Crystalline Polyester for Chemically Prepared Toner Having Low Energy Fusing

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Abstract

Regulations for the energy consumption of printers and copiers are getting more severe year by year. And with increasingly faster machine systems, the fusing of toner on the paper gets more difficult, so the toner which can be fused with lower energy is needed. Crystalline polyester (C-PES) is known as a very effective agent for toner fusing. C-PES dispersion size in toner is very important for fusing, and nano size CPES which shows very good fusing was reported by Fukuri et al.

On the other hand, chemically prepared toner (CPT,) especially emulsion aggregation toner (EA), was studied a lot in recent years. Toner from EA method can allow toner with core-shell structure, for example a low-Tg resin core that is covered with high-Tg resin shell. Therefore EA method is expected to provide both low energy fusing and good storage stability.

In this report, the study of CPT toner containing C-PES is done. The effect of conventional C-PES for CPT was very poor, so we studied the melting point of C-PES for improved performance in CPT. While studying the EA toner containing C-PES, it was observed that the particle size of C-PES emulsion is very sensitive to neutralization level. We evaluated several ways to prepare better C-PES emulsions by controlling the hydrogen bonding of C-PES during emulsification.

Introduction

Important technical requirements for electrophotographic toner recently are low-energy fusing, long developer life, quick charge ability and so on. Low-energy fusing is an especially important technology in the field of low-end as well as high-speed copiers and printers because it minimizes energy consumption of the machines and reduces problems in paper feed during fusing.

In recent years, the regulations or the standards have become stricter, for instance ZESM (Zero Energy Stand-by Mode) standards, which is for copiers in range of 20-40 copies per minute or faster, requires under 10W in sleep mode and under 10sec to restart from sleep mode.

So the toner which can be fused with low energy is desired. Conventional toners containing both amorphous polyester (A-PES) and C-PES scan show good fusing, and toners with lower melting point CPES can show better fusing as reported by Shirai et al. [1, 2] Additionally, control of the crystalline size of C-PES in toner using an annealing process was reported by Fukuri et al. [3, 4] It was reported that the melting point of C-PES can be controlled by the crystalline size of C-PES and smaller size of CPES shows lower melting point.. It was reported that C-PES and A-PES are miscible by kneading and CPES is crystallized by an annealing process.

In detail, by 90°C annealing, CPES crystals with a size of 100nm were observed. By annealing at 50°C, 20nm CPES crystals was observed. It was reported that toner annealed at 50°C provided better fusing than toner annealed at 90°C.

Recently chemically prepared toner (CPT), especially emulsion aggregation (EA) toner, has been studied a lot. In the EA method, toner is made from emulsified polymer of about 100nm particle size emulsion so the nano size control of structure can be done. For instance, core-shell or capsule structure could be designed where the core contains low-Tg resin and the shell contains high-Tg resin. This structure allows the design of toner with good fusing and good storage stability.

In this report, a study of CPT prepared by the EA method and containing C-PES is reported.

Emulsion of C-PES and emulsion of A-PES were prepared. CPT was prepared by blending C-PES and A-PES emulsions in certain ratios and by the process of aggregation and coalescence.

The performance of a conventional-type C-PES in CPT was very poor. It was supposed that the crystalline size of C-PES was quite large because the EA-method doesn't involve a kneading process, and the large crystal size caused the melting point of CPES to be high. In order to improve the fusing performance of CPES in CPT, we studied the effect of C-PES melting point on toner fusing in CPT's.

Additionally, it was observed that the emulsification of C-PES was more sensitive than that of A-PES. Particle size of C-PES emulsion changed rapidly by adjusting the neutralization ratio.

In this report, the effort of making C-PES emulsification less sensitive to neutralization ratio was done. CPES contains a high amount of hydrogen bonding between terminal carboxyl groups (COOH dimer) as shown by IR analysis. We suppose that the hydrogen bonding of the COOH dimmer is the cause of the sensitivity of particle size. We studied the breaking of hydrogen bonds with the following processes.

1: Addition of urea after resin is dissolved in solvent.

2: Treatment of C-PES with chloroform before emulsification.

Experimental

Preparation of amorphous polyester resin

A-PES-1; A 10L four-necked flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with the alcohols bisphenol A propylene oxide adduct and ethylene oxide adduct, terephthalic acid, dibutyltin oxide. The ingredients were reacted at 230°C for 5 hours, and further reacted at 8.3kPa for 1 hour. Then, fumaric acid and hydroquinone were added at 190°C, reacted for 4 hours at 210°C, and reacted at 8.3kPa until the desired softening point was attained.

A-PES-2; The above alcohols, terephthalic acid, alkenyl succinic anhydride and dibutyltin oxide were charged into a 10L four-necked flask. The ingredients were reacted at 230°C for 10 hours. Thereafter ingredients were reacted at 8.3kPa for 1hour.

Then, trimellitic anhydride was added at 210°C, and reacted for 1hr, and reacted at 8.3kPa until the desired softening point was attained.

The thermal properties of the reacted A-PES resins are listed in Table 1.

Table 1. Properties of the Experimental Polyester Resin

	Acid Value [1] (mg KOH/g)	T1/2 [2] (°C)	Tg [3] (°C)
A-PES-1	27	108	65 [4]
A-PES-2	21	116	64 [4]

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.

Preparation of crystalline polyester resin

C-PES-1; A 10L four-necked flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with 100 weight parts of 1,6-hexanediol as alcohol and 100 weight parts of Terephthalic acid. Dibutyltin oxide and hydroquinone were used to control the reaction. Then, the ingredients were reacted at 190°C and held for 5 hours in a glass flask. Thereafter, the temperature was raised to 210°C, reacted for 5 hours, and further reacted at 8.3kPa for 1 hour.

C-PES-2-3; Obtained by using the monomers listed in table 3 and the same procedure as C-PES-1.

The thermal properties of the crystalline polyesters are listed in Table 2, and the combinations of monomers of C-PES are shown in Table 3.

Table 2. Properties of the Experimental Crystalline Polyester Resin

	T1/2 (°C)	Tg [5] (°C)	AV [6] (KOHmg/g)
C-PES-1	144	146	Insoluble
C-PES-2	94	97	20
C-PES-3	78	74	16

5) Tg was read by the peak top. This value is called melting point.

6) The acid value was measured according to ASTM D-1980-67 solvent chloroform

Table 3. Combinations of monomers of C-PES

	Alcohol [7]			Acid [8]	
	1.6HD	1.5PD	1,9ND	TPA	SEBA
C-PES -1	100			100	
C-PES -2	60	40		100	
C-PES -3			100		100

7) 1,6HD: 1,6-Hexanediol 1,5PD: 1,5-Pentanediol 1,9ND: 1,9-Nonanediol

8) TPA: Terephthalic acid: SEBA: Sebacic acid.

Preparation of crystalline polyester emulsions

A 5L four-necked flask equipped with a dropping tube, a cooling tube, a stirrer, and a thermocouple was charged with C-PES-2, surfactant, and MEK. The ingredients were melted at 60°C for 2h. Thereafter the ingredients were stabilized at 60°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 60°C. To finish, deionized water was added dropwise and solvent was removed with vacuum. Emulsion containing finely prepared C-PES-2 was filtered through a wire mesh. In a similar method, C-PES-3 can be emulsified.

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 insoluble parts of C-PES Solution

The insoluble part of C-PES solution was measured by Dynamic light scattering.

Measurement of the amount of hydrogen bonding

The amount of hydrogen bonding was measured by IR spectroscopy.

Annealing treatment

The annealing treatment of the C-PES-3 was conducted by holding C-PES-3 in a heated oven at 60°C for 8 hours.

Preparation of toner sample

CPT TONER-A was prepared with common emulsification aggregation methods using polyester emulsion (A-PES-1), polyester emulsion (A-PES-2), and colorant (Pigment Blue 15:3)

TONER-B-C is the same procedure as TONER-A except a crystalline polyester emulsion was added. The prepared toner samples are listed in Table 4.

Table 4. Toner Samples

	A-PES-1	A-PES-2	C-PES-2	C-PES-3
TONER-A	62	38		
TONER-B	62	38	5	
TONER-C	62	38		5

Measurement of fusing property

Fusing performance was evaluated using an off-line fuser (Hot roll & Pressure roll). The silicone oil was removed completely for this study. The diameter of the heat roller was 30mm, the width of the nip was 4mm, and the pressure of the nip was 2kg/cm.

At first, each toner sample was developed and transferred on the paper so that the mass per area was 0.5mg/cm^2. Then the paper was passed through the fuser. The fusing speed was 40ppm.

The upper limit of the fusing temperature was defined as the upper limit temperature at which hot-offset was not observed.

And the fusing temperature was defined as the lower limit temperature at which cold-offset was not observed and at which

the fusing ratio of the toner exceeded 70%. The fusing ratio of the toner was calculated as the change in image density of a solid area image before and after stripping with Scotch tape.

The range from the fusing temperature to upper limit was defined as the fusing latitude of the each toner sample.

Results and Discussion

Fusing property of the toner

The results of fusing latitude are shown in Figure 1. The low fusing temperature was 140°C for Toner-A (without CPES) and 135°C for Toner-B (containing C-PES-2 mp97°C). The effect of C-PES-2 was only 5°C. Toner-B was prepared with 200nm C-PES emulsion, and the C-PES emulsion can further aggregate into even larger particles during aggregation and coalescence, so the crystalline size in Toner-B must be large compared to that of conventional toner. It is supposed that the reason why C-PES-2 provides just a 5°C improvement of fusing is that the crystalline size is large.

In contrast, the low fusing temperature of Toner-C (containing C-PES-3 mp74°C) was 120°C, which is 20°C improvement of fusing compared to Toner-A. This result indicates that even large crystalline size of CPES is effective when the melting point is lower.

In CPT, crystalline size of C-PES is large compared to conventional toner, so the effective melting point of C-PES for fusing is lower.

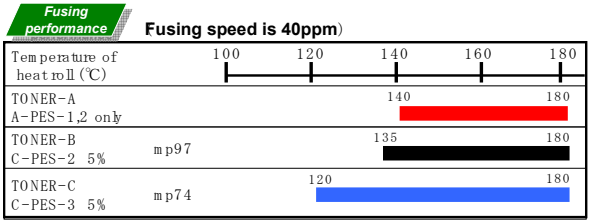

Figure 1 the fusing latitude of each TONER

Emulsification of C-PES

Emulsion of C-PES was prepared by typical solvent phase transfer method with MEK. C-PES-1 was difficult to dissolve in MEK, so an emulsion could not be prepared.

The relationship of neutralization ratio and average particle size of emulsion (D50) are shown in Figure 2. Particle size of A-PES emulsion was changed gradually with neutralization ratio. In contrast, the particle size of C-PES-3 emulsion changed rapidly with neutralization ratio. The particle size distribution charts of the emulsions with 60% neutralization are shown in figure 2. The chart of C-PES-3 emulsion has 2 peaks, one at 150nm and the other at about 10um. In the chart of APES just 1 peak is observed. By studying the characteristics of C-PES-3 in solvent using dynamic light scattering, we observed very small C-PES particles with a size of 3nm. We supposed this 3nm insoluble part is the source of the 10um peak for C-PES-3 and we investigated further.

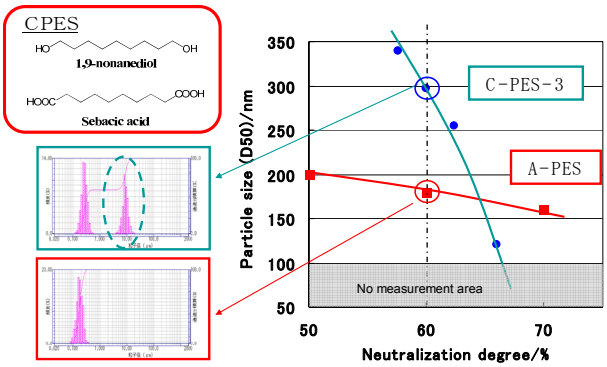

Figure 2 Change of particle size of emulsion

Quantitative determination of dimer in resin

An insoluble portion of C-PES-3 with 3 nm particle size was detected in MEK solution. . But in A-PES solution of MEK, no insoluble portion was detected. We speculated that the structure of the insoluble C-PES part involved the association between terminal carboxyl groups (dimer). So IR measurements of C-PES-3 were done at 100°C (which is higher than the melting point of CPES to eliminate the peak of crystallinity)..

Lorenz fitting was applied to the IR result of C=O stretching to separate each structure peak. The IR results are shown in Figure 3. Peak of C=O stretching in C-PES-3 was separated in three types. We focused attention on type 3 of hydrogen bonding which is between the terminal carboxyl groups (COOH dimer). 12% of COOH dimer was detected in C-PES-3. 0% of COOH dimer was detected in APES, so we theorized that this amount of COOH dimer is the insoluble part of C-PES-3 in MEK solution.

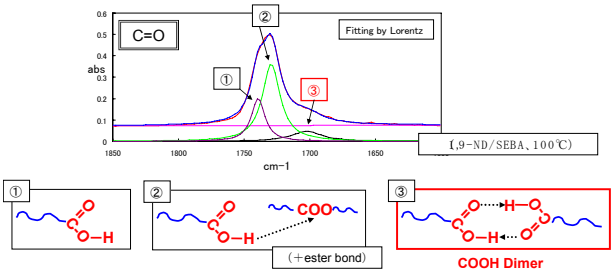

Figure 3 Measurement of C-PES by IR

Examination of elimination of hydrogen bonding in COOH dimer

We speculated that COOH dimerization from hydrogen bonding was the cause of high variation of D50 in C-PES-3 emulsions and the source of the 10μm peak in D50, so we tried to eliminate hydrogen bonding of the COOH dimer.

Elimination of hydrogen bonding in COOH dimer was examined by these methods.

1: Addition of urea (a hydrogen bond disrupter) after dissolving the resin in solvent.

2: Treatment of C-PES with chloroform before emulsification.

Urea is known as a material that disrupts the structure of hydrogen bonding we proposed to disrupt the hydrogen bonding in C-PES solution by adding urea to the dissolved resin. Results of emulsification with 3wt% of added urea are shown in Figure 4 (▲). By adding 3 wt% of urea, we found a more gradual change of D50 with neutralization ratio. And only one peak occurred in the particle size distribution chart of C-PES-3, as with A-PES. IR measurements indicated that the COOH dimer was reduced from 12% to 7% by adding urea. This result indicates that the 10μm peak in the C-PES-3 particle size distribution is caused by large amounts of COOH dimer, and control of the dimer amount is important for controlled production of C-PES emulsion.

Chloroform is known to create strong hydrogen bonding, so we predicted that when resin is dissolved in chloroform most of the COOH dimer would be broken by making hydrogen bonds with chloroform. Before dissolving resin in MEK, we applied the process of dissolving in chloroform and removing chloroform. In emulsification with chloroform-treated C-PES-3, the D50 changed more gradually with neutralization ratio and only one peak in particle size distribution occurred as shown in Figure 4. IR measurements indicated that COOH dimer content was reduced from 12% to 9% by chloroform treatment.

These results indicate that a stable emulsification process strongly depends on the control of COOH dimer in C-PES, and treatment with a hydrogen-bond disruptor like urea or chloroform is very effective for C-PES emulsification.

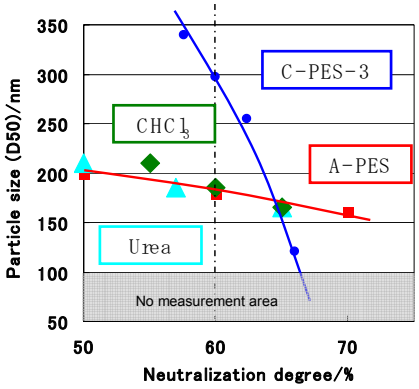

Figure 4 Particle size of emulsion with treatment

Conclusions

The investigation of the crystalline polyester for chemically prepared toner has led to the following conclusions:

1) Chemically prepared toners with good fusing performance can be prepared with low melting point C-PES.

2) For low-energy fusing, chemically prepared toners require a lower melting point C-PES than conventional toners.

3) The particle size of CPES emulsion varies strongly with neutralization ratio and has an additional peak at 10um with lower neutralization ratio.

4) C-PES solution contains a large amount of hydrogen-bonded COOH dimer,which is the cause of the difficulty of emulsification of CPES.

5) The addition of urea or treatment with chloroform can disrupt hydrogen bonding in C-PES, which provides a more gradual change of particle size with neutralization ratio.

References

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Author Biography

Hiroki Kakiuchi received his master degree in industrial chemistry from Nagoya Institute of Technology 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 toner binder with polyester resin.

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