Crystalline polyester for low energy fusing with high charging ability.

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Abstract

In recent years, environmental concerns 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, we are investigating crystalline polyester (C-PES). Toner made from amorphous polyester (A-PES) and C-PES with annealing process shows good fusing ability and durability, as already reported by Fukuri et al. in NIP24. But charging ability of aliphatic C-PES was insufficient because of its monomer structure. In this paper, we report a study to achieve high charging ability by changing the monomer of C-PES from aliphatic diol to aromatic diol. Furthermore, crystallinity of aromatic C-PES can be controlled by adding another monomer which disturbs the symmetrical structure of C-PES. It was observed that the crystal size of aromatic C-PES becomes smaller in the toner, as the amount of another monomer increases. Therefore melting point of C-PES can be decreased. As a result, low energy fusible toner with high charging ability can be obtained.

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. As already reported in NIP18&19 by Shirai et al., excellent toner fusing ability can be achieved through the use of crystalline polyesters (C-PES) as binder resins.[1,2] When C-PES is used in toner, amorphous polyester (A-PES) and C-PES are kneaded by a kneading machine in the production process. Although the use of C-PES is effective to improve the low energy fusing, the storage stability and durability of the toner is not enough. It is considered that the part of C-PES is not crystallized and the crystallinity can't be observed because the crystallization rate of C-PES is too slow in the production process. For the improvement of the storage stability and durability, the way to generate crystals in the toner was reported in NIP23 by Fukuri et al.[3] It was reported that the way of promoting crystallization was annealing treatment, which means treating the toner at a certain temperature. The crystallization mechanism of C-PES during treatment process and the proper condition of the annealing treatment were reported in NIP24 by Fukuri et al.[4] When annealing treatment was conducted, it was found by AFM analysis that crystals in the toner were dispersed with nano-size. In the case of an A-PES/C-PES blend without annealing treatment, crystalline domains couldn't be observed and a flat image was obtained (using phase modulation AFM to indicate hardness). It is considered that A-PES and C-PES are miscible in each other and no crystals remained in the blend. However, in A-PES/C-PES blend with annealing treatment, the crystalline domains could be observed. It is considered that part of the non-crystallized segment is crystallized and the crystals are generated uniformly in the blend with nano size. The compatibility with A-PES/C-PES is the key technology for the re-crystallization effect and speed of the annealing process. As reported in NIP25 by Ashizawa et al.[5], by controlling the compatibility of A-PES and C-PES, a toner with low energy fusing ability and high durability can be obtained even with short annealing time.

This A-PES/C-PES toner can allow a high-speed electrophotographic printing system, but in such high-speed printing situation, these toner had the insufficient charging ability. This insufficient charging ability is caused from low charging ability of C-PES because of its aliphatic monomer structure. In this paper, we report a study to achieve high charging ability by changing from aliphatic diol to aromatic diol of C-PES. The C-PES made from aromatic diol shows high charging ability, but the melting point is high in comparison with C-PES made from aliphatic diol.

We investigated the control of crystallinity of an aromatic C-PES by adding another monomer, adipic acid. It was observed that the melting point can be decreased. As a result, the toner containing aromatic C-PES can achieve low energy fusing, good durability and high charging ability.

Furthermore we investigated the morphology of C-PES in the toner by AFM. It was found that the crystal domain size became smaller by increasing the percentage of the other added monomer. It is thought that small domain size of CPES is effective for low energy fusing.

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, and hydroquinone. The ingredients were reacted at 230°C for 5 hours, and further reacted at 8.3kPa for 1 hour. Then, trimellitic anhydride was added, reacted for 1 hour, and reacted at 8.3kPa until the desired softening point was attained.

A-PES-2; The above alcohols, terephthalic acid, 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 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	17	123	66[4]
A-PES-2	6	112	65[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 fumaric acid. Dibutyltin oxide and hydroquinone were used to control the reaction. Then, the ingredients were reacted at 160°C and held for 5 hours in glass flask. Thereafter, the temperature was raised to 200°C, reacted for 1 hour, and further reacted at 8.3kPa for 1 hour.

C-PES-2-5; 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[5] (°C)	Tg[6] (°C)
C-PES-1	112	115
C-PES-2	144	146
C-PES-3	134	137
C-PES-4	122	125
C-PES-5	113	116

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

Table 3. Combinations of monomers of C-PES

	Alcohol	Acid		
	1.6HD	FA[7]	TPA[7]	APA[7]
C-PES-1	100	100		
C-PES-2	100		100	
C-PES-3	100		90	10
C-PES-4	100		80	20
C-PES-5	100		70	30

7) FA: Fumaric acid, TPA: Terephthalic acid: APA: Adipic acid.

Preparation of polyester resin blend for AFM

A-PES-1, A-PES-2 and each C-PES were premixed in a batch mixer and kneaded at 100°C using a kneading machine. The ratio of resins was: A-PES-1, A-PES-2 and C-PES = 30/55/15.

Preparation of toner samples

Toner samples were prepared comprising the polyester resins, a wax, a charge control agent, and a colorant. The colorant was Pigment Blue 15:3. These materials were premixed in a batch mixer, then kneaded, pulverized and classified. Toners having average size of about 5.5 μm were obtained. Each toner was blended with fumed silica. The prepared toner samples are listed in Table 4.

Table 4. Toner Samples.

	A-PES-1	A-PES-2	C-PES	
			Type	Percentage
TONER-A	30	70	-	-
TONER-B	30	55	C-PES-1	15
TONER-C	30	55	C-PES-2	15
TONER-D	30	55	C-PES-3	15
TONER-E	30	55	C-PES-4	15
TONER-F	30	55	C-PES-5	15

Annealing Treatment

The annealing treatment of the resin blend and toners was conducted during the toner making process. After the kneading process, toner samples were annealed at 70℃ for various time periods.

Measurement of charging ability

Charging ability was evaluated using Trek's Charge-to-Mass Ratio System (Model 210HS-2B). Ths process involved collecting the toner from a developer roll by vacuum filtration and measuring the weight and charge of the toner. Afterwards, Q/M(μC/g) was calculated.

Measurement of fusing property

Fusing performance was evaluated using an off-line oil-less fuser (hot roll & pressure roll),. The diameter of the heat roller was 45mm and the width of the nip was 6mm.

At first, each toner sample was developed and transferred on the paper so that the mass per area was 0.45mg/cm^2. The paper was J-paper of Xerox Corporation. Then the paper was passed through the fuser. The line speed was 42ppm.

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

The lower limit of the fusing temperature was defined as the lowest temperature at which the cold-offset was not observed and the fusing ratio of the toner exceeds 70%. The fusing ratio of the toner was calculated from the image density change before and after stripping with Scotch tape.

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

Measurement of the durability

The durability was tested by using the toner cartridge of the color laser printer. 30g of toner was put into a cartridge and the developer roll was rotated at 36ppm without developing the toner to OPC. The durability was defined as the time when the filming of the toner to a doctor blade occurred and the streak appeared at the toner layer on the developer roller.

Atomic Force Microscopy (AFM)

A flat cross-section of polyester resin blend was made using an ultra microtome (LEICA Ultracut EM UPR) for AFM measurements. AFM images of the cross-section of the polyester resin blend were obtained using a Nanoscope IIIa Multi Mode AFM (Veeco Instruments, Santa Barbara, CA) with a JV-Scanner. Tapping mode imaging was used to obtain topographic and phase images of the polyester resin blend. The difference in mechanical properties between A-PES and C-PES is substantial, so phase imaging in tapping mode AFM was used to differentiate the two components. The nominal spring constants of the cantilevers are reported by the manufacturer to be 20-100 N/m. All images presented in this work were obtained reproducibly over at least five spots on the sample surfaces. The images were acquired with a scan rate of either 0.5 or 1.0 Hz, and were flattened with a first-order polynomial before analysis.

Results and Discussion

Evaluation of charging ability of toners containing C-PES

We evaluated solid-area image quality with 42ppm printer. The image quality using Toner A was good. But image quality using Toner B was lower. This result suggested that aliphatic C-PES did not have enough charging ability to obtain good image quality, so we investigated the charge on the developing roller. The results are shown in Table 5. In addition, we confirmed the solid-area image quality for Toners C through F which used aromatic C-PES. These toners offered good image quality and showed high charging ability compared with TONER-B using aliphatic C-PES. Thus C-PES made from aromatic diol gave toner high charging ability. It is considered that terephthalic acid has an aromatic ring for π-conjugation. In other words, terephthalic acid has charging sites.

Table 5. The evaluated results print test, and charging ability on DR.

	Charging (-μ C/g)	Solid image quality
TONER-A	22	Good
TONER-B	13	insufficient
TONER-C	22	Good
TONER-D	21	Good
TONER-E	21	Good
TONER-F	20	Good

Fusing property of the toner

The fusing latitude of toners was investigated. The results are shown in Figure 1. The fusing property of TONER-B including 15wt% of C-PES-1 was improved compared with that TONER-A, which contained no C-PES. It is considered that when the toner passes through the heat roller, C-PES starts melting at the first step and then the amorphous parts are melted. So, toners containing C-PES showed good fusing compared to toners without C-PES .

On the other hand, TONER-C including 15wt% of C-PES-2 did not improve fusing as much. It is considered that the melting point of CPES-2 used in TONER-C was high compared with CPES-1 used in TONER-B. In order to confirm the effect of decreasing melting point, a toner including 15wt% of C-PES (C-PES-2-5) was investigated. As shown in figure 1, it becomes clear that the fusing property can be improved by decreasing the melting point of C-PES. The fusing property of TONER-F was same as TONER-B because of the similar melting points. Therefore TONER-F successfully achieved both good charging ability and low energy fusing.

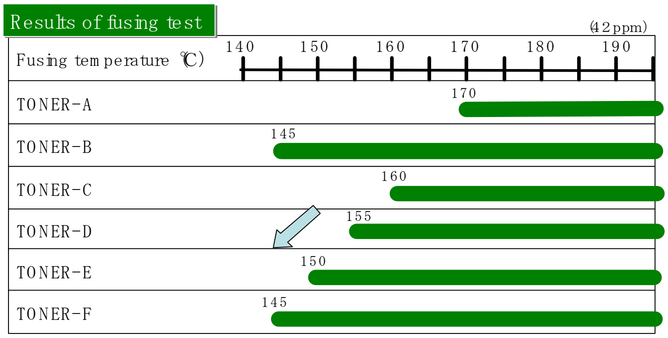


Figure 1The fusing latitude of each TONER

The durability of the toner

The durability of these toners was investigated by using a color laser printer. The results are listed in Table 6. The durability of toners B through F containing 15wt% C-PES was nearly the same as toner A which contained no C-PES. It is considered that toners B through F containing 15wt% C-PES had good durability because the annealing treatment increased the crystallinity sufficiently. Therefore TONER-F successfully achieved good charging ability, low energy fusing and good durability.

Table 6. The evaluated results durability test.

	The filming occurred time8)
TONER-A	6.0H
TONER-B	6.0H
TONER-C	6.0H
TONER-D	6.0H
TONER-E	5.5H
TONER-F	5.0H

8)The life of this developing unit is over 5.0H.

AFM observation of the crystallization state

We controlled the crystal size of aromatic C-PES in toner by adding adipic acid, and we confirmed the melting point decreased. Figure 2 shows the relationship between melting point and ratio of adipic acid (APA). Furthermore, the crystallization state of the toner was investigated by AFM. The results are shown in Figure 3. Crystal domains are seen as light color image. It is found that crystal domain size becomes small when the ratio of added adipic acid monomer is increased. It is thought that nano-size crystal domains are effective for improving low energy fusing.

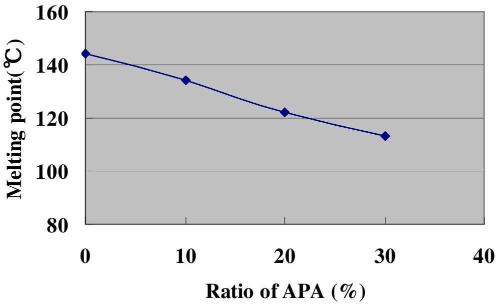
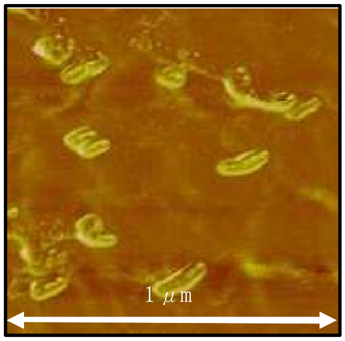
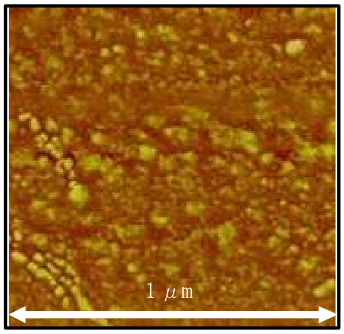


Figure 2. Additive amount of APA with melting point.

+adding 10% of APA



+adding 20% of APA



+adding 30% of APA

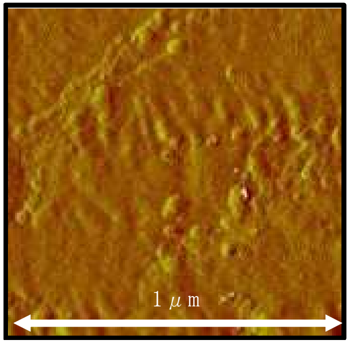


Figure 3. AFM images of TONER-D (top),TONER-E (middle), and TONER-F (bottom).

Conclusions

The investigation of the toner including crystalline polyester has led to the following conclusions:

1) Charging ability of C-PES can be improved by using aromatic monomer which has many charging parts in the structure,

2) Controlling the crystallinity of nano-size domains of aromatic C-PES with annealing treatment is a key technology for designing toner with high charging ability, low energy fusing and good durability.

References

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