Low energy fusing toner by controlling nano dispersion of crystalline polyester

Norihiro Fukuri1), Eiji Shirai1), Shigeto Inoue2), Masayuki Okamoto2) and Katsutoshi Aoki1) Kao Corporation, 1) Performance Chemicals Research Laboratories, 2) Analytical Science Research Laboratories, Wakayama, Japan

Abstract

In recent years, it is required that the toner can be fused at lower energy from the viewpoint of saving energy. As it has already been reported by Shirai et al, it is achieved good fusing ability by using amorphous polyester including crystalline polyester (C-PES). It is supposed that the good fusing ability is due to drastic change of elasticity of C-PES around melting point.

On the other hand, the toner including C-PES showed the poor storage stability. As it has already been reported by Fukuri et al in NIP23, the storage stability could be improved by anneal treatment. It was considered that the crystallization of C-PES was promoted and the crystallinity of the toner could be improved by anneal treatment, resulting in the improvement of the storage stability.

In this study, it is investigated the crystallization mechanism of the toner including C-PES in anneal treatment. It is found that crystals are dispersed with nano-size in the toner by AFM observation. Furthermore, it is found that by nano dispersion of C-PES, the toner that satisfied the low energy fusing, the storage stability, and the 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 be fusible at lower temperature, from the viewpoint of saving energy. It has already been 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 is reported in NIP23 by Fukuri et al.[3] It is reported that the way of promoting crystallization is anneal treatment, which means treating the toner at a certain temperature. By anneal treatment, both the storage stability and the low energy fusing of the toner could be satisfied.

However, it has not been fully cleared yet that the crystallization mechanisms of C-PES and the condition of C-PES in the toner by anneal treatment.

In this paper, it is investigated that the crystallization mechanism of C-PES and the condition of C-PES by anneal treatment. When anneal treatment is conducted, it is found that crystals in toner are dispersed with nano-size by AFM analysis. Furthermore, it is also found that the dispersion size of crystal is different when the anneal temperature is changed. As the result of the investigation of crystallization mechanism, it is cleared that nano-size dispersion is very effective on the improvement of the storage stability and the low energy fusing. In addition, it is found that the durability of the toner could be also improved by controlling the dispersion size of crystals in anneal condition.

Experimental

Preparation of amorphous polyester resin

A-PES-1; A 10L four necked flask equipped with a nitrogen intel 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, terephthalic acid, Dodecenylsuccinic acid 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 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	23	140	61[4)]
A-PES-2	12	100	63[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 intel 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[2] (°C)	Tg[3] (°C)
C-PES	112.5[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 and C-PES were premixed in a batch mixer and kneaded at 100°C by kneading machine. The ratio of them is; A-PES-1 and C-PES = 80/20.

Preparation of toner samples

Toner samples were prepared comprising the polyester resins, the wax (80°C polyethylene), the charge control agent (Fe azo-complex), and the carbon black. These materials were premixed in a batch mixer and kneaded at 100°C. Then they were pulverized and classified. And then, samples having average size of about 8.5 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. The ratio of APES-1 and APES-2 is prepared 50:30.

	APES-1	APES-2	C-PES
TONER-A	62.5	37.5	
TONER-B	50	30	20

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 line speed was 250mm/sec.

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

And the fusing temperature was defined as the lower limit temperature that the cold-offset was not observed and as the lower temperature which the fusing ratio of the toner exceeds 70%. The fusing ratio of the toner was calculated from the image density change of before and after Scooth 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. Put 30g of toner into a cartridge and rotated the developer roll at 70r/min 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 or TONER-B was conducted. The resin blend or TONER-B is kept into furnaces (Temperature condition; 50°C and 90°C) for 72 hours.

Wide-angle X-ray diffractometry (WAXD) measurement

WAXD measurement of C-PES and the toner including C-PES 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 $5º<2\theta<60º$ with an interval of 0.01º and a scan speed of 5º min^{-1}.

Atomic Force Microscopy (AFM)

A flat cross-section of A-PES-1/C-PES blend was made using a ultra microtome (LEICA Ultracut EM UPR) for AFM measurements. AFM images of the cross-section of A-PES-1/C-PES 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 A-PES-1/C-PES blend. The difference in mechanical properties between A-PES and C-PES was substantial, 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 prior analysis.

Result and discussion

Fusing property of the toner

The fusing latitudes of the toners were investigated. The results are shown in Figure 1. The fusing property of TONER-B including 20wt% C-PES was improved compared with that of TONER-A. These results are shown 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. In addition, the fusing property of TONER-B annealed at 50°C was same as TONER-B. Furthermore, as it is reported by Fukuri et al in NIP 23, the storage stability of the annealed toner was improved [3]. It is considered that crystallization was promoted in toner by anneal treatment.

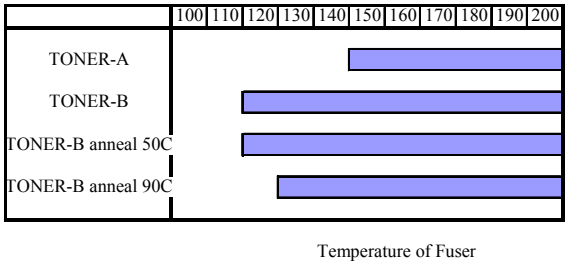

Figure 1 The fusing latitude of TONER-A, TONER-B, and TONER-B annealed at 50°C and 90°C

Crystallinity of TONER-B after anneal treatment

In order to confirm the crystallinity of C-PES and TONER-B with anneal treatment, crystallinity was investigated by WAXD. The results are shown in Figure 2. The peaks attributed to C-PES were observed in case of 50°C and 90°C anneal treatment. It is indicated that the crystallization was promoted by anneal treatment. Furthermore, crystallinity of 50°C and 90°C annealed toner is nearly same from WAXD analysis.

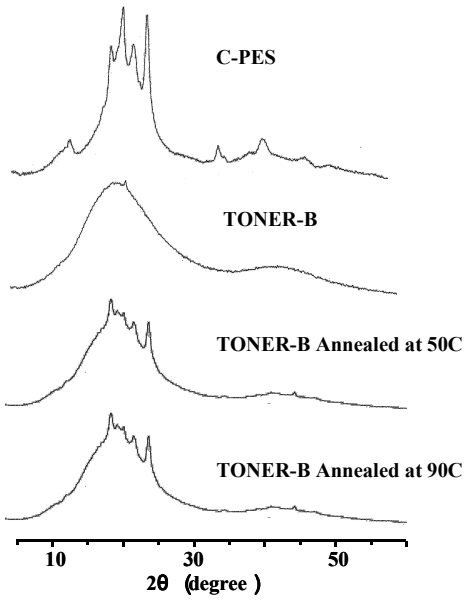

Figure 2 The WAXD measurement of C-PES, TONER-B, and TONER-B annealed at 50°C and 90°C

AFM observation of the blend with and without anneal

In order to analyze the crystallization condition of C-PES, AFM analysis of the A-PES-1/C-PES blend was investigated. The results are shown in Figure 3. Focusing on phase, in case of the A-PES-1/C-PES blend without anneal treatment, domain couldn't be observed and the flat image was obtained. It is considered that A-PES-1 and C-PES are miscible each other and there are no crystals in blend. However, A-PES-1/C-PES blend with 50°C anneal treatment, the domains could be observed, and their size was about 10~20 nm. It is considered that the part of non-crystallized segment is crystallized and the crystals are generated uniformly in blend with nano size. It is found that the size of dispersed crystals can be controlled by anneal temperature.

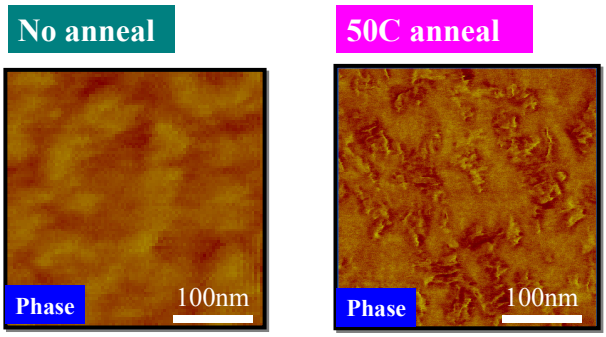

Figure 3 AFM images of blend without anneal (left), with anneal at 50°C (right)

The durability of the annealed toner

As it is indicated before, the effect of anneal treatment on toner is the increase of crystallinity. Furthermore, it is confirmed that, by AFM analysis, C-PES is crystallized and it is dispersed in nano size by anneal treatment. In order to confirm the effect of increase of crystallinity, the durability of the annealed toner was investigated by using color laser printer. The results are listed in Table 4. The durability of TONER-B was not enough compared with TONER-A. This is because that A-PES and C-PES are miscible and plasticizing and there are no crystals. However, in case of annealed toner, the durability was improved. Especially, in case of 50°C annealed toner, it was achieved that nearly same durability as TONER-A (only A-PES). It is considered that by 50°C anneal treatment, very small crystals (10~20 nm crystals from AFM analysis) are generated and dispersed well in toner, and the hardness of the toner was improved. Furthermore, in case of 90°C anneal, the durability gets worse compared with in case of 50°C anneal. Under 90°C anneal, generated crystal size should be bigger and disperse condition may be worse. Because of that, crystals may be bled out to the surface of toner, resulting in filming.

	The filming occurred time
TONER-A	6h
TONER-B	2h
TONER-B anneal 50C	6h
TONER-B anneal 90C	3h

Table 4 The durability of TONER-A, TONER-B, and TONER-B annealed at 50°C and 90°C

The anneal investigation and effect

As it is indicated before, A-PES-1/C-PES blend are miscible and there are no crystals. In order to promote crystallization in toner, it has been known that anneal treatment. Anneal treatment means treating the toner at more than glass transition temperature (Tg) and less than melting temperature (mp) of the toner. In this paper, 50°C and 90°C anneal temperature was investigated. In both condition, crystallization of C-PES was confirmed. Furthermore, it is found that generated crystal size can be controlled by anneal temperature and the dispersion size influences on durability of the toner. Especially, in 50°C anneal treatment toner, it is successfully generated that 10~20 nm size crystal in the toner and the durability of the toner is improved. The toner also satisfied the low energy fusing and the storage stability. It is found that the nano dispersion of C-PES is the key technology for the low energy fusing and high durability toner.

Conclusions

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

(1) The low energy fusing and the good storage stability were achieved by use of crystalline polyester and introducing anneal treatment.

(2) It was found that by anneal treatment, C-PES was crystallized in toner and is dispersed with nano size. Furthermore, by changing anneal condition, dispersed crystal size could be controlled.

(3) It was found that, by nano dispersion of C-PES, the toner that satisfied not only the low energy fusing and the storage stability, but also the durability could be obtained. The nano dispersion of C-PES is the key technology for the low energy fusing and high durability toner.

Reference

[1] E. Shirai, K. Aoki and M. Maruta, IS&T's NIP18 International Conference on Digital Printing Technologies, 258 (2002).
[2] E. Shirai, K. Aoki and M. Maruta, IS&T's NIP19 International Conference on Digital Printing Technologies, 119 (2003).
[3] N. Fukuri, E. Shirai, and K. Aoki, IS&T's NIP23 International Conference on Digital Printing Technologies, 258 (2007).

Author Biography

Norihiro Fukuri received his master degree in material and life science from Osaka University in 2005. Since 2005 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 and toner binder with polyester resin.

E-mail: fukuri.norihiro@kao.co.jp