes gradually increased. Also, the molecular weight was increased with the reaction time. The growing chains aggregate into micelles and the micelles grow by the addition of monomer from the aqueous solution whose concentration is replenished by a monomer feeding. However, this system is differs from the classical emulsion polymerization by the lack of the surfactant.

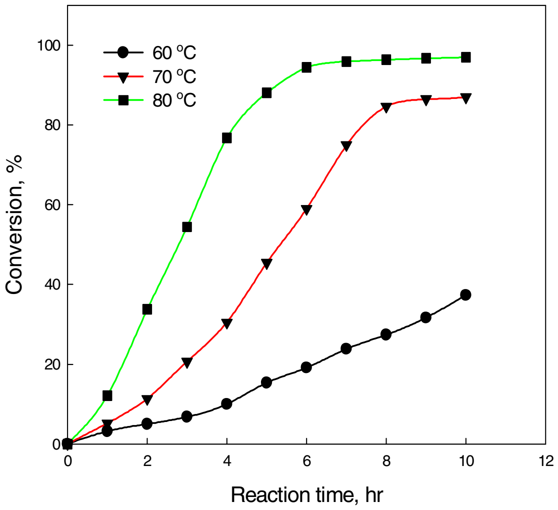

***Figure 1**. Conversions of the latex particles at various temperatures.*

The system produced emulsion latexes that are very stable, and their particles in sub-micron sizes are uniform and approaching monodisperse. It is reported that the introduction of PEG-EEM into the emulsion polymerization resulted in an increase in the overall monomer conversion and the stability of monomer-water emulsion increased with the increasing PEG-EEM concentration [5]. Also, the stability of polymerized toner latex increased with increasing the macromonomer concentration without using any surfactants. The particle diameters decreased with an increment of macromonomer concentration. The particle size of the toner latex can be controlled by the amount of macromonomers. The SEM picture of the resultant particles polymerized in the presence of PEG-EEM is drawn in Figure 3. As usual, spherical particles were obtained, implying that the macromonomer acts as a stabilizer in the emulsion polymerization.

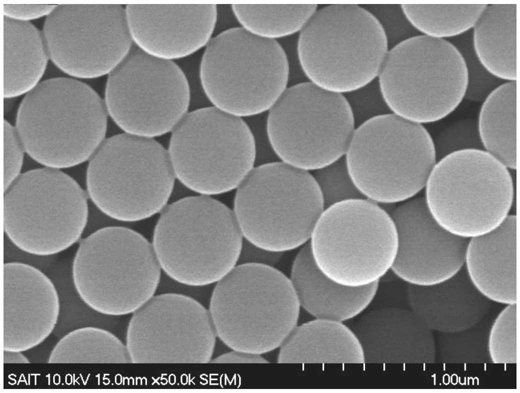

Figure 2. *SEM photographs of the latex particles.*

Effective macromolecules should posses both hydrophobic and hydrophilic moieties in order to act as a surfactant, which can form micelles in aqueous media. The long hydrophilic groups of the reacted macromonomer anchored on the surface of latex particles provide a permanent stabilization for the long-term stability of toner latexes. Furthermore, coagulum of the products was not observed in the presence of the macromonomer. The final toner latexes contain a polymerized resin, a colorant and a wax.

At the beginning of the aggregation process, the latex particles start to aggregate by adding a coagulant and by adjusting the pH. The range of particle sizes and the desired shape of the particle size distribution can be achieved by tailoring the stability of the toner latex particles during growth of the latex particles. The most important factor that affects the flocculation step is pH and the ionic strength. As the pH increases by adding alkali, the surface will become negative, or at least less positive. The negative charges on the particle surface were mainly due to the simultaneous presence of sulfate groups coming from the moieties of initiator and the macromonomer and acid groups [6]. For electrolyte concentrations higher than the critical coagulation concentration, the electrostatic repulsive forces are completely canceled and rapid coagulation occurs as a result of the Brownian motion of the polymer particles. Below this point, coagulation is slower. When one particle approaches near to other particle during the process, both particles have possibility to aggregate by ionic strength or to collide by stirring, producing a bigger particle. The aggregation step was carried out above the Tg of the resin and heated for coalescence. As temperature increases, the mean particle size increased. The mean particle size of the toner continuously grows with keeping the size distribution narrow. Thermodynamically, when the processing temperature exceeds over the Tg of the latex, the polymer chain in the particle has tendency to move freely as increase of the Gibbs free energy, so that viscous mobility of the molecular chain occurs in the particle. Thus, aggregated clusters have freedom to be coalesced together. As a consequence, the coalesced clusters of the aggregates result in smoother and more uniform shape under the given temperature condition. In this study, the toner particles are formed by simultaneous process of aggregation and coalescence. The average size of the toner particle is preferably in the range from 5 – 6.5 μm. The shape of a toner can be controlled through selection of the aggregation temperature and the heating time or through control of the Tg and the molecular weight of the resin. Decrease in the molecular weight of latexes can be made without altering the polymerization rate by using chain transfer agent. As the molecular weight decreased, the shape of the particles approaches to more uniform and spherical shape [7]. Morphological differences are due to the degree of interaction between interfacial tension on the particle and the viscous chain mobility of the toner depending on the molecular weight.

The cooled dispersion of coalesced toner particles is optionally washed and then dried. In this system, the washing process was minimized due to the surfactant –free process. This process is an environmentally friendly method by reducing wastewater. Also, the filtering and drying step is an important process to obtain desired toners. Figure 3 shows the CPT particles prepared by the method. The toner particles were blended with one or more surface additives (silica and titania) to improve the powder flow properties of the toner, or to tune the tribocharge properties. In the electrophotographic system, toner charge is one of the important factors to identify toner behaviors. The results of the printing test will be appeared in the presentation.

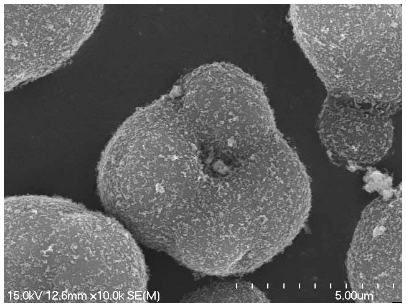

Figure 3. *SEM photographs of the Samsung CPT (black).*

4. Conclusions

In this study, the emulsion copolymerizaion of styrene, n-butyl acrylate and macromonomer produce toner latexes that are very stable, and their particles in sub-micron sizes are uniform and monodisperse. The toner latexes contain a polymerized resin, a colorant and a wax. Also, the stability of polymerized toner latex increased with increasing the macromonomer concentration without using any surfactants. During aggregation process, the ionic strength of aqueous aggregation medium is adjusted by pH and the concentration of electrolytes without the addition of surfactants. The size and shape of the toner can be controlled. This toner process is a simple, economical and environmentally friendly process by reducing the amount of wasting water in the washing step due to surfactant-free process. This study is the first attempt for developing a dry chemical toner using macromonomers.

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Chang Kook Hong received his Ph. D. in Polymer Engineering at the University of Akron, Ohio (2001). He worked as a post-doctoral fellow in the department of chemical engineering at University of Delaware for three years. Since then he has worked in the Digital Printing Division at Samsung Electronics in Korea. His work has focused on the research and development of imaging materials.