The excellent fusing toner by controlling polyester crystallinity

Norihiro Fukuri, Eiji Shirai and Katsutoshi Aoki
Kao Corporation, Performance Chemicals 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. It has already been reported by Shirai et al; good fusing ability is achieved by using amorphous polyester including crystalline polyester. It is supposed that the good fusing ability is due to drastic change of viscoelasticity of crystalline polyester around melting temperature.

On the other hand, the storage stability of the toner including crystalline polyester is not good compared with that of the toner without crystalline polyester. The thermal property of the toner including crystalline polyester is focused. As a result, glass transition temperature (Tg) of the toner is dramatically decreased compared with that of the toner without crystalline polyester. It is known that Tg of the toner including crystalline polyester is affected by the crystallinity of this toner itself. It means that crystal can't be kept in the toner by kneading process in case that crystalline polyester and amorphous polyester are miscible each other well. It is essential to improve crystallinity of the toner in order to improve the storage stability.

In this study, one method was investigated in order to improve the storage stability of the toner including crystalline polyester. The method is annealing treatment. The crystallinity of this toner was increased by treating at a temperature 50°C to 90°C. This temperature means more than Tg of the toner and less than melting temperature of crystalline polyester. It is found that Tg of the toner is also increased by annealing treatment. In addition, it is found that the fusing ability of this toner with the annealing treatment can be kept the lowest.

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 temperatures, 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 as binder resins.[1,2] It is considered that the excellent fusing ability characteristics are attributed crystalline polyester ability to quickly melt speed and lower viscoelasticity above melting temperature of crystalline polyester. As shown in Figure 1, the viscoelasticity of crystalline polyester is much different from that of amorphous polyester. The viscoelasticity of crystalline polyester dramatically decreases around melting temperature and that of amorphous polyester gradually decreases by increasing temperature.

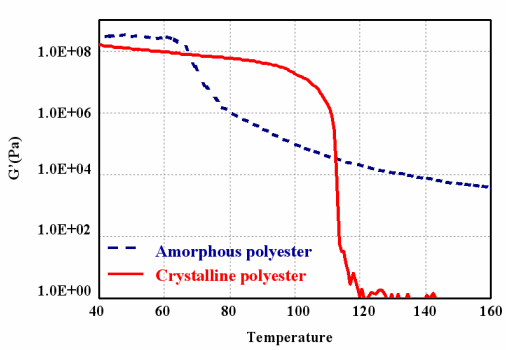

Figure 1 The relationship between temperature and viscoelasticity of amorphous polyester and crystalline polyester

As it has been reported by Shirai et al; the use of crystalline polyester is effective to improve the low energy fusing [1,2]. In that case, the amount of crystalline polyester was 20 wt% and that of amorphous polyester was 80 wt%. For further improvement of the fusing ability, it is considered that the amount of crystalline polyester is increased when the toner is prepared. When the amount of crystalline polyester is increased more than 20 wt%, the effect as plasticizer of crystalline polyester is remarkable. It is confirmed that crystalline polyester is not crystallized and the crystallinity can't be observed. The reason of that is the crystallization rate of crystalline polyester is too slow in the producing process. Furthermore, the thermal property such as glass transition temperature (Tg) of the toner is decreased more. The reason of that is crystalline polyester (Tg is very low) and amorphous polyester are miscible well. In that case, the further improvement of the low energy fusing is achieved but the storage stability gets worse.

In this paper, it is discussed that both the low energy fusing and the good storage stability of the toner are satisfied. In order to achieve both of them, the way to form enough crystal in the toner is reported. It is known that the way of promoting crystallization is annealing treatment, which means treating the toner at a certain temperature. As the result of annealing treatment, both the low energy fusing and the good storage stability can be obtained.

Experimental

Preparation of amorphous polyester resin

APES-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.

APES-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 amorphous 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)
APES-1	23	140	61[4]
APES-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)
CPES	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

APES-1 and CPES were premixed in a batch mixer and kneaded at 100°C. The ratio of them is; APES-1 and CPES = 80/20 (BLEND-A).

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	CPES
TONER-A	62.5	37.5	
TONER-B	50	30	20
TONER-C	44	26	30

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 (KP-cut paper; Kashiwai corporation) 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 Scocth 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 storage stability

The storage stability was measured by the cohesiveness, which was measure by Powder tester (manufactured by Hosokawa Micron Co.).

Put the toner into 45°C 60%H_2O environment for 48 hours, the cohesiveness was compared (under normal conditions the cohesiveness was almost zero).

Annealing Treatment

The annealing treatment of the resin blend or the toners was performed. The resin blend or the toners are kept into furnaces (Temperature condition; 50°C, 60°C, and 90°C) for a period.

Differential Scanning Calorimeter (DSC) measurement

Thermal properties of the resin blend and the toner samples without and with annealing treatment were measured by Q100 (TA instruments). Samples were added into aluminum pan. A temperature sweep was conducted from 0ºC to 150°C at 10°C /min.

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 5º<2θ<60º with an interval of 0.01º and a scan speed of 5º min^{-1}.

Rheometer measurement

Polyester viscoelastic properties were measured by ARES (TA instruments). 3 grams of resin was added to a parallel Serr plate with diameter of 8 mm. A temperature sweep was conducted from

40°C to 180°C at 10°C /min at frequency of 6.28 rad/sec. The strain was adjusted at 0.05%.

Result and discussion

Fusing property of the toner

The fusing latitudes of the toners were investigated. The results are shown in Figure 2. The fusing property of TONER-B (20 wt% CPES) was improved compared with that of TONER-A. In addition, that of TONER-C (30 wt% CPES) showed best result in these three toners and lowest energy fusing was achieved under this fusing test condition. These results show that when the toner passes through the heat roller, crystalline polyester starts melting at the first step and then the other amorphous resin are melted. Especially, in TONER-C, there are much parts of fast melting attributed to crystalline polyester, therefore, it is assumed that the toner is easier to fuse on the paper.

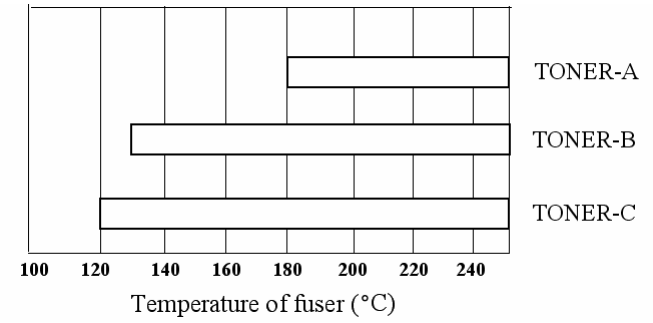

Figure 2 The fusing latitude of TONER-A, TONER-B, and TONER-C

Storage stability and crystallinity of the toner

The storage stability of the toner was investigated. The results are shown in Figure 3. The storage stability of TONER-B and TONER-C got worse compared with that of TONER-A and that of TONER-C showed the worst result. This is because the effect of plasticization by adding 30 wt% of crystalline polyester is remarkable. And, Tg is decreased by adding crystalline polyester whose Tg is about -30°C. When crystalline polyester and amorphous polyester were blended, both polyesters are miscible each other well in the kneading process, resulting in low Tg. As the results of those, it showed the worst storage stability.

Furthermore, the crystallinity of the TONER-C was investigated by WAXD. The result is shown in Figure 4. The peak attributed to crystalline polyester couldn't be observed. It is indicated that there is no crystallized part in TONER-C. It was considered that both polyesters are miscible each other well, therefore, the crystallization rate of crystalline polyester is too slow to form crystal during the producing process of TONER-C.

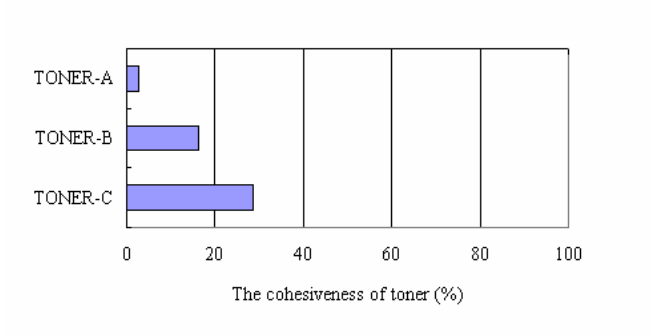

Figure 3 The storage stability of TONER-A, TONER-B, and TONER-C

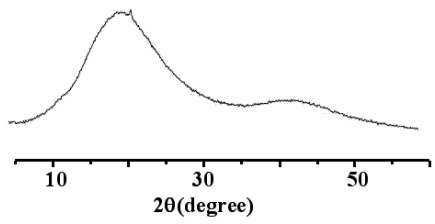

Figure 4 The WAXD measurement of TONER-C.

Thermal property and crystallinity of the BLEND after annealing treatment

It is confirmed that the crystallinity couldn't be observed in TONER-C by WAXD and it means that crystalline polyester is not crystallized. The reason of it seems as follows; the crystalline polyester in the toner was supercooled by cooling rapidly in the producing process, therefore, crystal can't be formed. Then, it is thought that if the thermal energy is given enough to the toner, crystalline polyester is crystallized. As a result, the annealing treatment was discussed in order to promote the crystallization. First, to remove the influences by additives such as wax, charge control agent, and carbon black, only crystalline and amorphous polyester blend (BLEND-A) was used in the annealing test. The thermal property of BLEND-A was investigated by DSC. Tg of BLEND-A was decreased (Tg:30°C) compared with that of APES-1 (Tg:61°C). It was also considered that both polyester are miscible and plasticize each other. On the other hand, annealing treatment of BLEND-A was performed. The treatment temperature was changed from 50°C to 90°C, which means more than Tg and less than melting temperature. The relationship between treatment time and Tg under the situation from 50°C to 90°C is shown in Figure 5. By annealing treatment, Tg of BLEND-A was increased as time goes by. It was considered that the part of non-crystallized segment of crystalline polyester was rearranged and crystallized, resulting in the increase of Tg. In addition, under 60°C and 90°C condition, the increase rate of Tg was bigger than in case of 50°C condition. It is considered that the crystallization rate of crystalline polyester was different by annealing temperature, and under 60°C and 90°C condition, it seemed faster.

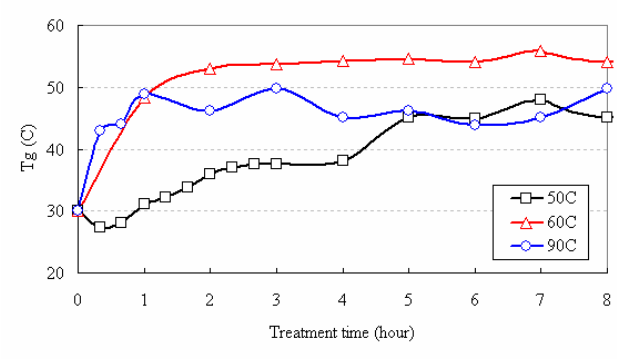

Figure 5 The relationship between annealing treatment time and Tg of BLEND-A.

Also, the crystallinity of BLEND-A with annealing treatment was investigated by WAXD. The results are shown in Figure 6. The peak attributed to crystalline polyester was observed under 50°C and 90°C condition. It was indicated that the crystallization was promoted by annealing treatment.

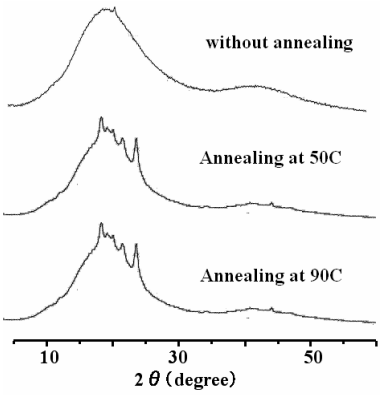

Figure 6 The WAXD measurement of the BLEND-A with and without annealing treatment.

The effect of annealing treatment on toner

It was confirmed that the effect of annealing treatment on blended polyester resin is the increase of Tg and crystallinity. Therefore, TONER-C was treated at the temperature from 50°C to 90°C. The results of the storage stability of TONER-C with annealing treatment are shown in Figure 7. By annealing treatment, the storage stability of the toner was improved compared with that of TONER-C. In case of 50°C, it was nearly same as TONER-B. Especially, in case of 60°C, the storage stability showed the best result. The reason of that seems as follows; From the result of the thermal property of BLEND-A with annealing treatment at 60°C, crystallization rate seems faster. In that case, it is considered that the crystalline polyester is crystallized enough and Tg is getting higher enough, resulting in the best storage stability. In addition, under 90°C condition, the storage stability was nearly same as 50°C. However, under 90°C condition, used wax in the toner may be melted.

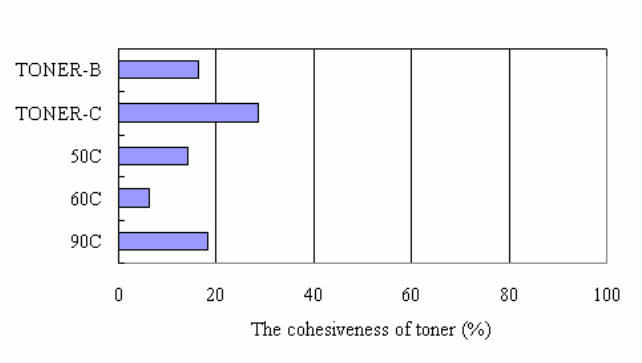

Figure 7 The storage stability of TONER-B, TONER-C, and TONER-C with annealing treatment temperature at 50ºC, 60ºC, and 90ºC.

Furthermore, the results of the fusing property of TONER-C with annealing treatment are shown in Figure 8. With annealing treatment at temperature 50°C, the excellent low energy fusing (120°C) could be kept. The excellent low energy fusing is attributed to not only the effect of plasticization by adding crystalline polyester but also the formation of crystal. On the other hand, the fusing property of the toner with 60°C and 90°C treatment was a little worse. It is hypothesized that by 60ºC and 90°C treatment, the crystallization is promoted and the effect as plasticizer is decreased, resulting in worse of low energy fusing.

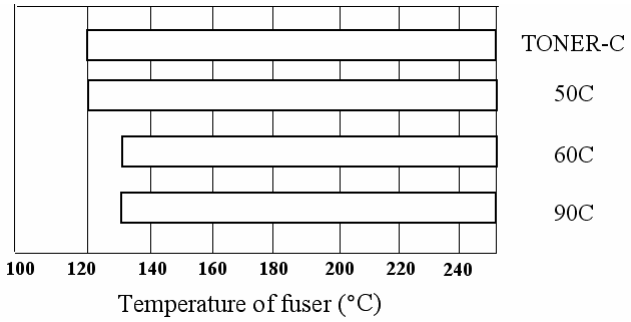

Figure 8 The fusing latitude of TONER-C, and TONER-C with annealing treatment temperature at 50°C, 60°C, and 70°C.

In addition, the pulverized ability of TONER-C and TONER-C with annealing treatment was investigated. The results are shown in Table 4. Pressure is the power of machine in pulverizing toner and the small value means easy to be pulverized. The pulverized ability of TONER-C with annealing treatment was improved compared with TONER-C. It is considered that by annealing treatment, the part of plasticizer is decreased, resulting in easy to be pulverized.

Table 4 The pulverized ability of Toner.

	Pressure	Particle size (μm)
TONER-C	0.56	8.51
50°C	0.40	8.29
60°C	0.38	8.53
90°C	0.42	8.56

From these results, it was found that in TONER-C with annealing treatment at 50°C, the storage stability kept good result as TONER-B, and the excellent low energy fusing could be achieved compared with TONER-B. In addition, the pulverized ability was improved.

Conclusions

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

(1) The low energy fusing was affected by the ratio of crystalline polyester and 30 wt% of crystalline polyester in the toner showed the excellent low energy fusing.

(2) The storage stability of the toner including 30 wt% crystalline polyester was improved by annealing treatment.

(3) In the toner including 30 wt% crystalline polyester with annealing treatment at 50°C, keeping the same cohesiveness level as the toner including 20 wt% crystalline polyester, the fusing property was improved 10°C lower. Furthermore, pulverized ability was also improved by annealing treatment.

(4) It was found that Tg of the toner was increased and the crystallization is promoted by annealing treatment. Furthermore, the increase ratio of Tg was affected by annealing treatment temperature. It is indicated the crystallization rate of the toner is different by annealing treatment temperature.

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).

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