Novel Process for Aqueous-based Polyester Chemically Prepared Toner

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Abstract

In recent years, environmental issues and energy costs have created a need for lower energy consumption in the fusing systems of printers and copiers. To develop toner for low-energy fusing systems, there are several methods to manufacture polyester chemically prepared toner. But there are still environmental concerns due to the use of organic solvent during manufacturing process. We developed a novel process for aqueous-based polyester chemically prepared toner by using nonionic surfactant. In this study, we report that nano-size emulsions can be obtained for the synthesis of toner particles without any organic solvent. We indicate the relationship between nonionic surfactant and the emulsification of 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. On the other hand, 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 environmental concerns due to the use of organic solvent during manufacturing process. It has been required that polyester chemically prepared toner should be manufactured without any organic solvent. However polyester can't be emulsified without any plasticizers because of their very high viscosity. We focused on nonionic surfactants which have properties of high plasticity, emulsifier and easy removal below cloud point, instead of organic solvent.

We investigated the control of viscosity and emulsifiability of polyester resin during emulsification by adding nonionic surfactants which have cloud points near the emulsification temperature. It was observed that the viscosity of the polyester resin can be decreased. As a result, nano-size polyester emulsions can be obtained without any organic solvent.

We developed a novel process for aqueous-based polyester chemically prepared toner by using nonionic surfactant.

Experimental

Preparation of amorphous polyester resin

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, fumaric acid, hydroquinone, and dibutyltin oxide. The ingredients were reacted at 210°C for 5 hours, and further reacted at 8.3kPa until the desired softening point was attained.

PES-2 : The alcohols 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-3 : The above alcohols, terephthalic acid, trimellitic anhydride, dodecylsuccinic 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.

PES-4 : A 10L four-neck flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with 1,6-hecanediol, 1,4-buthanediol, fumaric acid, hydroquinone, and dibutyltin oxide. The ingredients were reacted at 160°C for 5 hours. Thereafter temperature was raised to 200°C, reacted for 1hour, and further reated 8.3kPa for 1hour.

The thermal properties of the reacted PES resins are listed in Table1.

Table1. Properties of the Experimental Polyester Resin

	Acid Value[1] (mgKOH/g)	T1/2[2] (C)	Tg[3] (C)
PES-1	22	98	56[4]
PES-2	24	111	67[4]
PES-3	21	125	65[4]
PES-4	25	83	84[5]

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

2) The softening point (T1/2) was measured according to ASTM E-28-67

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

4) Tg was read by the tangential way

5) Tg was read by the peak top

Preparation of polyester emulsions

A 5L four-necked flask equipped with a dropping tube, a cooling tube, a stirrer, and a thermocouple was charged with PES-1 and nonionic surfactant (C12EO12). The ingredients were melted at 150°C for 30min. Thereafter the ingredients were stabilized at 95°C and aqueous sodium hydroxide (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 was obtained through a wire mesh. In a similar method, PES-2, 3, and 4 can be emulsified.

Also, we investigated the influence of emulsifiability on the structure of nonionic surfactants. There are nonionic surfactants having cloud points above and below the emulsification temperature (table2).

Table2. Properties of the nonionic surfactants

Structural formula	Cloud point (°C)	HLB
C12EO5	< 25	9.7
C12EO12	98	15.3
C12EO19	> 100	16.3

Preparation of toner sample

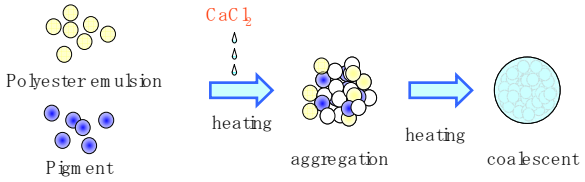


Fig.1 scheme of aggregation and coalescent process

The resulting polyester emulsion (PES-1) and colorant (Pigment Blue 15:3) dispersion were mixed in a 2L vessel at room temperature (25°C). Next, an aqueous solution containing calcium chloride as a coagulant was added to the mixture, and the pH was adjusted to 7 with an aqueous sodium carbonate. Thereafter, the mixture was stirred with a homo mixer at room temperature for 1 hour. The resulting mixed dispersion was transferred to a 2 L four-neck flask, heated to 80° C, and stirred for 4.5 hours, to form aggregate particles.

Thereafter, the mixed dispersion was heated to 99° C, and stirred for an additional 1 hour to unify aggregate particles. Subsequently, the mixed dispersion was subjected to a suction filtration step, a washing step, and a drying step, to give a fine colored resin particle powder. The fine colored resin particle powder had a volume-median particle size (D50) of 5.4 µm. Each toner was blended with fumed silica.

Measurement of charging ability

The two-component developer was prepared by adding silicone-coated ferrite carrier (commercially available from Kanto Denka Kogyo Co., Ltd.) having an average particle size of 60 µm. Charging ability was evaluated using Q/M meter (commercially available from Epping GmbH). This process involved collecting the toner from a sieved developer in NN and HH conditions by vacuum filtration and measuring the weight and charge of the toner. Afterwards, Q/M (µC/g) was calculated.

Measurement of the particle size distribution of the emulsions

The particle size distribution of the emulsions was measured by LA-920 (Laser scattering, HORIBA Co.,Ltd).

Measurement of the particle size distribution of the toner

The particle size distribution of toner was measured Coulter Multisizer II with the 100µm size aperture.

Measurement of the toner shape

The toner shape was observed by scanning electron microscope (SEM) photograph.

Measurement of the image quality

The toner was developed by a non-magnetic dual component printer. The dot image on the paper before fusing was observed.

Results and Discussion

Evaluation of the influence of type of nonionic surfactant on emulsifiability

Table3 viscosity of polyester during emulsification process

Polyester	Surfactant	Viscosity	D50 (nm)
PES-1	C12EO9	Very high	Not emulsified
PES-1	C12EO12	low	160
PES-1	C12EO19	Very high	Not emulsified

Table 3 shows the viscosity (mixing torque) of the polyester during the emulsification process. Initially the viscosity of the PES-1 increased with any nonionic surfactant. But the viscosity finally decreased in case of C12EO12 and polyester could be emulsified.

In case of C12EO19, the viscosity of the polyester went up with an increasing the amount of water. Most of the surfactant existed in the water due to high hydrophilicity. The polyester could not be plasticized efficiently and emulsified

In case of C12EO9, the reason is different, but the same phenomenon happened. Most of the surfactant existed in polyester because of high hydrophobicity. And so the polyester could be plasticized, but it couldn't be emulsified due to low emulsifying. Finally phase separation was observed.

C12EO12 has a cloud point near the emulsification temperature. It can exist not only in polyester but also in the water phase. As a result, the polyester could be plasticized and emulsified successfully.

Evaluation of influence of emulsifiability on the type of polyester (emulsification temperature: 95°C, nonionic surfactant: C12EO12)

Fig. 2 shows that all kinds of polyester can be emulsified in this method. This figure indicates that the emulsifiability of polyester declines with decreasing acid value and with increasing softening point of the polyester.

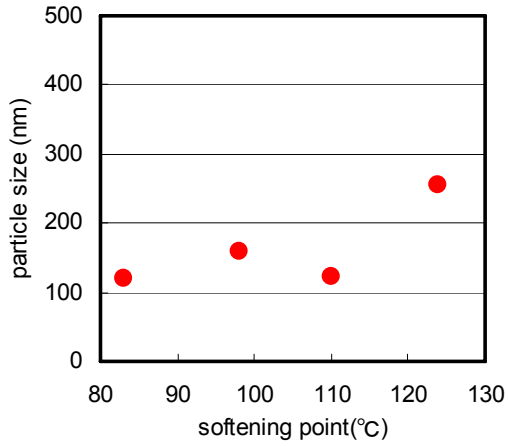


Fig.2 Particle size of emulsion

The particle size distribution and shape of aqueous-based polyester chemically prepared toner

Fig. 3 shows the particle size distribution of aqueous-based polyester chemically prepared toner. It has small and narrow particle size distribution.

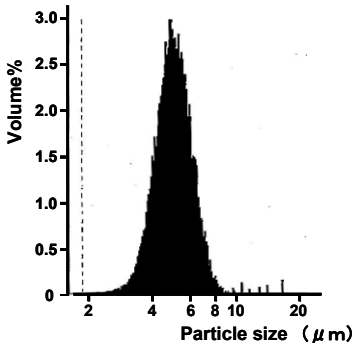
Particle size distribution (vol)	
D50(μm)	5.4
CV	23

Fig. 3 The particle size distribution of the toner

Fig. 4 shows SEM photograph of the toner. The shape of the toner is spherical.

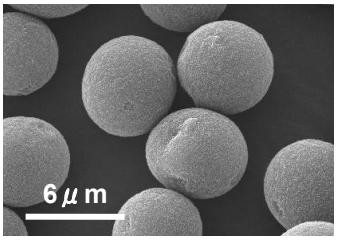


Fig.4 The SEM investigation of the toner

Evaluation of charging ability of toner

Fig. 5 shows that the toner (PES-1) has the quick charging ability at the NN condition. And at the HH condition, charging level is also stable because of removal of nonionic surfactant.

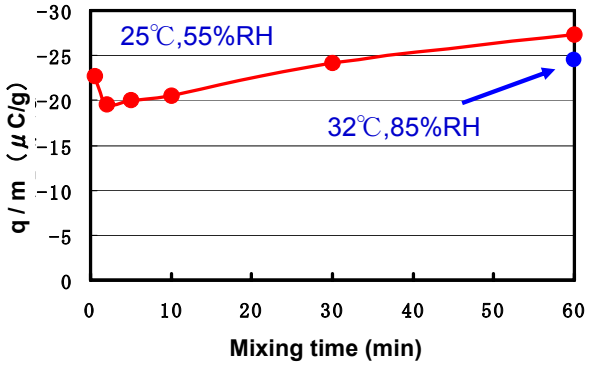


Fig. 5 Charge ability of the toner

Image Quality Evaluation

Small particle size, narrow distribution and spherical shape can achieve high quality transfer performance in electrophotographic systems. Fig. 6 shows the photograph of fine dot image on the paper. Compared to pulverized toner, aqueous-based polyester chemically prepared toner shows considerably better reproduction.

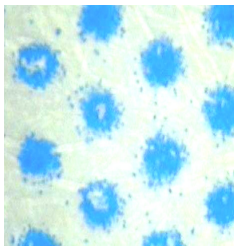
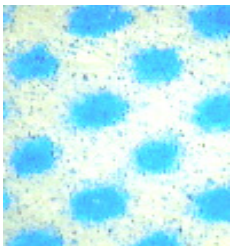
	pulverized toner	Aqueous-based polyester chemically prepared toner
D50(μm)	8.0	5.4
dot image		

Fig. 6 The comparison of the image quality of each toner

Conclusions

The investigation of the process of the aqueous-based polyester chemically prepared toner has led to the following conclusions:

1) Nano-size polyester emulsion can be obtained by using nonionic surfactant without any organic solvent,

2) All kinds of polyester emulsions can be prepared by using this method,

3) Aqueous-based polyester chemically prepared toner can be manufactured by using these emulsions.

Reference

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

Author Biography

Nobumichi Kamiyoshi received his master degree in applied chemistry from Osaka University in 2002. Since 2002 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 emulsification of polyester and its application.

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