Advanced Process for Polyester Chemically Prepared Toner in Aqueous Phase

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Abstract

In the full color laser printers and copiers, the performance features of high print speed, fine image quality and environmental friendliness are required. Therefore the special toner also has been required for high speed printing and fine image quality. Recently many chemically prepared toners have been proposed, and these toners are suitable to achieve small and narrow particle size distribution. But most of these toners use styrene acrylic resin, and only a few toners use polyester which is superior to styrene acrylic resin in low-energy fusing. The polyester chemically prepared toners remain a matter of improvement in the point of environment friendliness, due to the use of organic solvent in the manufacturing process.

Previously we reported on a solvent-free polyester chemically prepared toner in aqueous phase by using several surfactants, but it is not desirable to prepare polyester emulsions for toner with a large amount of surfactant. In this study it is found that the combination of anionic surfactants and nonionic surfactants is effective for preparing the polyester emulsion. In addition, it is found that hydrolysis of the polyester resin during emulsification can be inhibited by controlling the pH for neutralization of carboxyl terminal groups of the polyester.

Introduction

In recent years, environmental issues have received a considerable amount of attention. As part of that focus, it has been required that electrophotographic toners should be fusible at lower temperature for the purpose of saving energy. In addition, it has been required that the toners should have small particle size and narrow particle size distribution for fine image quality.

To develop toner for low energy fusing and high image quality system, there are several methods to manufacture polyester chemically prepared toner [1]. But there are still concerns due to the use of organic solvents during the manufacturing process. It has been desired to manufacture polyester chemically prepared toner without any organic solvent.

We have already reported the use of nonionic surfactant instead of organic solvents at NIP27 [2]. The polyester emulsion of small particle size and narrow particle size distribution is prepared by this method, and by aggregation and unifying of this emulsion the polyester chemically prepared toner has been obtained.

But to prepared polyester emulsion, a large amount of nonionic surfactant was used. Therefore nonionic surfactant remained in the toner even after the filtration and rinsing process, which is not preferable for the toner.

We developed an advanced process for polyester chemically prepared toner which requires a lower amount of surfactant.

Experimental

Preparation of amorphous polyester resins

PES-1; A 10L four-neck flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with bisphenol A propylene oxide adduct and ethylene oxide adduct, terephthalic acid, and dibutyltin oxide were reacted at 230°C for 10 hours and further reacted at 8.3kPa for 1 hour. Then, fumaric acid and hydroquinone were added, and reacted at 210°C for 3 hours. Thereafter ingredients were reacted at 8.3kPa until the desired softening point was attained.

PES-2; The above alcohols, terephthalic acid , trimellic anhydride, dodecenylsuccinic acid anhydride and dibutyltin oxide were reacted at 230°C for 5 hours. Thereafter ingredients were reacted at 8.3kPa until the desired softening point was attained.

The thermal properties of reacted amorphous resins are listed in Table 1.

Table 1. Properties of the Experimental Polyester Resin

	Acid value[1)] (mgKOH/g)	T 1/2 [2)] (°C)	Tg [3)] (°C)
PES-1	24	108	64 [4)]
PES-2	21	121	63 [4)]

1) The acid value was measured according to ASTM D-1980-67.

2) The softening point (T 1/2) was measured according to ASTM E-28-67.

3) The glass transition temperature (Tg) was measured by a differential scanning calorimeter (DSC).

4) Tg was read by the tangential way.

Preparation of polyester emulsions: Studying surfactants

Exp1; A 5L four-necked flask equipped with a dropping tube, a cooling tube, a stirrer, and a thermocouple was charged with PES-1, PES-2, and nonionic surfactant (polyoxyethylene lauryl ether). The ingredients were melted at 150°C for 30min. Thereafter the ingredients were stabilized at 95°C and aqueous sodium hydroxide solution (concentration: 5% by weight) was added dropwise thereto as a neutralizing agent. Subsequently, deionized water was added dropwise to the mixture. During the addition, the temperature of the system was kept at 95°C. Emulsion containing finely prepared PES-1 and PES-2 was obtained through a wire mesh. In a similar method, by use of nonionic surfactant and / or anionic surfactant emulsion of polyester was obtained (Exp2 – Exp5).

Preparation of polyester emulsions: Studying neutralizing agents

A 5L four-necked flask equipped with a dropping tube, a cooling tube, a stirrer, and a thermocouple was charged with PES-1, PES-2, nonionic surfactant (polyoxyethylene oleyl ether), anionic surfactant (sodium dodecylbenzene sulfonate), and aqueous sodium hydroxide solution (concentration: 5% by weight) as a neutralizing agent. The ingredients were stabilized at 95°C for 2 hour. Subsequently, deionized water was added dropwise to the mixture. During the addition, the temperature of the system was kept at 95°C. Emulsion containing finely prepared PES-1 and PES-2 and colorant was obtained through a wire mesh.

In case of the use of the buffer solution as neutralizing agent, it was used the buffer solution (pH 8.0) of phosphate / potassium hydroxide in stead of aqueous sodium hydroxide solution (Exp6).

Preparation of toner samples

Toner-A; The resulting polyester emulsion (Exp1), colorant (Pigment Blue 15:3) dispersion, and wax emulsion containing carnauba wax were mixed in a 2L four-neck flask at room temperature (25°C). Next, an aqueous solution containing ammonium sulfate as a coagulant was added to the mixture. Thereafter the mixture heated to 55°C, and kept at 55°C, and stirred for 4 hours, to form aggregate particles.

Thereafter, the mixture was heated to 80°C, and stirred for 3 hours to unify the aggregated particles. Subsequently, the mixed dispersion was subjected to a suction filtration step, a rinsing step, and drying step, to give a fine colored resin particle powder, particle size of 5.0μm. Each toner was blended with fumed silica as fluidizing agent. In similar method, Toner-B and Toner-C were prepared from polyester emulsion Exp5, and Toner-D was prepared from polyester emulsion Exp6.

Measurement of the particle size distribution of emulsions and toners

The particle size distribution of emulsions was measured by LA-920 (Laser scattering particle size analyzer, HORIBA Co., Ltd.). The particle size distribution of toners was measured by Multisizer II (Beckman Coulter, Inc.) with the 100μm size aperture.

Measurement of fusing property

Fusing performance was evaluated using an off-line fuser. (Hot roll & Pressure roll), oil free type.

At first, each toner sample was developed and transferred on the paper so that the mass per area was 0.45mg/cm2. The paper was J-paper by Xerox Corporation. Then the paper was passed through the fuser. The line speed was 40ppm.

The upper limit of the fusing temperature was defined as the upper temperature limit at which the hot-offset was not observed. And the fusing temperature was defined as the lower temperature limit at which the cold-offset was not observed and the fusing ratio of the toner exceeds 80%. The fusing ratio of toner was calculated as the change in image density before and after Scotch tape (3M) stripping.

The fusing latitude was defined as the temperature difference between the fusing temperature and the upper limit of fusing temperature.

Measurement of heat storage stability

Each toner sample (20 g) was placed in a polyethylene bottle (capacity: 20 mL) and was allowed to stand at 55°C for 12 hours. Heat storage stability was determined by the amount of blocked toner and aggregated toner observed in the sample. In the case of good storage stability, blocking and aggregating of toner was not observed.

Results and discussions

Evaluation of preparation the emulsion by using nonionic surfactant and anionic surfactant

The polyester emulsion can be prepared in aqueous phase by using nonionic surfactant, and polyester chemically prepared toner has been obtained. But when using a large amount of nonionic surfactant, the finished toners contain residual nonionic surfactants because it is difficult to remove nonionic surfactant by the filtration process. Table 2 shows the glass transition temperature (Tg) of the toner from this emulsion. The Tg of this toner is lower than the Tg of polyester resin. The low Tg of the toner is damaging to the heat storage stability of the toner. In the test of heat storage stability of Toner A, blocking occurred because of low Tg.

Table 2. Properties of polyester resin and toner

	Tg (°C)	Heat storage stability
Polyester resin (PES-1 & PES-2)	63	-
Toner-A [1]	54	Blocked

[1] The toner was made from aggregation and unifying of emulsion with nonionic surfactant.

During emulsification in aqueous phase, the nonionic surfactant works as an emulsifying agent and as a plasticizer for the polyester. By plasticizing the polyester, the neutralization of the terminal carboxyl groups of polyester occurrs easily and efficiently. As shown in Table 3, when the amount of nonionic surfactant was reduced, the neutralizing ratio declined and it became difficult to emulsify the polyester in aqueous phase.

In general, anionic surfactants are good as emulsifying and dispersing agents for various cases, for example, emulsion polymerization and suspension polymerization. If this effect contributed to allow the neutralization of carboxyl groups, it is supposed that the polyester emulsion with fine particle size could be prepared by combination of nonionic surfactant and anionic surfactant. Table 3 shows the case of the combination of anionic surfactant and nonionic surfactant (Exp4, Exp5). In comparison between Exp2 and Exp4, or between Exp3 and Exp5, the neutralizing ratio of terminal carboxyl group by using a combination surfactant was approximately the same as with the use of a large amount of nonionic surfactant. Thus the polyester emulsion with fine particle size distribution was obtained. It is supposed that efficient neutralization by anionic surfactant led to the improved emulsification of the polyester. By combination of nonionic surfactant and anionic surfactant, a polyester emulsion was obtained with a smaller amount of surfactant.

In addition, the anionic surfactant dodecylbenzene sulfonate has a large hydrophobic group, so it has been effective in adsorption to polyester resin. Therefore polyester emulsion which has fine particle size was obtained in spite of using a lower amount of surfactant. In fact, when dodecylbenzene sulfonate was replaced with sodium stearate, an anionic surfactant with a smaller hydrophobic group, the, emulsification properties got worse.

Table 3. Properties of polyester emulsion

	Nonionic surfactant[1]	Anionic surfactant[2]	Neutralizing ratio[3] (%)	Emulsion diameter D50 (μm)
Exp1	20wt%	-	84	0.11
Exp2	6.7wt%	-	73	Not emulsified
Exp3	2.0wt%	-	67	Not emulsified
Exp4	6.7wt%	1.0wt%	82	0.41
Exp5	1.0wt%	1.0wt%	75	0.15

1) The nonionic surfactant was polyoxyethylene lauryl ether.

2) The anionic surfactant was sodium dodecylbenzene sulfonate.

3) The neutralizing ratio was calculated by acid value of polyester resin before and after emulsification.

Thermal properties of toner

Table 4 shows the Tg of toner and polyester. Toner-B was prepared from emulsion with combination of anionic surfactant and nonionic surfactant. The Tg of toner prepared from the emulsion by this method was similar to the polyester resin, and it was higher than by the previous method. It is indicated that the toner from this method has good heat storage stability.

Table 4. Properties of polyester resin and toner

	Tg (°C)	Heat Storage stability
Polyester resin (PES-1 & PES-2)	63	-
Toner-B[1]	60	Good

1) The toner was made from aggregation and unifying of emulsion with combination of anionic surfactant and nonionic surfactant.

Inhibiting hydrolysis of polyester during emulsification

Under the alkaline conditions of emulsification, molecular breakdown of the polyester resin can occur by hydrolysis . During emulsification, the hydrolysis of polyester has been observed even when using a combination of anionic surfactant and nonionic surfactant.

Figure 1 is the molecular weight distribution of Toner-C determined by gel permeation chromatography. Toner-C was prepared from a polyester emulsion using a combination of anionic and nonionic surfactant and using a low amount of total surfactant,. This figure indicates that the high molecular weigh component was decreased and the low molecular weight component was increased due to hydrolysis of polyester.

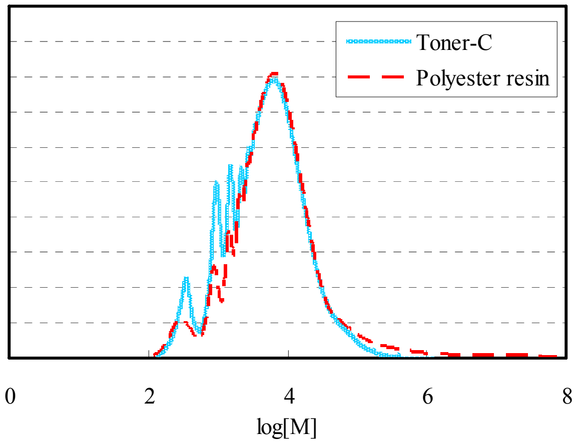

Figure 1. *Molecular weight distribution of toner*

Using strong alkali such as sodium hydroxide as the neutralizing agent increased the polyester hydrolysis. But by using a weak alkali instead of strong alkali, the emulsification properties became worse because the neutralization of polyester terminal carboxyl groups was not enough to allow the polyester to emulsify into particles with fine particle size. It is necessary to select the proper neutralizing agent for preparation of polyester emulsion.

Particularly, it is effective for inhibiting hydrolysis of polyester to use a base of mild pH as the neutralizing agent. Table 5 shows the properties of emulsions prepared using the alkali with mild pH. The polyester emulsion with fine particle size was obtained with neutralizing agent of pH8 (Exp7) and pH10 (Exp8).

Table 5. Emulsification properties by various bases

	Neutralizing agent		Emulsion diameter D50 (μm)
	alkali	pH	
Exp6	Potassium hydroxide	14	0.12
Exp7	Phosphate acid / potassium hydroxide buffer	10	0.25
Exp8	Phosphate acid / potassium hydroxide buffer	8	0.21

1) In this case PES-1 & PES-2 were used.

The buffer solution of phosphate acid / potassium hydroxide was used as neutralizing agent for polyester. This buffer consists of strong alkali and weak acid. The mild pH was effective to inhibit hydrolysis of polyester, and the strong alkali was effective to neutralize the terminal carboxyl groups of the polyester. The buffer solution has to work to maintain the pH of the system. In this case, the buffer maintained a mild pH and supplied a strong alkali for emulsification of the polyester.

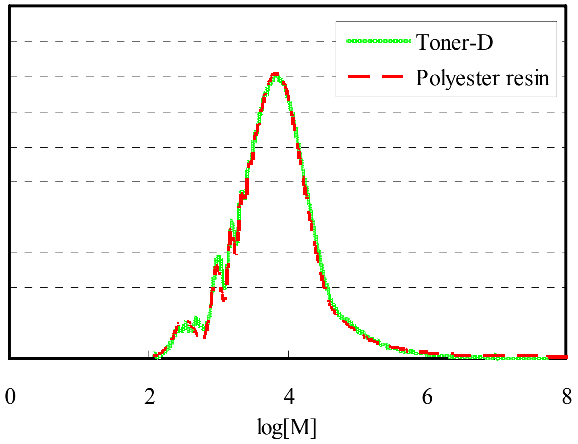

Figure 2. *Molecular weight distribution of toner prepared from emulsion in use of buffer solution as neutralizing agent*

Figure 2 shows that hydrolysis of the polyester during emulsification is inhibited by using a buffer solution of pH8 as the neutralizing agent . Toner-D was prepared from the polyester emulsion which used this buffer solution (pH8). There was less decrease of high molecular weight component in Toner D than in Toner C, which used potassium hydroxide as the neutralizing agent.

Evaluation of fusing property

The fusing latitudes of the toners were investigated and the results are shown in Figure 3. Toner-D was prepared from polyester that was emulsified using a buffer solution as the neutralizing agent. The fusing property of Toner D was improved compared with that of Toner C (previous method). By inhibiting hydrolysis of the polyester resin, the high molecular weight component of the toner was kept, and the toner's resistance to hot-offset was improved.

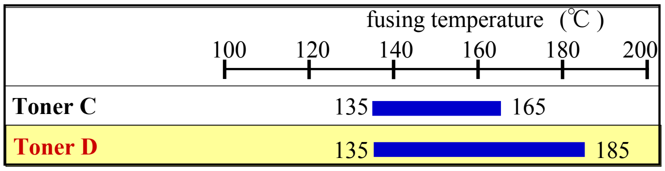

Figure 3. *Fusing property of polyester chemically prepared toner*

Conclusions

The investigation of the advanced process of polyester chemically prepared toner in aqueous phase has led to the following conclusions:

1) Polyester emulsion with fine particle size was obtained by using a combination of nonionic and anionic surfactants with a low amount of total surfactant.

2) Durng emulsification, molecular breakdown of the polyester by hydrolysis was inhibited by using a buffer solution (pH8) as the neutralizing agent.

3) Polyester chemically prepared toner with good toner performance can be made from this method..

Reference

[1] T. Nanya, F. Sasaki, S. Yagi, N. Shimota, H. Higuchi, J. Awamura, M. Tomita, IS&T's NIP20 international Conference on Degital Printing Technologies, 143 (2004)

[2] N. Kamiyoshi, S. Sata, Y. Ishikawa, IS&T's NIP27 International Conference on Digital Printing Technologies, 429 (2011)

Author Biography

Hiroshi Mizuhata received his master's degree in engineering from Nagoya Institute of Technology in 2000. Since 2005, he has been working for Kao Corporation in the Performance Chemicals Research Laboratories in Wakayama, Japan. He has been engaged in research and development of toner and toner binder with polyester.