The Toner for Low Energy Fusing by using Crystalline Polyester

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Abstract

To achieve the low energy fusing, the application of the crystalline polyester is studied. To compare with usual polyester, the crystalline polyester melts very quickly when it comes to the melting point. To compare with wax, crystalline polyester is very hard. So the toner that contains crystalline polyester can be fused in low energy but has enough durability.

It is not popular yet because of some problems (One of the problems is poor storage stability because this resin is plasticizated for mixing usual resin, the other one is low anti-offset property because of low elasticity.) though.

This report shows the properties of the toner that contains crystalline polyester, or how well that toner works for low energy fusing. In this study, the way to overcome problems of toner that contains crystalline polyester, or the better way to use crystalline polyester for toner is reported. e.g.1) Which melting point's crystalline polyester is better for toner. 2) How to control the dispersion size of the crystalline polyester. 3) Which dispersion size of the crystalline polyester is better for low energy fusing and storage ability.

Introduction

The speed of printers and copiers are getting faster year by year. Also from the point of saving energy, the way to fuse toner in lower energy is expected. In these years, the regulations or the standards have gotten strict, for instance ZESM(Zero Energy Stand-by Mode) standards requires under 10W sleeping energy and under 10sec to restart.

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

To improve the fusing performance, it is also known to use toner which contains some amount of crystalline polyester. Because crystalline polyester melts faster than resin and show large endothermic energy.

But the crystalline polyesters which has been reported are not fit to use for toner. Most of them show low melting point(under 100 degree Celsius). So durability and storage ability of toner which contains those crystalline polyester are very poor. And some of the combination of monomers which are reported show very low reactivity. So it takes lots of hours to synthesize, and the crystalline polyester itself contains lots of residue monomers and oligomers. That means it'll cost a lot, and show very poor storage ability.

In this paper, first, the way to get proper crystalline polyester is reported. Then the comparison of fusing ability of toner between the one which doesn't contain crystalline polyester and the one which contains crystalline polyester 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 Polyester Resin 3,4

A 5-liter four-necked flask equipped with a nitrogen intel tube, a dehydration tube,a stirrer, a reflux condenser and a thermocouple was charged with Etyl glycol, Neopenthyl glycol, Terephthalic 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

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.

Table 1. Properties of the Experimental Polyester Resin

Resin	Acid Value[1)] (mg KOH/g)	T1/2[2)] (°C)	Tg[3)] (°C)
PES-1	26	145	62[4)]
PES-2	12	100	63[4)]
PES-3	55	140	66[4)]
PES-4	46	100	62[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)
CPE-1	125	124[5)]

5. Tg was read by the peak top way.

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 5.

Table 3. Toner Samples

Toner Name	PES-1 (parts)	PES-2 (parts)	PES-3 (parts)	PES-4 (parts)	CPE-1 (parts)
A	50	50			
B	50	30			20
C	50	20			30
D			50	20	30

Measurement of the Dispersion Size of Crystalline Polyester

The dispersion size of the crystalline polyester was observed by a microscope, the sample was prepared as follow. 1) A little toner was scattered on a slide glass. 2) A slide glass was put on the hot plate which was 150°C for 1 minute.

Measurement of the Fusing Ability

The 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 (250g and 50g paper; Xerox corporation) so that the mass per area was 0.6mg/cm2. 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 lower limit of 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 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 lower limit of 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 was compared (under normal conditions the cohesiveness was almost zero).

Results and Discussion

The Way to Make Good Crystalline Polyester for Toner

The combination of monomers and the melting point of crystalline polyester which has been reported is on table 4.

Table 4. The Melting Point of the Crystalline Polyester

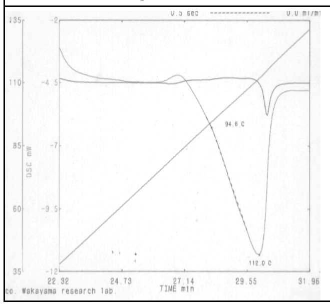
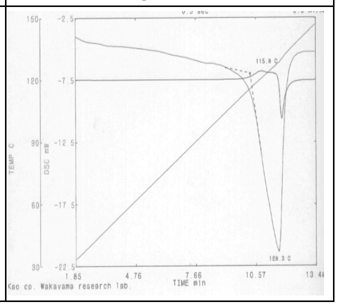
	Acid	Oxalic acid	Succinic acid	Adipic acid
Alcohol	N[*1]	2	4	6
Ethylene glycol	2	172°C	108°C	65°C
Trimethylene glycol	3	89°C	52°C	46°C
1,4-Butanediol	4	103°C	121°C[*2]	48°C
1,5-Pentanediol	5	49°C	87°C	36°C
1,6-Hexanediol	6	66°C	57°C	56°C

*1 The number of carbon.

*2 This crystalline polyester is called 'CPE-2'.

This table indicates crystalline polyester from most of the combination of monomers shows melting point under 100°C. Usually toner is required the storage stability enough to be stored at 45°C, but when the crystalline polyester which has melting point under 100°C was used, to achieve that requirement would be difficult, since polymer has molecular weight distribution and contains some monomers and oligomers. The combination of succinic acid and 1.4-butanediol could be used, but the reaction rate is low and it would be difficult to control the other properties. So the peak of the crystalline polyester which can be gotten by a differential scanning calorimeter(DSC) is very broad as in table 5. That means part of these crrystalline polyester start melting in low temperature, and so the storage ability gets worse. The combination of etylene glycol and oxalic acid show very high melting, but it is hard to synthesize, because while synthesizing monomers are sublimed a lot.

Table 5. The DSC Chart of Crystalline Polyester

CPE-2	CPE-1
	

The absorption energy peak of the crystalline polyester from fumaric acid and 1.4-butanediol which was gotten by a differential scanning calorimeter is shown in table 5. This table indicates crystalline polyester from fumaric acid and 1.4-butanediol shows very narrow peak and about 130°C melting point. Narrow peak indicates high crystallinity from high reacting rate. Over 100°C melting point is from the rigid structure of fumaric acid.

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

The fusing latitude of Toner A ,Toner B and Toner C are shown in Figure 1.

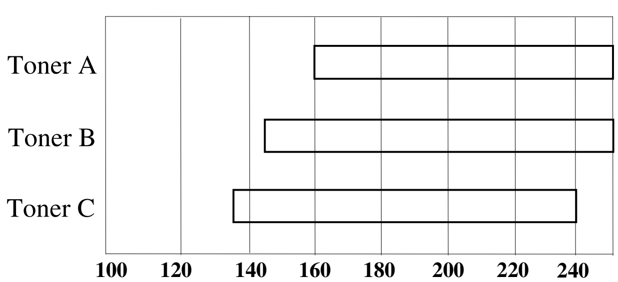


Figure 1. Fusing ability of Toner A and Toner B

This figure indicates that the toner which contains crystalline polyester shows good lower limit of the fusing temperature, and the lower limit of the fusing temperature is controlled by the amount of crystalline polyester. This result means that the crystalline polyester starts melting faster and causes other resin to melt when the toner passes through the heat roller.

The Influence of the Dispersion Size of the Crystalline Polyester on the Fusing Ability and the Storage Ability of the Toner

The dispersion size of crystalline polyester of Toner B was controlled by the strength of the kneading. Same with other additives, the stronger the strength of the kneading was, the finer dispersion size of crystalline polyester could be gotten.

The storage stability of toner in each dispersion size of the crystalline polyester is shown in Figure 2. And the fusing latitude of toner in each dispersion size of crystalline polyester is shown in Figure 2. In this case, dispersion size was controlled by changing kneading strength.

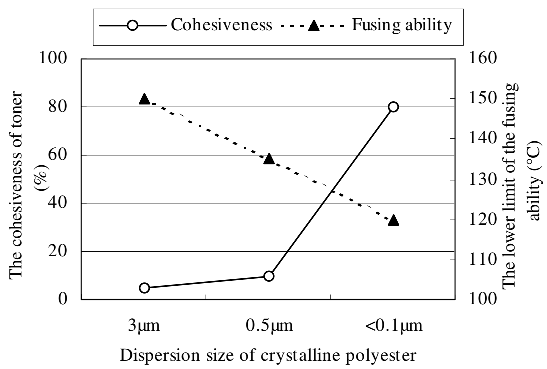


Figure 2. The dependency of the storage stability and the fusing ability on the dispersion size of the crystalline polyester

This figure indicates the smaller dispersion toner shows good lower limit of the fusing temperature. At the same time, it indicates that the toner which dispersion size of crystalline polyester is small shows poor storage stability because of plasticizated of base resin. So to control dispersion size of the crystalline polyester is very important.

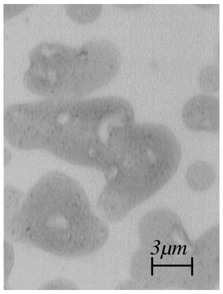
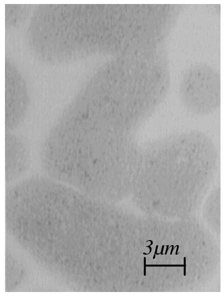
The way to get the fine dispersion size (<0.1μm) of crystalline polyester in usual kneading strength.

The very strong kneading strength is required to get the fine dispersion size (<0.1μm) of crystalline polyester. So the improved kneading machine or the long kneading hours are required.

The effort to get the fine dispersion size by usual kneading strength has been done.

The dispersion size of crystalline polyester of Toner B and Toner D are shown in table 6(the base resin of Toner B contains Bisphenol A propylene oxide adduct, ethylene oxide adduct but the base resin of Toner D doesn't contain them). The very difference of dispersion size can be seen. Big particles of crystalline polyester are found in Toner B. But the picture of Toner D shows good dispersion. This result indicates when the monomers of the crystalline polyester and the usual polyester resin are similar, the good dispersion toner can be gotten.

Table 6. Dispersion Size of the Crystalline Polyester

Toner B	Toner D
	

From this point, the best suited dispersion size of crystalline polyester would be gotten by controlling the monomer of base resin, not depending on the strength of the kneading.

Conclusion

The influences and the way to use crystalline polyester in the polyester toner can be summarized as follows:

(1) Adequate melting point crystalline polyester was synthesized by using fumaric acid and 1.4-butanediol for monomers.
(2) The crystalline polyester works a lot for the lower limit of the fusing temperature.
(3) When the crystalline polyester is dispersed enough, the good lower limit of the fusing temperature will be shown.
(4) If the dispersion size of crystalline polyester can't be observed, the toner will be plasticized and will show poor storage stability.
(5) The fine dispersion size of crystalline polyester can be gotten by choosing the monomer of the base polyester.

References

1. Japan Patent 49,129,540, March 1974, Xerox Corp., Rochester, N.Y., Erhardt, Peter F., Richards, William C.

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: 309957@kastanet.kao.co.jp