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Crystalline Polyesters for Use in High Durability Electrophotographic Toner

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Abstract. *Recently, requests have been made that toners be able to fuse to paper with lower energy utilization. It has been reported previously that toners containing crystalline polyesters exhibited excellent fusing ability and that the lowering of these polymers' melting points was an effective means of improving fusing performance. On the other hand, the speed of printers and copiers has been increasing year by year, requiring the toner to have excellent durability properties. It is extremely difficult to satisfy both the durability and lower energy fusing requirements with the same toner as the properties work against each other. In this study, we have developed high molecular weight crystalline polyesters which allow us to obtain a high durability toner that also exhibits low energy fusing performance. Durability was achieved by increasing the molecular weight of the crystalline polyester, which is believed to also contribute to better dispersion of the toner additives. Moreover, it was found that the crystalline polyester's melting point was not affected by the molecular weight changes made in this study. Consequently, we were able to obtain both high molecular weight and a low melting point in these crystalline polyesters. As an added benefit, it has been observed that the high molecular weight crystalline polyesters also exhibit melt elasticity properties important for good toner antihot offset performance. © 2007 Society for Imaging Science and Technology.*
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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 be fusible at lower temperatures, from the viewpoint of saving energy. It has been reported that excellent toner fusing ability can be achieved through the use of crystalline polyesters as binder resins. It is believed that the excellent fusing characteristics are attributed crystalline polyester's ability to quickly melt and obtain lower melt elasticity properties compared with an amorphous polyester resin having the same softening temperature ($T_{1/2}$) as shown in Fig. 1. It has also been noted by decreasing the crystalline polyester's melting point one can further decrease the lower limit of the fusing window.

The printing speed of printers and copy machines is getting increasingly faster which means that mechanical stress to the toner by friction with carrier will be higher. So the toner that shows not only excellent fusing ability but also high durability is required. Generally, it is said that decreasing low molecular weight component or increasing molecular weight of polymer is effective to improve durability of the toner. But for the toner containing only amorphous polyester resin, the fusing ability deteriorates with increasing molecular weight because $T_{1/2}$ and the glass transition temperature (T_g) of the resin become higher correlatively. However, in case of crystalline polyester, its melting point is not affected by increasing its molecular weight. It is a characteristic property of the crystalline polyester. So in this report, we investigated the relationship between molecular weight of crystalline polyester and durability to obtain a toner with both excellent fusing ability and high durability.

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EXPERIMENT

Preparation of Amorphous Polyester Resin

The monomers and other raw materials including: Bisphenol A propoxylate (Sigma-Aldrich Japan K.K.), Bisphenol A ethoxylate (Sigma-Aldrich Japan K.K.), Terephthalic acid (Wako Pure Chemical Industries, Ltd., purity over 95%), Dodecenylsuccinic anhydride (Sigma-Aldrich Japan K.K., purity is 90%), Trimellitic anhydride (Wako Pure Chemical Industries, Ltd., purity over 97%), and Dibutyltin oxide (Wako Pure Chemical Industries, Ltd., purity over 95%), were first mixed. The mixture was heated to 230 °C in a glass flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and thermocouple. Thereafter, the ingredients were reacted at 8 kPa until the desired softening point was attained. The amorphous polyester resins are listed in Table I.

Preparation of Crystalline Polyester Resin

The monomers listed in Table II, Dibutyltin oxide (Wako Pure Chemical Industries, Ltd., purity over 95%) and Hydroquinone (Wako Pure Chemical Industries, Ltd., purity

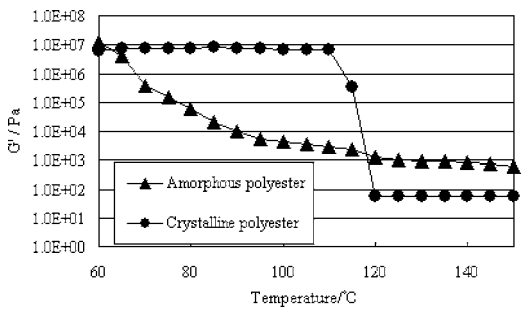

Figure 1. Viscoelasticity of amorphous and crystalline polyester (both resins have the same $T_{1/2}$ (110 °C)).

Table I. Properties of amorphous polyester resin.

Resin	Acid value[a] (mg KOH/g)	$T_{1/2}$[b] (°C)	T_g[c] (°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

[a]The acid value was measured according to ASTM D-1980-67.

[b]The softening point ($T_{1/2}$) was measured by a flowtester "CFT-500D" manufactured by Shimadzu Corporation.

[c]The glass transition temperature (T_g) was measured by a differential scanning calorimeter "DSC model 200" manufactured by Seiko Instruments Inc., at heating rate of 10°C/min.

Table II. Monomers used to synthesis the crystalline polyesters.

	Mol ratio			
Resin	1,4-Butanediol	1,6-Hexanediol	Fumaric acid	Adipic acid
CPES-1	70	30	100	
CPES-2	70	30	100	
CPES-3	70	30	100	
CPES-4	90	10	85	15
CPES-5	92	10	85	15

over 99%), were combined. The mixture was heated to 160 °C and held there for 5 h in a glass flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and thermocouple. Thereafter, the temperature was raised to 200 °C and the ingredients further reacted for 1 h followed by a final reaction at 8 kPa until a resin having a desired molecular weight was obtained. The crystalline polyester resins are listed in Table III.

Preparation of Toner Samples

Toner samples were prepared comprising the polyester resins, wax, charge control agent, and carbon black. The materials were premixed in a batch mixer and the toner was kneaded, pulverized and classified to an average size of 8 μm. Finally, each toner sample was blended with fumed silica to get adequate flowability and tribocharge properties. The toner samples are listed in Table IV, part (a).

Measurement of Toner Viscoelasticity

Toner viscoelastic properties were measured by Dynamic Mechanical Analysis (DMA; Dynamic Analyzer RDA), 8 g of resin was added to a cuvette with diameter 25 mm and length 32 mm. A temperature sweep was conducted from 70 to 160 °C at a frequency of 2.0 rad/s.

Measurement of Toner Electrical Resistance

Toner (5 g) was added to a 59 mm press die for tabletting and the toner surface was evened out. The die was set in an

Table III. Properties of crystalline polyester.

Resin	T_{mp}[a] (°C)	M_w[b]
CPES-1	106.7	9.9*E*+03
CPES-2	104.2	3.6*E*+04
CPES-3	105.8	7.2*E*+04
CPES-4	93.4	8.4*E*+03
CPES-5	91.2	5.6*E*+04

[a]T_{mp} was read by the peak of the differential scanning colorimetry endotherm and is called melting point.

[b]M_w (molecular weight) was measured according to ASTM D-3536-91.

Table IV. Toner samples.

(a)1	Toner	PES-1 (wt %)	PES-2 (wt %)	CPES-1 (wt %)	CPES-2 (wt %)	CPES-3 (wt %)
	A	60	40	—	—	—
	B	60	20	20	—	—
	C	60	20	—	20	—
	D	60	20	—	—	20
(b)2	Toner	PES-3 (wt %)	PES-4 (wt %)	CPES-4 (wt %)	CPES-5 (wt %)	
	E	50	50	—	—	
	F	50	30	20	—	
	G	50	30	—	20	

electric sample-molding machine (C/N:9302/30), and a pressure of 10 MT (measured by the scale on a Boudon's tube pressure gauge) was applied for 10 s, to create a toner pellet having a diameter of 59 mm and a thickness of about 1.7 mm.

Electric loss tangent and capacitance of the toner pellet were measured at 1 kHz at a temperature of 25 °C, using a precision LCR meter; HP4284 and HP16451B. Electrical resistance was calculated from these two values.

Measurement of Toner Durability

Toner (140 g) and 3860 g of fluoro/acrylic resin-coated magnesium-based carrier (saturation magnetization 60 A m^2/kg, average particle size 100 μm) were mixed in a Nauta mixer. The two component developer was loaded in a contact two-component development device. Ten images with a print ratio of 8% were printed using continuously fed paper having a basis weight of 11×18 in. Thereafter, the ratio of spent toner to carrier was determined by total organic carbon (TOC) (EMIA-110).

Measurement of Toner Triboelectric Properties

The triboelectric behavior of the toner was measured by a q/m meter (Epping GmbH); 1.75 g of toner and 48.25 g of

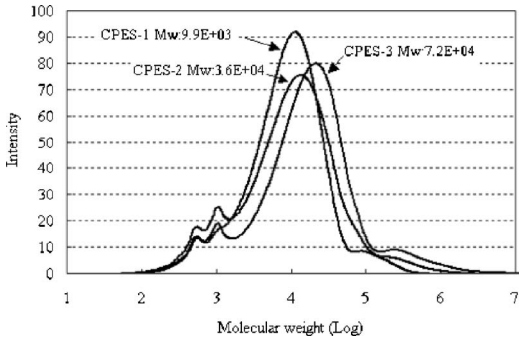

Figure 2. GPC chart of crystalline polyester.

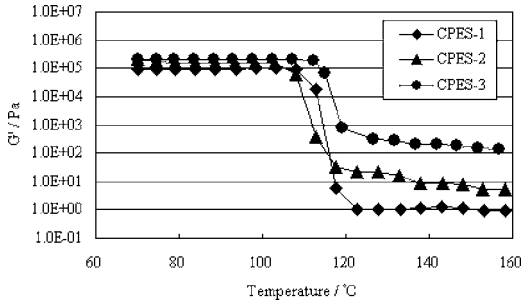

Figure 3. Viscoelasticity of the experimental crystalline polyesters.

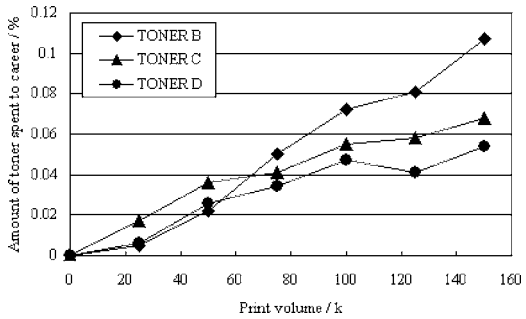

Figure 4. Ratio of spent toner to carrier as a function of print volume.

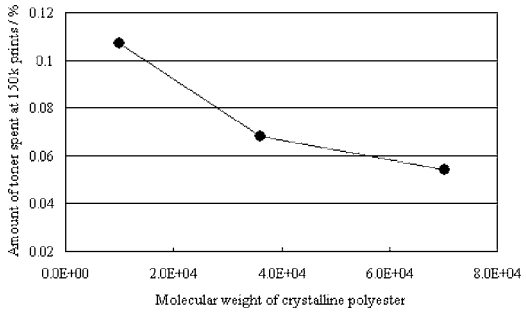

Figure 5. Relationship between the amount of toner spent at 150 000 prints and the molecular weight of crystalline polyester.

fluoro/acrylic resin-coated magnesium-based carrier (average particle size of 100 μm) were mixed together in a ball mill at 250 rpm. The toner's charge characteristics were measured after a mixing time of 1200 s (20 min).

Measurement of Toner Fusing Properties

Fusing performance was evaluated using an off-line fuser (hot roll and pressure roll). Silicone oil was completely removed for this study. The diameter of the heat roller was 30 mm, the width of the nip was 4 mm, and the pressure of the nip was 2 kg/cm.

Each toner sample was developed and transferred to the paper (50 g weight from Xerox Corporation), so that the mass per unit area was 0.6 mg/cm^2. The paper was then passed through the offline fuser at a linear speed of 250 mm/s.

The lower limit and upper limit of the fusing temperature window was defined as the lowest temperature where cold offset and highest temperature where hot offset, respectively, was not observed.

Measurement of Crystalline Polyester Resin Hardness

Crystalline polyester resin (20 g) was melted in an aluminum cup at 160 °C, then cooled to 25 °C, and held there for 3 h. The hardness property was evaluated using a durometer (Asker-D).

RESULTS AND DISCUSSION

Molecular Weight and Viscoelasticity of the Crystalline Polyester Resins

Molecular weight distribution and viscoelasticity of CPES-1, CPES-2, and CPES-3 are shown in Figs. 2 and 3. It was found that storage modulus (G') increased as molecular weight increased as measured at 140 °C. On the other hand, the melting point (T_{mp}) of the crystalline polyesters did not appear to be affected by its molecular weight during this study.

Toner Durability and the Effect of Crystalline Polyester Molecular Weight

The toner durability properties were evaluated by measuring the amount of toner spent on the carrier during the course of a long print test. It is hypothesized that good toner durability is associated with a low amount of spent toner adhered to the carrier for this experiment. Figures 4 and 5 show the TOC results for these toner print tests.

Up through 50,000 prints, the amount of toner spent was the same for the three toner samples. After 50,000, however, it was found that the amount of toner spent decreased as the molecular weight of the crystalline polyester increased. Figure 5 shows amount of spent toner after 150,000 prints for the three toner samples.

It has been hypothesized that there are two reasons for this durability dependence on molecular weight. First, the physical properties of the crystalline polyester resins improved by increasing molecular weight. Second, the dispersion of additives in the toner gets better through the use of a higher molecular weight crystalline polyester (higher viscosity). The dispersion of wax is thought to greatly influence durability, because wax is easily affected by heat and mechanical stress. Both of these hypotheses were further investigated.

Table V. Properties of crystalline polyesters.

	CPES-1	CPES-2	CPES-3
Under 500 g/mol (wt %)[a]	4.2	3.2	1.8
Hardness	54	53	55

[a]Ratio of low molecular weight polymer under 500 g/mol measured by GPC.

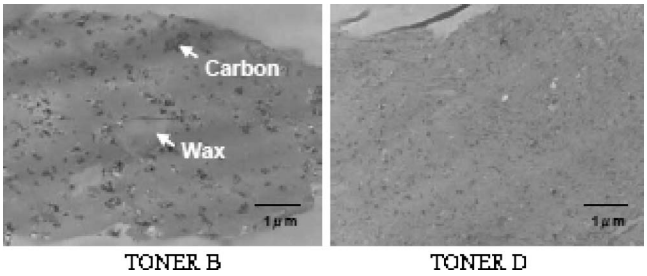

Figure 6. TEM images of Toner B and Toner D.

Physical Properties of the Crystalline Polyesters

The physical properties of crystalline polyesters were investigated by quantifying the amount of low molecular weight polymer and through hardness data. The results from this comparison are listed in Table V. Generally, it is considered that residual monomers and low molecular weight polymer have a bad influence on toner durability. The amount of low molecular weight component (<500 g/mol) was measured by gel permeation chromatography (GPC). It was found that by increasing the crystalline polyester's average molecular weight, the amount of low molecular weight component was reduced.

In contrast, the hardness properties are almost the same for the crystalline polyester resins despite the molecular weight differences. Consequently, it has been hypothesized that the hardness is not affected by molecular weight, but by the structure of monomer used to synthesize these polymers.

Dispersion of Additives in the Toner

Next, the dispersion of toner additives was studied by three distinct methods. First, transmission electron microscopy (TEM) was used to observe the additive dispersion. Figure 6 shows the TEM images of Toner B and Toner D. Large wax domains can easily be found in the photograph of Toner B, which contains the low molecular weight crystalline polyester (CPES-1). Toner D contains CPES-3, which has a higher molecular weight than CPES-1. In the photograph of Toner D, large wax domains were not found. Furthermore, it was also confirmed that Toner D also had better carbon black pigment dispersion compared to Toner B.

Next, the toner additive dispersion was investigated by measuring the electrical resistance properties of the toner. For toners containing conductive materials such as carbon black, it has been found that toner electrical resistance decreases as dispersion of this conductive additive becomes less uniform. Figure 7 shows that there is a direct correlation between electrical resistance and molecular weight of the crystalline polyester. As the molecular weight increases, the resistance also increases, suggesting improved carbon black dispersion. This result is consistent with the TEM images.

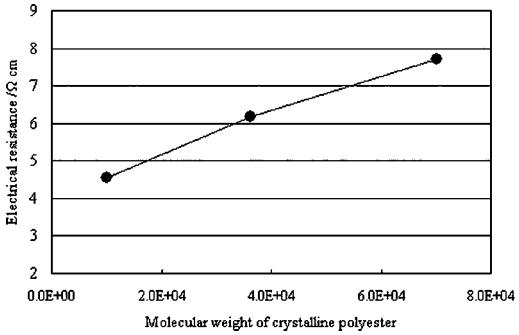

Figure 7. Relationship between electrical resistance and molecular weight of the crystalline polyesters.

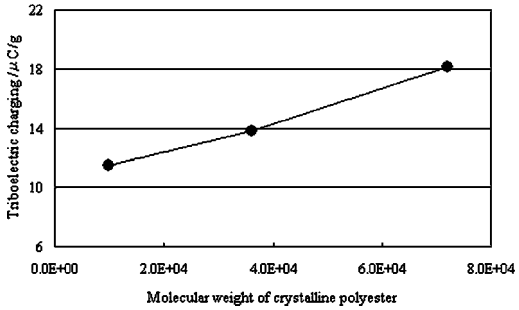

Figure 8. Relationship between triboelectric charging and molecular weight of the crystalline polyesters.

Finally, the tribocharge properties of the toner were found to improve through the use of higher molecular weight crystalline polyester. This is shown in Fig. 8. Figure 8 appears to be exactly the same as Fig. 7. It has been theorized that the dispersion of charge control agent is also improved by using crystalline polyester with higher molecular weight. This result is consistent with the electrical resistance findings.

All of the results described above support the hypothesis that the dispersion of additives in the toner is improved by using higher molecular weight crystalline polyester compared to lower molecular weight crystalline polyester. These results correlate to the kneaded toner's melt elasticity at 140 °C as shown in Fig. 3. The elasticity can be improved by increasing the molecular weight of crystalline polyester allowing for adequate kneading which results in good toner additive dispersion. This high quality dispersion enables the achievement of excellent toner durability, especially with regards to wax, since wax can be easily affected by mechanical force and temperature.

Fusing Properties

The fusing latitude of Toners A, B, C, and D were investigated. The results are shown in Fig. 9. Regardless of molecular weight, it has been found that toner containing this type of crystalline polyester exhibits good fusing performance. Furthermore, it was confirmed that the lower limit of fusing

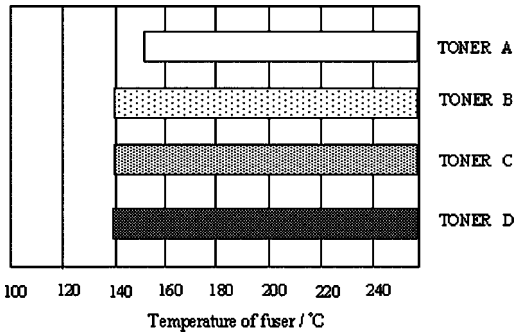

Figure 9. Fusing latitude of the first group of toners.

latitude is not detrimentally affected, even if the molecular weight of the crystalline polyester is increased.

Generally speaking, increasing a polymer's (toner resin) molecular weight tends to cause degradation in the toner's low energy fusing ability, as $T_{1/2}$ and T_g will normally increase. However, in case of these crystalline polyesters, the melting point did not seem to vary with molecular weight, as shown in Table III. As a consequence, the toner containing the high molecular weight crystalline polyester (CPES-3) also exhibited excellent low energy fusability.

To achieve an even greater improvement in the toner's low energy fusing properties, research focused on additional modifications of both the amorphous and crystalline polyesters. This work is described below. Table IV, part (b) lists the binder resin compositions for the three new toner samples E, F, and G. PES-3 and PES-4 are the new amorphous polyesters and they have lower softening temperatures, $T_{1/2}$, compared to PES-1 and PES-2. The T_{mp} for the crystalline polyesters decreased from CPES-1 and CPES-3 to the new CPES-4 and CPES-5.

Finally, the ratio of high molecular weight to low molecular weight resin in the toners was reduced for the amorphous polyesters, as shown in Table IV, part (b). Previously, 60/40 and 60/20/20 were the ratios explored (high molecular weight amorphous / low molecular weight amorphous / crystalline polyester). In the follow-on study, the ratios were changed to 50/50 and 50/30/20, respectively, to attempt to achieve even better low energy fusability.

The fusing latitudes of Toner E, Toner F and Toner G is shown in Fig. 10. It can be observed that the lower fusing limit (cold offset) of Toner F (containing low molecular weight crystalline polyester) was about 30 °C lower (better) than Toner E (containing no crystalline polyester). Unfortunately, however, the upper fusing limit (hot offset) also decreased (worse) for Toner F compared to Toner E. It has been hypothesized that this detrimental effect is related to the lower elasticity of CPES-4 crystalline polyester compared to the amorphous polyester at temperatures above the melting point.

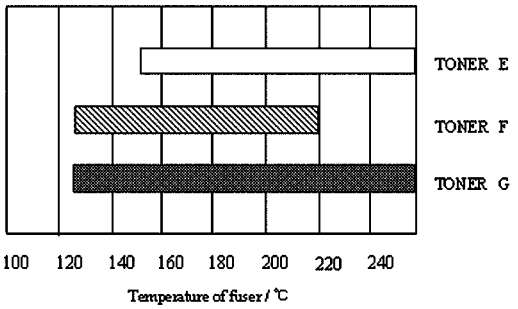

Figure 10. Fusing latitude of the second group of toners.

Toner G was made with high molecular weight crystalline polyester, CPES-5, in contrast to Toner E. Figure 10 shows that even though Toner G has the same good lower fusing limit as Toner F, the upper fusing limit is much improved and equivalent to the control Toner E. It is believed that the high molecular weight crystalline polyester has a melt elasticity similar to that of the amorphous polyester resin, enabling it to avoid the hot offset issues observed with Toner F. Nevertheless, the use of 20% crystalline polyester allows for the 30 °C reduction in lower fusing limit.[1,2]

CONCLUSIONS

The present investigation of high molecular weight type crystalline polyester and the toners containing it have led to the following conclusions.

(1) The melting point of the crystalline polyester was not affected by molecular weight despite the advantageous increase of elasticity above its melting point.

(2) Durability of the toners containing crystalline polyester was improved by increasing the molecular weight of the crystalline polyester.

(3) The dispersion of the toner's additives was improved by increasing molecular weight of the crystalline polyester. This leads to an improvement in toner durability.

(4) The use of high molecular weight crystalline polyester in toner has been found to decrease the lower limit of the fusing latitude by up 30 °C without changing upper limit, resulting in a much larger fusing window.

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