The Effect to the Toner of Various Properties of the Crystalline Polyester

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Abstract

The regulation for the energy consumption of printers and copiers are getting severe year by year. And with the speed up of the machine system, the fusing of toner on the paper gets more difficult. So the toner which can be fused in lower energy is expected. There are still several ways for that problem. To use low Tg and low Tm resin for binder is the typical one for instance, but there is a barrier to improve more by just controlling the Tg and Tm of the resin.

In NIP18 the effect of crystalline polyester for low energy fusing was reported; the properties of the toner that contains crystalline polyester, the quantitative effect of crystalline polyester for toner, the effect of the dispersion size of crystalline polyester in toner and the way to disperse the crystalline polyester.

In this report, by controlling the kinds of monomers and the reaction hours, various kinds of crystalline polyester are prepared. And the effects of its melting point and molecular weight for the fusing ability and the storage stability of toner are investigated. Also the property of the toner which contains the crystalline polyester with small amount of the monomer which has a long chain is investigated. As the result, one type of crystalline polyester, which is better for toner, is reported.

Introduction

Important technological requirements for electrophotographic toner in these days are low energy fusing, developer long life, quick charge ability and so on. Especially, low energy fusing is one of the most important technologies in the field of low end as well as high speed copier or printer, because it brings minimization of consumed energy of the overall machines and less trouble in paper feed or paper burning, and so on.

In these years, the regulations or the standards have gotten strict, for instance ZESM (Zero Energy Stand-by Mode) standards, which is for the copier in range of 20-40 copies per minute or faster, requires under 10W in sleep mode and under 10sec to restart from sleep mode.

So the toner which can be fused in low energy is desired. It is well known that polyester can be designed to have wide molecular weight distribution and good affinity to paper and therefore lower energy fusing can be achieved. Particularly toner using polyester having high acid value (AV) shows good fusing ability, because of large cohesive energy caused by its many polar groups such as COOH or COOR groups with OH group. Furthermore, polyester toner has potentially long life in developer by its toughness and quick charge ability.

Also it is well known the toner using polyester with soft segment side chain such as long alkyl or alkenyl group shows lower energy fusing. Since the side chain can move at under glass transition temperature, which is called β dispersion, much lower energy fusing can be achieved. However, it is not enough for recent requires.

For further improvement of the fusing ability, it is also known to use some amount of crystalline polyester for toner.

It is because the crystalline polyester melts faster than the amorphous resin and shows large endothermic energy.

In NIP 18, it was reported that even the high melting point (over 100 degree Celsius) crystalline polyester works well for the fusing ability of the toner, and from the point of high crystallinity and appropriate melting point, the crystalline polyester which is from fumaric acid and 1.4-butandiol is one of the best candidate for toner.

Also the effect of crystalline polyester for fusing ability highly depends on its dispersion size so it should be controlled carefully was reported.

In this paper, first, the way to get various properties of crystalline polyester is reported. Second the comparison of fusing ability and storage stability of toner among several melting points' crystalline polyester. Third, the influence of the molecular weight of crystalline polyester on the fusing ability and storage stability of the toner is reported.

Experimental

Preparation of Polyester Resin[1,2]

A 5-liter 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, Terephthalic acid, Fumaric acid, Trimellitic anhydride, and Dibutyltin oxide, and the ingredients were reacted at 220°C for 8 hours, and thereafter further reacted at 8.3 kPa until a given softening point was reached.

Preparation of Crystalline Polyester Resin CPE-1-3

A 5-liter four-necked flask equipped with a nitrogen intel tube, a dehydration tube,a stirrer, and a thermocouple was charged with 1,4-butandiol, 1,6-hexanediol, Fumaric acid, Dibutyltin oxide and Hydroquinone, and the ingredients were reacted at 160°C for 5 hours. Thereafter, the temperature was raised to 200°C and reacted for 1 hour, and further reacted at 8.3 kPa for 1 hour.

Preparation of Crystalline Polyester Resin CPE-4-6

Use same ingredient and do the same reaction way with CPE-1-3, but after the evacuated rate was 30kPa and the evacuated hour was 0.5 hour.

Preparation of Crystalline Polyester Resin CPE-7-9

Add Stearic acid as the ingredient and made reacted like CPE-1-3.

Table 1. Properties of the Experimental Polyester Resin

Resin	Acid Value[1] (mg KOH/g)	T1/2[2] (°C)	Tg[3] (°C)
PES-1	23	140	61[4]
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 "DSC Model 200" manufactured by Seiko Instruments Inc., at a heating rate of 10/min.
4) Tg was read by the tangential way.

Table 2. Properties of the Experimental Crystalline Polyester Resin

Resin	T1/2[2] (°C)	Tg[3] (°C)	Mn[7]
CPE-1	129[5]	129[6]	3545
CPE-2	113[5]	116[6]	3470
CPE-3	101[5]	104[6]	3610
CPE-4	126[5]	130[6]	2470
CPE-5	111[5]	115[6]	2530
CPE-6	98[5]	103[6]	2605
CPE-7	127[5]	129[6]	2930
CPE-8	113[5]	116[6]	2800
CPE-9	99[5]	102[6]	2920

5) These values are called melting point.
6) Tg was read by the peak top.
7) Mn was measured according to ASTM D-3536-91 (in chloroform).

Preparation of Toner Samples

Toner samples were comprised of this resin, the wax(140°C,Polypropylene), the charge control agent(Fe-azo-complex) 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 9.5μm were obtained. Each toner was blended with fumed silica to get efficient flow ability and charging ability for the test operation.

The toner samples are listed in table 3.

Table 3. Toner Samples

Toner Name	PES-1 (parts)	PES-2 (parts)	CPE-1 (parts)	CPE-2 (parts)	CPE-3 (parts)
A	50	50			
B	50	30	20		
C	50	30		20	
D	50	30			20

In every evaluation of the crystalline polyester, the toner is from PES-1/PES-2/crystalline polyester=50/30/20

Measurement of the Fusing Ability

Using the off-line fuser tested the fusing ability. (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 (250g and 50g paper; Xerox corporation) so that the mass per area was 0.6mg/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 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 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°C60%H2O environment for 48 hours then the cohesiveness were compared (under normal conditions the cohesiveness was almost zero).

Results and Discussion

The Way to Control the Melting Point of the Crystalline Polyester

The combinations of monomers of CPE-1,2,3 are shown on table 4. And the difference of the DSC chart of these crystalline polyester is shown in Figure 1.

Table 4. The Melting Point of the Crystalline Polyester

	Alcohol	Acid	
	1,4-Butanediol	Fumaric acid	Adipic acid
CPE-1	100	100	
CPE-2	100	85	15
CPE-3	100	75	25

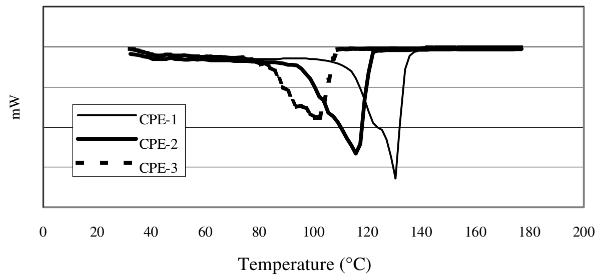

Figure 1. The DSC chart of the crystalline polyester

The combination of 1.4-Butanediol and Fumaric acid is chosen as the base combination because of high crystallinity from high reacting rate and the rigid structure of fumaric acid. (The crystallinity is judged from the value of Tm and Tg. When the value of Tm and Tg is not so different, we say it has high crystallinity.)

Table 4 and Figure 1 indicate the melting point of the crystalline polyester depends on the combination of the monomer, and just by adding small amount of the Adipic acid, the melting point can be easily controlled.

Certainly the DSC chart of CPE-3 is a little broader than that of CPE-1 and this result indicates the crystallinity is broken a little by adding Adipic acid, but still it keeps high crystallinity, still the value of Tm and Tg isn't so different.

The Evaluation of Fusing Ability of the Polyester Toner which Contains Crystalline Polyester

The fusing latitude of Toner A, Toner B, Toner C and Toner D are shown in Figure 2.

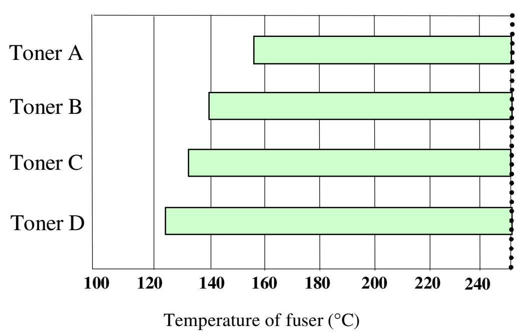

Figure 2. Fusing latitude of Toner A, B, C and Toner D

This figure indicates that the toner B, C, and D which contain crystalline polyester, show much better lower limit of the fusing temperature, and the lower limit of the fusing temperature is affected by the melting point of the crystalline polyester. This result means that when the toner passes through the heat roller, the crystalline polyester starts melting at the first step and then the other amorphous resin are melted. So the main factor for the lower limit of the fusing temperature depends on how fast the crystalline polyester starts melting.

The Influence of the Molecular Weight of the Crystalline Polyester on the Fusing Ability and the Storage Stability of the Toner

The fusing latitude and the storage stability of the toner, which contains 20% of crystalline polyester, is shown in Figure 3. Six types of crystalline polyester were prepared. Three of them are Mn=3500 which is indicated in the circle marks. And the melting point is 100°C, 115°C and 130°C respectively. Other three of them are Mn=2500 which is indicated in the triangle marks. Also the melting point is 100°C, 115°C and 130°C respectively.

When the molecular weight of the crystalline polyester gets lower, residual monomer and oligomer get larger, and the viscosity after melting gets lower.

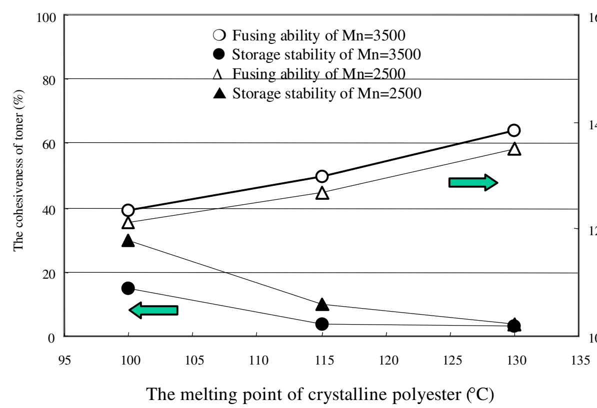

Figure 3. The dependency of the storage stability and the fusing ability on the molecular weight of the crystalline polyester

This figure shows, the fusing ability is affected by the molecular weight of the crystalline polyester, but the effect is not visible. On the other hand the storage stability is affected a lot by the melting point and molecular weight of the crystalline polyester.

From this result, it is indicated the main factor that has an effect on the fusing ability is the melting point of the crystalline polyester not the viscosity after melting or the residual monomer and oligomer of the crystalline polyester. In other words, the parts which start moving in lower temperature in toner is very important for the low energy fusing is indicated.

And it is also indicated the factors that have an effect on the storage stability are not only the melting point of the crystalline polyester but also the residual monomer and oligomer. These are thought that the crystalline polyester with low melting point starts melting lower temperature so when it is used for toner there is a limitation of the melting point, and the residual monomer and oligomer easily interact with the amorphous resin and make the storage stability worse.

The Challenge to Make the Crystalline Polyester That Has Good Fusing Ability but Does Not Makes the Storage Stability Worse

The way to improve the lower fusing ability of the crystalline polyester of high melting point is studied, and the monomer with long alkylic chain was investigated.

The comparison of the fusing ability of the toner, which contains crystalline polyester without stearic acid and with stearic acid, is shown in Figure 4.

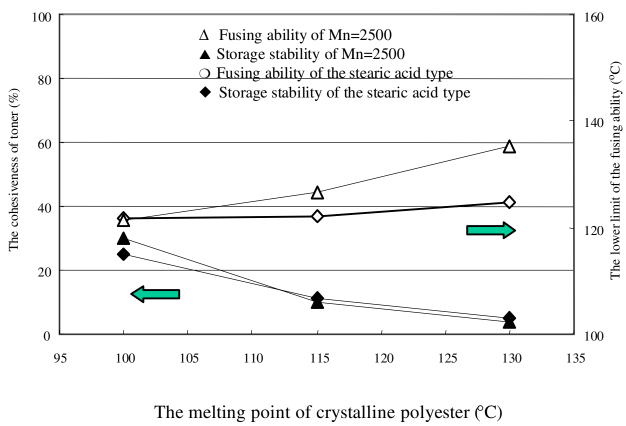

Figure 4. The storage stability and the fusing ability of the crystalline polyester from a little stearic acid

That figure shows the toner, which contains crystalline polyester with stearic acid shows good lower fusing ability but the storage stability is not so different from usual ones.

From this result the things below can be thought.

With or without stearic acid, the amount of the residual monomer and oligomer doesn't change, so the storage stability doesn't change, either.

Still it is under investigation but the reason the crystalline polyester with a little stearic acid works quite well (even when it has high melting point) for the fusing ability is thought as below.

The crystalline polyester from a little stearic acid has long alkylic chain and that long chain.

So even if the melting point of crystalline polyester is high, the crystalline polyester with stearic acid works quite well for the fusing ability.

Conclusion

The influences of the properties of the crystalline polyester in the polyester toner can be summarized as follows:

(1) The melting point of the crystalline polyester can be controlled easily by adding small amount the monomer which is different from the basic combination of monomer.
(2) The crystalline polyester with low melting point works more for the fusing ability.
(3) The fusing ability isn't affected a lot by the molecular weight of the crystalline polyester.
(4) The molecular weight, especially the residual monomer and oligomer of the crystalline polyester affects a lot to the storage stability of the toner.
(5) The crystalline polyester with high melting point, which has the long alkylic chain monomer, shows good fusing ability and good storage stability.

References

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Biography

Eiji Shirai received his master degree in chemical from Waseda University in 1997. Since 1997 he has been working for Kao Corporation in the Performance Chemicals Research Laboratories in Wakayama, Japan. His work has primarily focused on the development of toner and toner binder with polyester resin, including the design of full color toner regarding CCA, wax, colorant, and surface treatment agent. E-mail: shirai.eiji@kao.co.jp