Study of Seed Polymerized Polyester Emulsion for Chemically Prepared Toner

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Abstract

In full color laser printers and copiers, the performance requirements include high printing speed, fine image quality, and environmental friendliness. Specially designed toners are needed to achieve these requirements. To develop the toner for low-energy fusing, hot-offset resistance, and good storage stability, chemically prepared polyester toner was developed (core-shell typed toner) by emulsion aggregation method. Polyester emulsion is usually made by phase inversion emulsification with organic solvent. Unfortunately higher molecular weight polyesters, which provide resistance against storage stability and hot-offset, have limited solubility in organic solvent. To solve these problems, some cross-linking techniques like urethane reaction and oxazoline-polymer reaction have been developed. But these techniques resulted in disappearance of carboxyl groups which play a role in the dispersion stability of emulsion, so emulsions with small and narrow particle size distribution could not be made. It is a challenge to design resins that have both larger molecular weight and dispersion stability.

In this study, to support larger molecular weight and dispersion stability of polyester emulsion at the same time, we introduced seed polymerization which allows radical polymerization inside emulsion without disappearance of carboxyl groups. In addition, it is found that seed polymerization could control the thermal properties of polyester emulsion like storage elastic modulus and glass-transition temperature. With this method, we could design polyester chemically prepared toners having a wider range of thermal properties.

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 high performance of hot-offset for wide range of use because of high printing speed. We have already reported about polyester chemically prepared toner [1, 2].

To develop toner for low energy fusing and high performance of hot-offset, some cross-linking techniques of polyester emulsion like urethane reaction and oxazoline-polymer reaction have been developed. But these techniques resulted in disappearance of carboxyl end groups in the resin which play a role in the dispersion stability of the emulsion. so emulsions with small and narrow particle size distribution could not be made. It is a challenge to design resins that have both larger molecular weight and good dispersion stability.

In this paper, we tried to apply new technology to achieve larger molecular weight and dispersion stability of emulsion at the same time to design a binder resin that can be used widely for chemically prepared toner. In CPT synthesis, it is necessary for polyester to dissolve in an organic solvent like MEK before emulsification, so to maintain good solubility in organic solvent, it is better to increase the molecular weight of the polyester after doing emulsification.

To increase the molecular weight after emulsification, it is necessary to introduce functional groups which can form cross-linkage without using carboxyl groups. Therefore we tried to introduce double bonds to polyester which could polymerize by radical polymerization, and we tried to do radical polymerization within the polyester emulsion. This method was able to support larger molecular weight and dispersion stability of emulsion at the same time without disappearance of carboxyl groups.

Experimental

Preparation of 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, isophthalic acid, succinic 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-2–3; In a similar method, PES-2 and PES-3 were obtained. PES-2 and PES-3 used reduced amounts of fumaric acid as compared with PES-1. Table 1 shows the amount of fumaric acid included in each polyester. (The order in amount of fumaric acid is as follows: PES-1>PES-2>PES-3).

PES-4; Bisphenol A propylene oxide adduct and ethylene oxide adduct, terephthalic acid, dodecenylsuccinic acid anhydride, trimellic 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 and acid value of reacted polyester resins are listed in Table 1.

Table 1. Properties of the Experimental Polyester Resin

	Amount of FA[1] (mol%)	Acid value[2] (mgKOH/g)	Tg [3] (°C)	Mn [4]
PES-1	20	21	59	3660
PES-2	10	20	58	3760
PES-3	5	18	61	3530
PES-4	0	18	52	4200

1) Amount of fumaric acid was indicated by mol% of acid components.

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

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

4) The molecular weight (Mn) was measured by gel permeation chromatography (GPC) with THF.

Preparation of polyester emulsions by phase inversion emulsification

Polyester emulsion which is used for shell and core emulsion was made by phase inversion emulsification with methyl ethyl ketone (MEK).

Em-1; At first, a 2L four-necked flask equipped with a dropping tube, a cooling tube, a stirrer, and a thermocouple was charged with PES-1 and MEK. Then PES-1 was dissolved in MEK by stirring at 25°C for 3 hours. Secondly, PES-1 was neutralized by ammonia water (concentration: 25% by weight). Neutralizing ratio is listed in table 2. Thirdly, emulsification was achieved by adding ion-exchanged water over 30 minutes. Finally, an emulsion of PES-1 was obtained by removing MEK under reduced pressure at 60°C. Then the emulsion of PES-1 was filtered through a wire mesh after cooling.

Em-2-4; In a similar method, PES-2, PES-3 and PES-4 emulsions were obtained (Em-2–Em-4).

The particle size of obtained polyester emulsions are listed in Table 2.

Table 2. Properties of the polyester emulsion

	Polyester	Neutralizing ratio[1) (%)	Particle size (nm)
Em-1	PES-1	75	96
Em-2	PES-2	75	102
Em-3	PES-3	75	98
Em-4	PES-4	75	116

1) Degree of neutralization was calculated by acid value of polyester resin before and after emulsification

Preparation of high molecular weight polyester emulsions by seed polymerization

SP-1; A 2L five-necked flask equipped with a dropping tube, a cooling tube, nitrogen gas substitution tube, a stirrer, and a thermocouple was charged with Em-1. Next, Em-1 was heated to 80°C. Then, initiator (potassium persulfate) was added dropwise to Em-1, and the temperature of the mixture was kept at 80°C for 6 hours. Finally, the polyester emulsion was filtered through a wire mesh after cooling.

SP-2; In similar method, a 2L five-necked flask was charged with Em-1. Next, styrene monomer was added dropwise to Em-1, and the mixture was stirred for 30 minutes at 25°C. The amount of styrene is listed in table 3. After that, the mixture was heated to 80°C. Then initiator (potassium persulfate) was added dropwise to the mixture, and the temperature of the mixture was kept at 80°C for 6 hours. Finally, seed polymerized polyester emulsion was obtained by filtering through a wire mesh after cooling.

SP-3–5; In a similar method, seed polymerized polyester emulsions were obtained using different polyesters (SP-3–SP-4), and a seed polymerized polyester emulsion with decreased amount of styrene was obtained (SP-5).

The thermal properties and the particle size of obtained seed polymerized polyester emulsions are listed in Table 3.

Table 3. Properties of the seed polymerized polyester emulsion

	PES Em	PES/St (ratio)	Tg[1) (°C)	Particle size (nm)	Mn
SP-1	Em-1	100/0	59	96	3660
SP-2	Em-1	80/20	65	98	Insoluble
SP-3	Em-2	80/20	65	103	Insoluble
SP-4	Em-3	80/20	66	102	Insoluble
SP-5	Em-3	90/10	63	101	Insoluble

1) The glass transition temperature (Tg) was measured by a differential scanning calorimeter (DSC). Freeze-dried emulsions were used.

2) The molecular weight (Mn) was measured by gel permeation chromatography (GPC) with THF. Freeze-dried emulsions were used.

Preparation of toner samples

TONER-A; A core ingredient was prepared from polyester emulsion (Em-4), colorant dispersion (Pigment Blue 15:3) and wax emulsion (carnauba wax) with common emulsification aggregation methods. Next, a shell ingredient was prepared from polyester emulsion (Em-3) in the methods similar to the core. Thirdly, the prepared 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. The colored resin particle powder was blended with fumed silica as fluidizing agent.

TONER-B; A core ingredient was prepared from polyester emulsion (Em-4), colorant dispersion (Pigment Blue 15:3) and wax emulsion (carnauba wax) with common emulsification aggregation methods. Next, a shell ingredient was prepared from seed polymerized polyester emulsion (SP-5) in the methods similar to the core. Thirdly, the prepared 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. The colored resin particle powder was blended with fumed silica as fluidizing agent.

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 storage elastic modulus of seed polymerized emulsions

Storage elastic modulus of seed polymerized emulsion was measured by rheometer ARES (TA instruments). Freeze-dried emulsion was used.

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 160mm/sec.

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 exceeded 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 and was allowed to stand at 55°C for 8 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

Polymerization reactivity of polyester emulsions

As noted earlier, the emulsion of polyester including fumaric acid was prepared by phase inversion emulsification. An initiator was added to prepared emulsion to initiate radical polymerization in the emulsified resin (SP-1). But molecular weight of the treated emulsion did not change compared with an untreated one (table 1 and 3). It was found that radical polymerization inside emulsion did not happen. Mobility of double bond segments attached to polyester are lower as compared with the mobility of small size monomer for radical polymerization. Radical polymerization did not happen because each double bond could not come close together.

Therefore we tried to add the other radical monomer to form cross-linking chain between double bonds in the polyester chain. In this case, radical polymerization could happen inside emulsion because mobility of added radical monomer is higher compared with the double bond in the polyester chain. In this report, styrene monomer was used in point of cost and ease. The styrene monomer was added into polyester emulsion. The initiator was added to do radical polymerization after the styrene monomer was introduced into emulsion (SP-2–5).

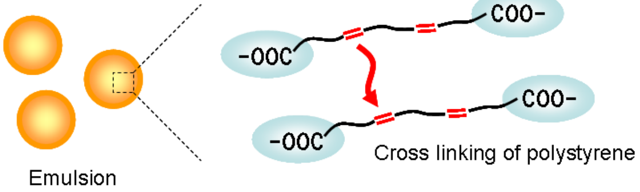

Figure 1. Concept of radical polymerization inside polyester emulsion

The molecular weight of seed polymerized polyester emulsion could not be determined by gel permeation chromatography because the resin could not be dissolved in organic solvent. The solubility test was measured using freeze-dried powder of emulsion. Figure 2 shows the reduced solubility of the treated emulsion in tetrahydrofuran (THF). It is found that seed polymerized polyester emulsion could not dissolved in THF. But the reduced solubility of the seed polymerized polyester emulsion is evidence that the molecular weight was increased successfully by radical polymerization.

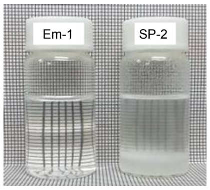

Figure 2. The reduced solubility of the treated emulsion in THF

Thermal properties of seed polymerized polyester emulsions

The copolymerization of polyester and polystyrene was confirmed by measurements of glass-transition temperature (Tg) and storage elastic modulus. If polymerization of only styrene happened inside emulsion, Tg would indicate double peaks (PES Tg and polystyrene Tg). So, it was found that copolymerization happened because Tg indicated a single peak (table 3). Figure 3 and 4 show storage elastic modulus of seed polymerized polyester emulsions.

widespread The magnitude of the storage elastic modulus of seed polymerized polyester emulsion could be controlled by adjusting the amount of fumaic acid in the polyester and the amount of added styrene monomer. As shown in figure 3, seed polymerized polyester emulsion indicated high storage elastic modulus at high temperature compared with non-reacted polyester. Moreover, the storage elastic modulus increased from 1.0×10^4 to 1.0×10^6 when the amount of fumaric acid included in the polyester was increased from 5mol% to 20mol% with keeping a constant amount of styrene monomer.

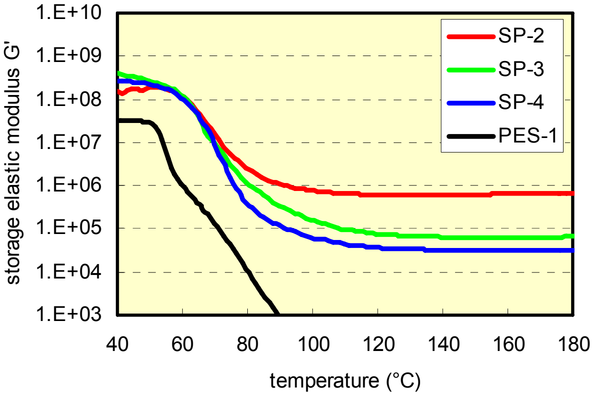

Figure 3. Impact of amount of fumaric acid on storage elastic modulus

In addition, as shown in figure 4, it is found that the amount of added styrene monomer could control the magnitude of storage elastic modulus. Also, the glass-transition temperature could be controlled by the amount of styrene monomer (table 3). As not shown in detail, it is found that the common radical monomer like 2-ethylhexyl acrylate could be used to control Tg. It is important for controlling the property of toner to control the thermal properties like storage elastic modulus and glass-transition temperature. Our proposed method will be optimum for controlling the thermal properties of polyester emulsion through the position of selecting widespread radical monomers.

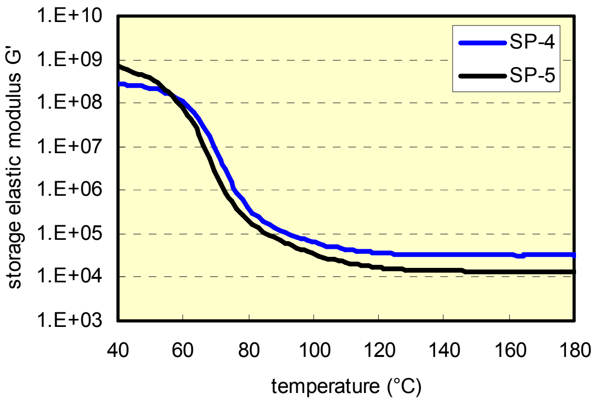

Figure 4. ***Impact of amount of styrene to strage elastic modulus***

Evaluation of heat storage stability

As already shown, chemically prepared toner was prepared with common emulsification aggregation methods (Toner-A, B). The same emulsion for core was used in each toner (Em-4),but different emulsions were used for each toner shell. Shell of Toner-B was prepared from seed polymerized polyester emulsion (SP-5) of which Tg was high compared with that of Toner-A (Em-1). Table 4 shows heat storage stability of toner at 55°C for 12 hours. As expected, Toner-B was better than Toner-A. It is found that heat storage stability was improved because chemically prepared toner formed core-shell structure. The shell resin indicated lower solubility to the core resin because the gap of molecular weight between core resin and shell resin was very large. Each polymer which has the gap of molecular weight usually indicates lower solubility by Flory-Huggins theory.

Table 4. Heat storage stability of toner

	Heat Storage stability[1)]
Toner-A	Bad (12.0 g)
Toner-B	Good (0.1 g)

1) Heat storage stability of toner was determined by the amount of blocked toner and aggregated toner observed in the sample.

Evaluation of fusing property

The fusing latitudes of the toners were investigated and the results are shown in Figure 5. The fusing property of Toner B was improved compared with that of Toner A. Although low energy fusing property of Toner-B was slightly inferior to Toner-A, the resistance to hot-offset of Toner-B was improved greatly because of the high molecular weight component of seed polymerized emulsion.

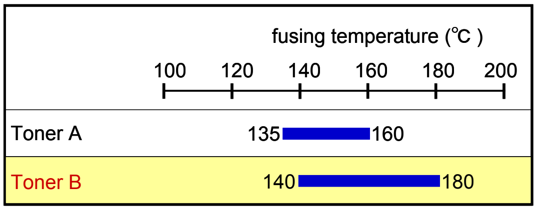

Figure 5. *Fusing property of toner*

Conclusions

The study of seed polymerized polyester emulsion for chemically prepared toner has led to the following conclusions:

1) Styrene copolymerization inside emulsion of polyester including fumaric acid achieved larger molecular weight.

2) The amount of fumaric acid included in the polyester and the amount of added styrene monomer could control the magnitude of storage elastic modulus of seed polymerized polyester emulsion.

3) The glass-transition temperature of seed polymerized polyester emulsion could be controlled by the amount of styrene monomer.

4) The chemically prepared toners using seed polymerized polyester emulsion for shell indicated wide fusing latitude compared with non-reacted emulsion.

In this report, we introduced the concept of seed polymerization to polyester emulsion to achieve larger molecular weight. With this method, we could design polyester chemically prepared toners having a wider range of thermal properties.

Reference

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Author Biography

Yuta Matsumoto received his master's degree in applied molecular science and engineering from Kyushu University in 2006. Since 2006, 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 polyester emulsion for chemically prepared polyester toner.