Low Energy Fusing Toner by Controlling Compatibility of Crystalline Polyester with Amorphous Polyester

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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 with amorphous polyester (A-PES) and C-PES had good fusing ability, but showed insufficient storage stability and durability. As already reported by Fukuri et al. in NIP24, the storage stability and durability could be improved by an annealing treatment. In the annealing process, C-PES crystalline size was controlled on a nanometer scale. In this study, we report further methods to control the crystallization of C-PES in A-PES. We found it was important to control compatibility between C-PES and A-PES in addition to annealing for adequate crystal growth. We controlled solubility parameters by varying the acid monomer in A-PES polymerization. Lower compatibility between A-PES and C-PES improved the speed and degree of C-PES crystallization during annealing. From this study, a low energy fusing toner with improved storage stability, and durability 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 electro-photographic toners should be fusible at lower temperature, from the viewpoint of saving energy. As already reported 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 kneading machine in the production process.

Although the use of C-PES is effective to improve the low energy fusing, the storage stability 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. The reason of that is the crystallization rate of C-PES is too slow in the producing process. For the improvement of the storage stability, 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 anneal 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 anneal treatment were reported in NIP24 by Fukuri et al.[4] When anneal treatment was conducted, it was found by AFM analysis that crystals in toner were dispersed with nano-size. Focusing on phase for indicator of hardness, in case of the A-PES/C-PES blend without anneal treatment, crystalline domains couldn't be observed and the flat image was obtained. It is considered that A-PES and C-PES are miscible each other and there are no crystals in the blend. However, in A-PES/C-PES blend with anneal treatment, the domains could be observed. It is considered that the part of non-crystallized segment is crystallized and the crystals are generated uniformly in the blend with nano size. The dispersion of C-PES is the key technology for the low energy fusing and high durability toner.

In this paper, we report further methods to control the crystallization of C-PES in A-PES. We found it was important to control compatibility between C-PES and A-PES in addition to annealing for adequate crystal growth. We controlled solubility parameters by varying the acid monomer in A-PES polymerization. Lower compatibility between A-PES and C-PES improved the speed and degree of C-PES crystallization during annealing. From this study, holding a low energy fusing, storage stability and durability toner can be obtained by short anneal treatment time.

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 Bisphenol A propylene oxide adduct, ethylene oxide adduct as alcohols, Fumaric acid, Dibutyltin oxide, and hydroquinone. The ingredients were reacted at 180°C for 1 hour, the temperature was gradually raised to 210°C, reacted 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, Fumaric acid, and Dibutyltin oxide were charged into a 10L four necked flask. The ingredients were reacted at 210°C for 3 hours. Thereafter ingredients were reacted at 8.3kPa until the desired softening point was attained.

A-PES-3; The above alcohols, terephthalic acid, and Dibutyltin oxide were charged into a 10L four necked flask. 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-4; 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 reacted A-PES 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	28	145	60[4]
A-PES-2	20	100	60[4]
A-PES-3	17	123	66[4]
A-PES-4	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

A 10L four necked flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with 100 mol% of 1,6-hexanediol as alcohol, 100mol% Fumaric acid, Dibutyltin oxide, and hydroquinone. 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. The thermal properties of crystalline polyester are listed in Table 2.

Table 2. Properties of the Experimental Crystalline Polyester Resin

	T1/2[5] (°C)	Tg[6] (°C)
C-PES	112[5]	115[6]

5) This value is called melting point.

6) Tg was read by the peak top.

Preparation of polyester resin blend

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

A-PES-3, A-PES-4 and C-PES (Blend 2) were premixed in a batch mixer and kneaded at 100°C by kneading machine. The ratio of resins was: A-PES-3, A-PES-4 and C-PES = 30/55/15.

Preparation of toner samples

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

Table 3. Toner Samples.

	APES-1 (FA)[1]	APES-2 (FA)[1]	APES-3 (TPA)[1]	APES-4 (TPA)[1]	C-PES (FA)[1]
TONER-A	30	55			15
TONER-B			30	55	15
TONER-C			30	70	

1) Used acid monomer

Measurement of fusing property

Fusing performance was evaluated using an off-line fuser (hot roll & pressure roll), oil-free type. The diameter of the heat roller was 45mm, 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 by Xerox Corporation. Then the paper was passed through the fuser. The line speed was 15ppm.

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

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

The range from the 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.

Anneal Treatment

The anneal treatment of the resin blend, TONER-A, and TONER-B was conducted. These samples were kept in furnaces at 70°C for various hours.

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 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.

Wide-angle X-ray diffractometry(WAXD) measurement

WAXD measurement of the toner including crystalline polyester was made on an X-ray diffractometer (RIGAKU RINT2000) with monochromatized Cu Kα radiation (λ=0.15406 nm) operated at 40 KV and 120 mA. The data was corrected in the range of 5°<2θ<40° with an interval of 0.01° and a scan speed of 5° min^{-1}.

Results and Discussion

AFM observation of Blend 1 and Blend 2

The crystallization state of the Blend 1 and Blend 2 was investigated by AFM. The results are shown in Figure 2.

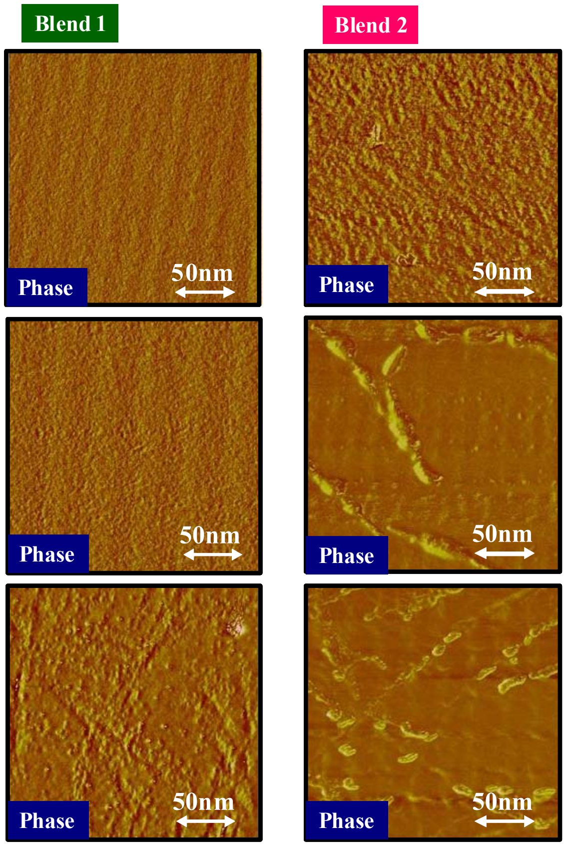

Figure2 AFM images of Blend 1 (left) and Blend 2 (right).Without anneal(upper),with anneal at 70℃ for 1 hours(middle) and 70℃ for 24hours(under).

In case of the Blend 1 without anneal treatment and 1hr treatment, crystal domain couldn't be observed and the flat image was obtained. And 24 hours anneal treated Blend 1 can be observed crystal domain. Domain size was very small(about 10-20nm). However, without anneal treatment Blend 2 was observed nano-meter size crystal domain(about 10-20nm). Furthermore, Blend 2 was grown crystallization by anneal treatment. This result indicates that low compatibility of C-PES and A-PES enhance the effect of anneal process. In other words, C-PES in Blend 2 shows better growth than Blend 1 in anneal process.

The influence of resin compatibility on re-crystallization.

In general, the compatibility of polymer blends can be determined by crystallinity degree. In order to confirm the crystallinity of Blend 1 and Blend 2 with anneal treatment, crystallinity was investigated by WAXD. The results are shown in Figure 3. The crystallinity degree of Blend 2 was higher than Blend 1 after anneal treatment. Furthermore, re-crystallization speed of Blend 2 is higher than Blend 1. It is thought that the difference of crystallinity degree is attributed to the difference of acid monomer of A-PES in samples. Because the A-PES and C-PES in Blend 2 had low compatibility with each other, C-PES crystal growth in TONER-B proceeded rapidly.

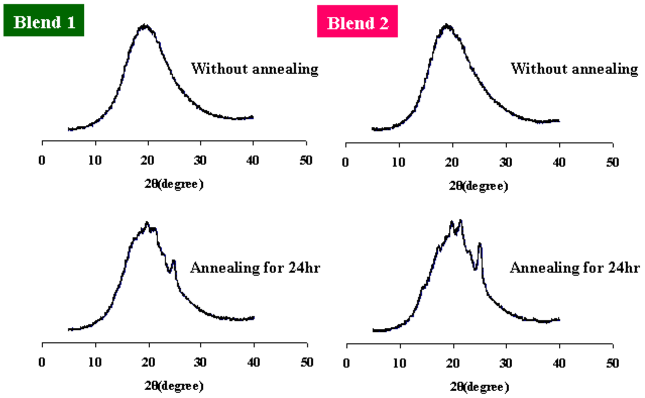

Figure3 The WAXD measurement of the Blend 1 and Blend 2 with and without annealing treatment.

The durability of the annealed toner

As mentioned before, the effect of anneal treatment on toner is the increase of crystallinity degree. Furthermore, it is confirmed by AFM analysis that C-PES is crystallized and it is dispersed in nano-meter size domain by anneal treatment. In order to confirm the effect of increase of crystallinity degree, the durability of the annealed toner was investigated by using a color laser printer. The results are listed in Table 4. The durability of TONER-A was very low compared with TONER-B at the same anneal time. It is considered that TONER-A has less non-crystalline part in C-PES. From the value of crystallinity degree and AFM analysis, this insufficient growth of crystallization is the reason why TONER-A showed poor durability. So, TONER-A showed poor durability, when shortening anneal treatment time.

The durability of TONER-B was same compared with TONER-C, when shortening anneal treatment time. It is considered that TONER-B has enough to grow of crystalline.

	anneal condition	The filming occurred time
TONER-A	70℃／48hr	4.0hr
	70℃／24hr	2.5hr
TONER-B	70℃／24hr	6.0hr
	70℃／12hr	6.0hr
TONER-C	-	6.0hr

Table 4 The durability of TONER-A, TONER-B and TONER-C, annealed at 70°C for various time.

Fusing property of the toner

The fusing latitudes of the toners were investigated. The results are shown in Figure 5. The fusing property of TONER-A and TONER-B including 15wt% C-PES was improved compared with that of TONER-C, 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 other amorphous parts are melted. So, TONER of contained C-PES was showed good fusing, compared contained no C-PES of TONER.

TONER-B maintained of good durability, and low energy fusing can be obtained even the short anneal treatment time.

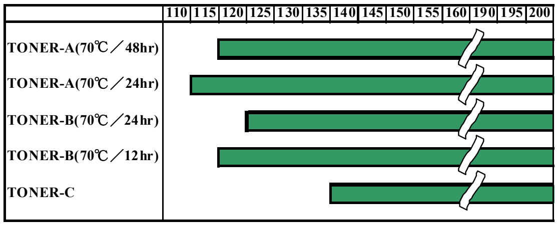

Table 5 The fusing latitude of TONER-A, TONER-B and TONER-C, annealed at 70°C for various time.

Conclusions

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

(1) Key technology for high re-crystallization effect is controlling the compatibility of C-PES and A-PES in combination with anneal process.

(2) Even the short anneal treatment time, the toner with low energy fusing and good storage stability can be obtained by controlling compatibility of C-PES and A-PES.

(3) Proper control of compatibility affects not only crystallization but also crystallization speed in anneal process.

References

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Author Biography

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