Crystalline Polyester for High Durability

Takashi Kubo, Eiji Shirai and Katsutoshi Aoki
Kao corporation, Performance Chemicals Research Laboratories
Wakayama, Japan

Abstract

In recent years, from the viewpoint of saving energy, it is requested that the toner can be fused at lower energy. In NIP19, it was reported that the toner containing crystalline polyester exhibited excellent fusing ability. And the melting point of crystalline polyester is effective on fusing ability.

On the other hand, the speed of machine system is increasing year by year. So high durability toner is requested as well. However, it was very difficult to satisfy high durability and excellent fusing ability at the same time.

In this study, we developed high molecular weight crystalline polyester. Durability of the toner containing crystalline polyester is improved by increasing molecular weight of crystalline polyester. And the melting point of crystalline polyester is not changed even if its molecular weight is higher. So its good fusing ability can be kept. Furthermore, high molecular weight crystalline polyester shows high elasticity above its melting point. Because of that, anti-hot offset property of the toner is also improved.

Introduction

Recently, environmental problem has received considerable attention. It is required that the toner is fused at lower temperature, from the viewpoint of saving energy. In NIP19, it was reported that excellent fusing ability was acheived by using crystalline polyester. It is considered that the excellent fusing ability is attributed to faster melting speed and lower elasticity after melting of crystalline polyester than amorphous polyester resin as Figure1 shows. The lower limit of the fusing ability of the toner is improved by decreasing the melting point of crystalline polyester.

From now on, printing speed of printer and copy machine will be getting faster. It means that stress to the toner by friction with career will be higher. So the toner which shows not only excellent fusing ability but also high durability is necessary. Generally, it is said that decreasing low molecular weight component or increasing its molecular weight of polymer is effective to improve durability of the toner. But in case of amorphous polyester resin, fusing ability of this toner is getting worse by increasing molecular weight because the softening point (T1/2) and the glass transition temperature (Tg) of the resins become higher correlatively. However, in case of crystalline polyester, its melting point is not affected by increasing its molecular weight. So in this report, it was investigated the relationship between molecular weight of crystalline polyester and durability to get the toner with excellent fusing ability and high durability.

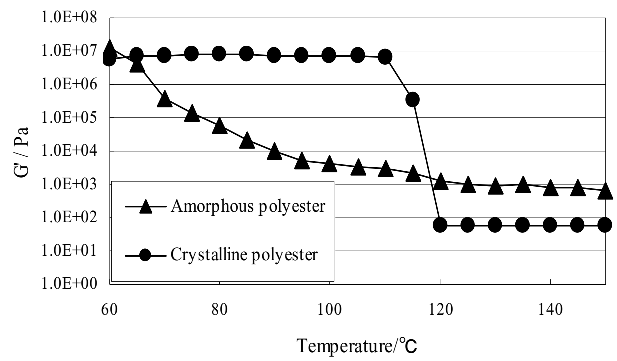

Figure 1. Viscoelasticity of amorphous polyester and crystalline polyester

Experimental

Preparation of Amorphous Polyester Resin

The raw material monomers, propylene oxide adduct of Bisphenol A, ethylene oxide adduct of Bisphenol A, Terephthalic acid, Dodecenylsuccinic acid anhydride, Trimellitic anhydride, and Dibutyltin oxide, were combined, and the ingredients were reacted at 230°C for 10 hours in the grass flask equipped with a nitrogen intel tube, a dehydration tube, a stirrer, and thermocouple. Thereafter ingredients were reacted at 8.3kPa until the desired softening point was attained. Amorphous polyester resins are listed in Table 1.

Table 1. Properties of Amorphous Polyester Resin

Resin	Acid Value[1)] (mgKOH/g)	T1/2[2)] (°C)	Tg[3)] (°C)
PES-1	7.0	148.1	63.2
PES-2	10.6	103.1	61.7
PES-3	27.8	141.9	59.9
PES-4	13.5	100.3	62.7

1) The acid value was measured according to ASTM D-1980-67.
2) The softening point (T1/2) was measured by flowtester "CFT-500D" manufactured by Shimadzu Corporation.
3) The glass transition temperature (Tg) was measured by a differential scanning calorimeter "DSC Model 200" manufactured by Seiko Instruments Inc., at heating rate of 10°C/min. And Tg was read by the tangential way.

Preparation of Crystalline Polyester Resin

The raw material monomers, as shown in table 2, and Dibutyltin oxide and Hydroquinone, were combined, and the ingredients were reacted at 160°C for 5 hours in the grass flask equipped with a nitrogen intel tube, a dehydration tube, a stirrer, and thermocouple. Thereafter, the temperature was raised to 200°C and the ingredients reacted for 1 hour, and further reacted at 8.3kPa until a resin having a desired molecular weight was obtained. Crystalline polyester resins are listed in table 3.

Table 2. The Material Monomers of Crystalline Polyester

(Mol ratio)

Resin	1,4-Butane diol	1,6-Hexane diol	Fumaric acid	Adipic acid	stearic acid
CPES-1	70	30	100		
CPES-2	70	30	100		0.5
CPES-3	72	30	100		
CPES-4	90	10	85	15	
CPES-5	92	10	85	15	

Table 3. Properties of Crystalline Polyester

Resin	Tmp[4] (°C)	Mw[5]
CPES-1	106.7	9.9E+03
CPES-2	104.2	3.6E+04
CPES-3	105.8	7.2E+04
CPES-4	93.4	8.4E+03
CPES-5	91.2	5.6E+04

4) Tmp was read by peak top of DSC and called melting point.
5) Mw was measured according to ASTM D-3536-91.

Preparation of Toner Samples

Toner samples were comprised of this resin, the wax, the charge control agent and the carbon black. Those samples were prepared through the same process. The materials were premixed in a batch mixer; then they were kneaded, pulverized and classified. And then, samples having average size of 8 μ m were obtained. Each toner was blended with fumed silica to get efficient flow ability and charging ability for the test operation. Toner samples are listed Table 4.

Table 4-1. Toner Samlpes-1

TONER	PES-1 (wt%)	PES-2 (wt%)	CPES-1 (wt%)	CPES-2 (wt%)	CPES-3 (wt%)
A	60	20	20		
B	60	20		20	
C	60	20			20

Table 4-2. Toner Samples-2

TONER	PES-3 (wt%)	PES-4 (wt%)	CPES-4 (wt%)	CPES-5 (wt%)
D	50	50		
E	50	30	20	
F	50	30		20

Measurement of Viscoelasticity

Viscoelasticity was measured by Dynamic Mechanical Analysis (DMA; DYNAMIC ANALYZER RDA II). The amount of 8g of a resin was supplied in a quette with diameter of 25mm and length of 32mm. The temperature was swept from 70°C to 160°C at frequency of 2.0 rad/s.

Measurement of Electric Resistance

The amount of 5g of a toner was supplied in a press die for tabletting having an inner diameter of 59 mm so that the toner surface was even. The die was set in an electric sample-molding machine (C/N:9302/30), and pressure of 10 tons by the scale on a Boudon's tube pressure gauge provided in the machine was applied for ten seconds, to give a toner pellet having a diameter of 59mm and a thickness of about 1.7mm.

Electric loss tangent and capacitance of the resulting toner pellet was determined at 1kHz under the environmental of a temperature 25, using a precision LCR meter; HP4284 and electric determination; HP16451B. And from these values, electric resistance of the toner was calculated.

Measurement of Durability

The amount of 140g of a toner and 3860g of fluororesin/acrylic resin-coated magnesium-based carrier having a saturation magnetization of 60Am^2/kg (average particle size:100 µm) were mixed with a Nauta Mixer. The two component developer was loaded in a contact two-component development device. Ten print patterns with a print ratio of 8% were continuously printed using continuous feeding paper having different basis weight (11×18 inches). There after, the amount of toner spent to the carrier was determined by TOC (EMIA-110).

Measurement of Electric Charging

Electric charging was measured by q/m meter (Epping GmbH). The amount of 1.75g of toner and 48.25g of fluororesin/acrylic resin-coated magnesium-based carrier carrier (average particle size: 100 µm) were mixed together with a ball mill at 250r/min. And electric charging at a mixing time of 1200s were measured by q/m meter.

Measurement of Fusing Ability

Fusing ability was tested by using the off-line fuser. (Heat roller/Pressure roller) The silicone oil was removed completely. 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 (50g paper; Xerox Corporation) so that the mass per area was 0.6 mg/cm^2. Then the paper was passed through the fuser. The line speed was 250mm/sec.

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

Results and Discussion

Molecular Weight and Viscoelasticity of Crystalline Polyester

Molecular weight distribution and viscoelasticity of CPES-1, CPES-2 and CPES-3 are shown in Figure 2 and Figure 3. It was confirmed that storage modulus (G') after melting of crystalline polyester was higher by increasing its molecular weight. The melting point of crystalline polyester was not affected by its molecular weight. Then durability of the toners made with each three types of crystalline polyester was tested.

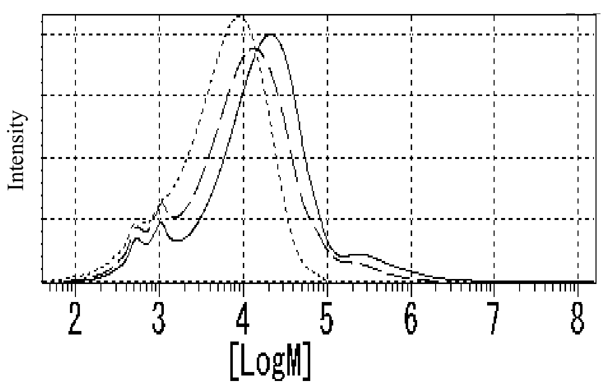

Figure 2. GPC chart of crystalline polyester. 1) Dotted line: CPES-1, 2) Dashed line: CPES-2, 3) Solid line: CPES-3

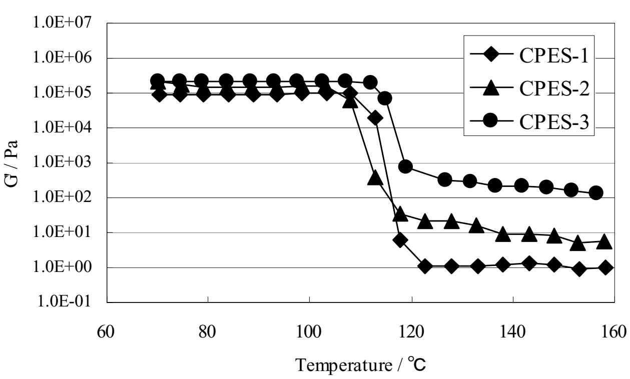

Figure 3. Viscoelasticity of crystalline polyester

The Effect to Durability by Increasing Molecular Weight of Crystalline Polyester

Durability of the toner was evaluated by the amount of toner spent to career during long time printing. Figure 5 and Figure 6 show the results of printing test.

As shown in Figure 4, at first, the amount of spent was almost same. But after 50k printing, the ratio of increase in the amount of spent was getting lower by increasing molecular weight of crystalline polyester. And as shown in Figure 5, it was confirmed that the amount of spent at 150k was depended on the molecular weight of crystalline polyester. It is suggested that there are two reasons. One is that the toughness of crystalline polyester was improved by increasing its molecular weight. The other is that the dispersion of additions gets better by using crystalline polyester having higher elasticity after melting. Especially the dispersion of mechanically weak wax is thought to affect on durability. Then dispersion of additions was investigated as follows.

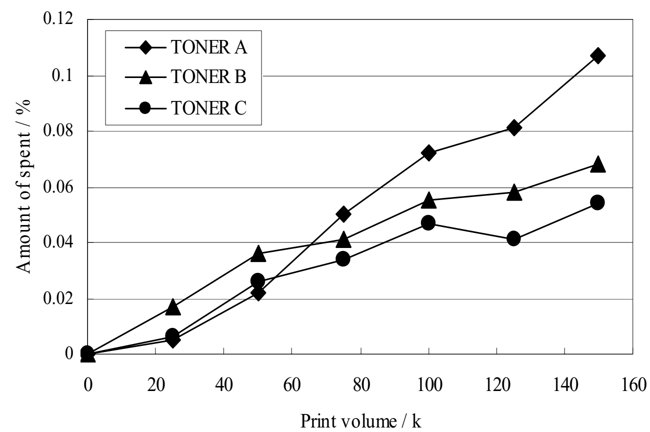

Figure 4. Variation of the amount of spent to career with print volume

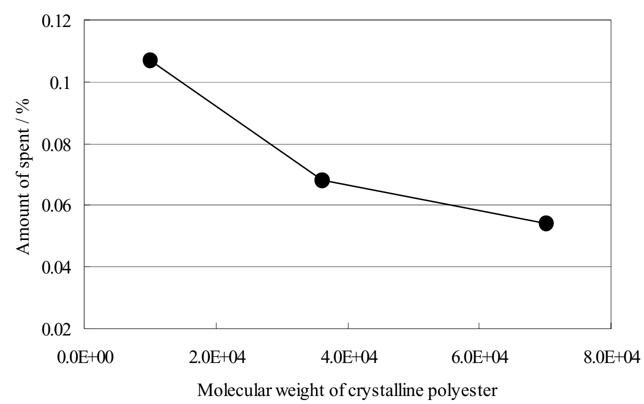

Figure 5. Relationship between amount of spent at 150k and molecular weight of crystalline polyester

Dispersion of Additions in the Toner

Dispersion of additions was investigated by measuring the electric resistance of the toner. If such a conductive material as carbon black is cohered, the electric resistance of toner gets lower.

From Figure 6, it was indicated that the resistance of the toner was higher by increasing molecular weight of crystalline polyester. It means that additions in the toner are dispersed better by using high molecular weight crystalline polyester. This result is related to the elasticity after melting of toner. As shown in Figure 3, the elasticity after melting of crystalline polyester is within suitable range by increasing its molecular weight. So the toner with crystalline polyester having high elasticity above its melting point is kneaded strongly.

Furthermore, as shown in Figure 7, it was confirmed that charging ability of the toner containing high molecular weight crystalline polyester was also improved .It is suggested that dispersion of charge control agent is improved by using crystalline polyester with higher molecular weight. And this result is consistent with the result of electric resistance.

From these results, it is supported that the dispersion of additions in the toner is improved by using higher molecular weight crystalline polyester.

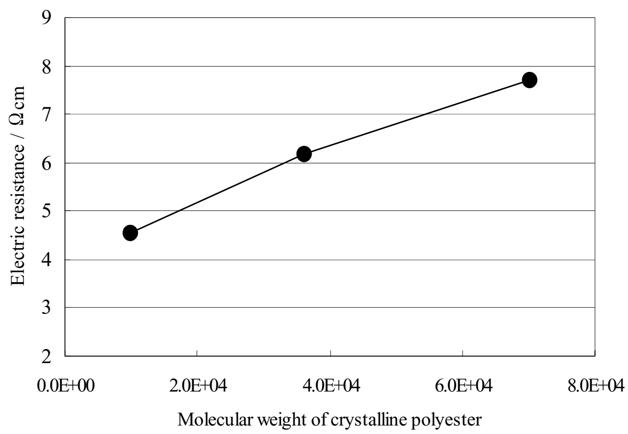

Figure 6. Relationship between electric resistance and molecular weight of crystallie polyester.

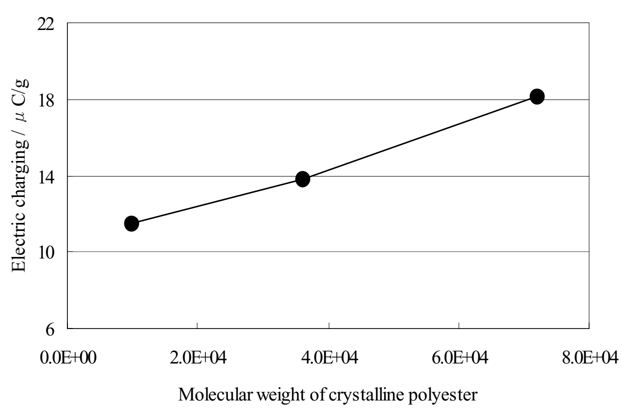

Figure 7. Relationship between electric charging and molecular weight of crystalline polyester.

Fusing Property

The fusing latitude of the TONER D, TONER E and TONER F were shown in Figure 8. From this result, the lower limit of fusing ability of TONER E was improved about 30°C compare to the TONER D without crystalline polyester. And the lower limit of the fusing ability was not changed by increasing molecular weight of crystalline polyester. As shown in table 3, the melting point of crystalline polyester was almost same even if the molecular weight was increased. As a result, the toner containing high molecular crystalline polyester also gives excellent fusing ability.

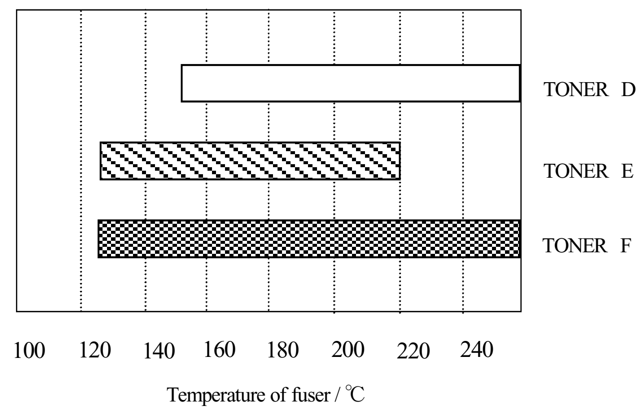

Figure 8. Fusing latitude of each sample

On the other hand, upper limit of the fusing latitude of TONER E was declined compare to the toner D without crystalline polyester. It is related to the low elasticity of crystalline polyester after melting as Figure 1 shows. However, the upper limit of the TONER F containing high molecular weight crystalline polyester was improved. As Figure 3 shows, it is considered that high elasticity of CPES-3 works like amorphous polyester resin with high molecular weight.

Conclusions

The present investigation of high molecular weight type crystalline polyester leads to the following conclusions.

1. The molecular weight of crystalline polyester was increased without changing its melting point.
2. Durability of the toner containing crystalline polyester was improved by increasing its molecular weight.
3. The dispersion of the additions in the toner was improved by increasing molecular weight of crystalline polyester.
4. By using the toner containing high molecular weight crystalline polyester, upper limit of anti-offset latitude is improved without changing lower limit of fusing ability.

References

1. E. Shirai, K. Aoki and M. Maruta, IS&T's NIP 18 International Conference on Digital Printing Technologies, 258(2002)
2. E. Shirai, K. Aoki and M. Maruta, IS&T's NIP 19 International Conference on Digital Printing Technologies, 119(2003)

Biography

Takashi Kubo received his master degree in applied chemistry from Keio University in 2001. Since 2001 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: kubo.takashi@ kao.co.jp