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The Effects of Crystalline Polyester on Toner Properties

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The regulation of energy consumption for printers and copiers is becoming increasingly strict each year. Also, with increasing speeds of the machine system, the fusing of toner on paper becomes even more difficult. Thus, toner that fuses at lower energy is expected. There are several solutions to address this issue. A typical method is to use low Tg and low Tm resins for binder. This solution, however, offers limited improvement. Crystalline polyester (CPES) is a long studied candidate that shows great promise. However CPES is not yet widely used due to its poor storage stability and low anti-offset properties. This report explains how to overcome problems encountered with toner containing CPES, improved uses of CPES in toner, and the enhanced properties of CPES. The properties of toner containing CPES, and how that toner works for low energy fusing, are described.

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Introduction

Important technological requirements for electrophotographic toner include low energy fusing, long-life developer, and quick charging. Low energy fusing is especially important in both the low and high speed copiers and printers. It minimizes not only the overall energy consumption of the machines but also any issues in the paper feed.

In recent years, the regulations and standards have become more stringent. For example, ZESM (Zero Energy Stand-by Mode) standard requires under 10W in sleep mode and under 10 sec to restart from sleep mode for copiers in the range of 20–40 copies per minute or faster. Therefore, low energy fusing toner is most desirable.

It is well known that polyester can be designed to have a wide molecular weight distribution and good affinity to paper. These characteristics can lead to lower energy fusing. For example, toner comprising polyester with high acid value (AV) results in good fusing ability. Many polar groups, such as COOH or COOR groups with the OH group, lead to large cohesive energy. Furthermore, polyester toner has potentially long life in developer owing to its toughness and quick charging ability.

It is also well known that toners using polyester with soft segment side chains, such as long alkyl or alkenyl groups, show lower energy fusing. Since the side chain can move below the glass transition temperature, called β dispersion, much lower energy fusing can be achieved. However, it is not sufficient for recent requirements.

TABLE I. The Melting Points of Crystalline Polyesters

	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	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 atoms.

For further improvement of the fusing ability, crystalline polyester (CPES) may be applied. CPES melts faster than the amorphous resin and shows a endothermic energy. The CPES that have thus far been reported, however, are not suitable for toner. As Table I shows, most of the reported CPES have a low melting point (under 100°C). Toners using this type of CPES have poor durability and storage stability. Some of the reported combinations of monomers also show very low reactivity. Synthesis may require more hours, and such CPES itself will contain lots of residual monomers and oligomers. Figure 1 includes data on CPES from succinic acid. Measurements from a differential scanning calorimeter (DSC) show a very broad absorption energy peak. This indicates that a part of the CPES starts melting at low temperature, so the storage stability is fairly poor.

On the other hand, CPES from fumaric acid and 1,4-butanediol have very high crystallinity. As shown in Fig. 1, the high reactivity of fumaric acid results in a narrow DSC absorption energy peak. Our study therefore concerns CPES from fumaric acid. This article not only describes the effects of CPES in the toner but also illustrates how various characteristics of CPES can affect

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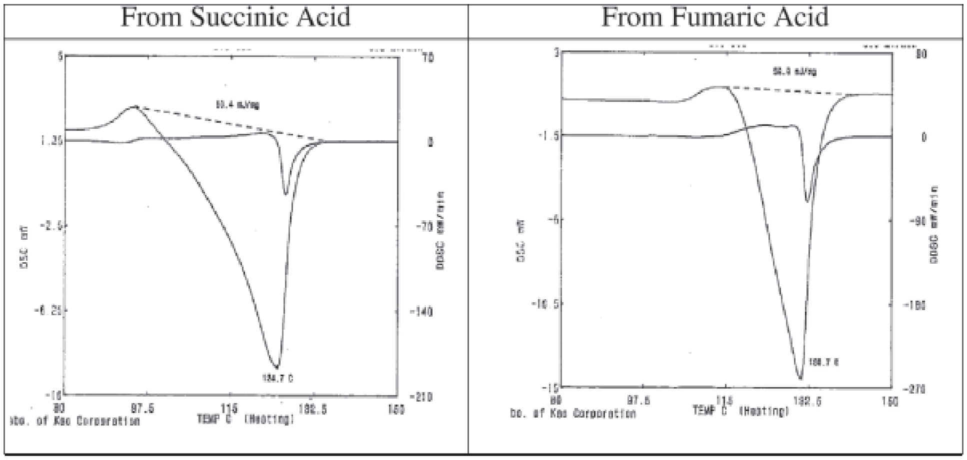

Figure 1. The DSC Chart of Crystalline Polyester

TABLE II. Monomer Composition of the Crystalline Polyester

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 tangentially.

TABLE III. Toner Samples

	Alcohol 1,4-Butanediol	Acid Fumaric acid	Adipic acid	Stearic acid
CPE-1, 4	100	100		
CPE-2, 5	100	85	15	
CPE-3, 6	100	75	25	
CPE-7	100	98		4
CPE-8	100	85	13	4
CPE-9	100	75	23	4

TABLE IV. Properties of the Experimental Crystalline Polyester Resin

Toner Name	PES-1 (parts)	PES-2 (parts)	CPE-1 (parts)	CPE-2 (parts)	CPE-3 (parts)	CPE-7 (parts)
A	50	50				
B	50	30	20			
C	50	20	30			
D	50	30		20		
E	50	30			20	
F	50	30				20

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

the toner. These CPES characteristics include dispersion size within the toner, melting point, molecular weight, and type of additive monomer used.

Experimental

Preparation of Polyester Resin 1,2

A 5 liter four-necked flask equipped with a nitrogen inlet 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. Monomer compositions of all CPES preparations are given in Table III.

Preparation of Polyester Resin 3,4

A 5 liter four-necked flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, a reflux condenser and a thermocouple was charged with etheylene 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. Moromer compositions of all CPES preporations are given in Table II.

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

Same ingredients and reaction conditions were used as with CPE-1-3, but the subsequent evacuation rate was 30 kPa for 0.5 hour.

Preparation of Crystalline Polyester Resin CPE-7-9

Stearic acid was added and reaction conditions were the same as for CPE-1-3.

Preparation of Toner Samples

Toner samples were comprised of the resin, wax (140°C, polypropylene), charge control agent (Fe-azo-complex) and carbon black. All samples were prepared by the same process. The materials were premixed in a batch mixer; then they were kneaded, pulverized and classified. Samples having average size of 9.5 µm were obtained. Each toner was blended with fumed silica to get efficient flow and charging ability for test operation. The toner samples are listed in Table IV.

Measurement of Thermal Properties

The softening point (T1/2) was measured according to ASTM E-28-67.

The melting point (MP) of the crystalline polyester was also measured according to ASTM E-28-67.

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°C/min, and was read by the tangential method.

The melting peak top (Mpt) of the crystalline polyester was also measured by differential scanning colorimetry at a heating rate of 10°C/min, and was read by the peak top method.

Measurement of Molecular Weight of the Crystalline Polyester

The molecular weight of the crystalline polyester was measured in chloroform according to ASTM D-3536-91.

Measurement of Fusing Ability

The fusing ability was tested with a off-line fuser. The silicone oil was removed completely. 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.

At first, each toner sample was developed and transferred onto paper (250 g and 50 g paper; Xerox Corporation) so that mass per area was 0.6 mg/cm^2. Then the paper was passed through the fuser. The line speed was 250 mm/sec.

The upper limit of the fusing temperature was defined as the upper limit temperature at which hot offset was not observed.

The fusing temperature was defined as the lower limit temperature that the cold offset was not observed, and as the lower temperature at 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 each toner sample.

Measurement of Storage Stability

The storage stability was tested by measuring the cohesiveness with the Powder-Tester (manufactured by Hosokawa Micron Co.) .The toner was put into a 45°C 60% RH environment for 48 hours, then the cohesiveness was measured (under normal conditions the cohesiveness was almost zero).

Measurement of Dispersion Size of Crystalline Polyester

The dispersion size of the crystalline polyester was observed under a microscope. The sample was prepared as follows: 1) a little toner was scattered on a slide glass; 2) a slide glass was then put on the hot plate at 150°C for 1 minute.

Measurement of Viscoelasticity of the Toner

The viscoelasticity of the toner was measured by parallel plate Dynamic Analyzer RDA2 manufactured by Rheometrics Co., at 1 Hz frequency and 10 Pas.sec strain.

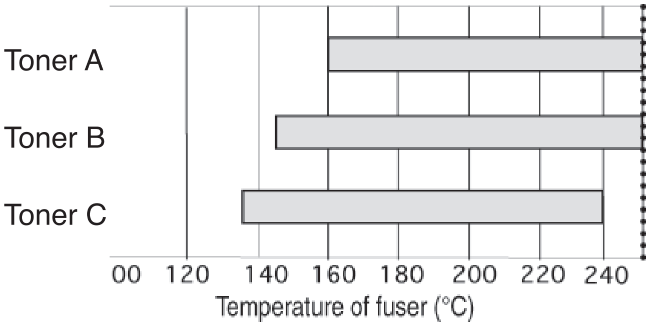

Figure 2. Fusing ability of Toners A, B and C

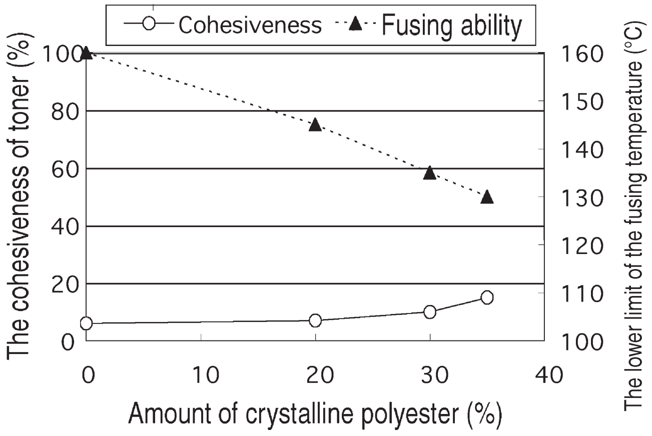

Figure 3. The dependency of the storage stability and the fusing ability on the amount of the crystalline polyester

Results and Discussion

Evaluation of Fusing Ability for Polyester Toner Containing CPES

First, the fusing ability of the toner with CPES was measured. For this experiment, CPE-1 of melting point 129°C was used. The fusing latitudes of Toner A, Toner B and Toner C (Table III) are shown in Fig. 2.

Figure 2 demonstrates that toner containing CPES shows good lower limit of the fusing temperature. The lower limit of fusing temperature is controlled by the amount of CPES. When CPES melts earlier, it causes other resin to melt when the toner passes through the heat roller.

Figure 3 demonstrates the linear relationship between the fusing ability and amount of CPES. Storage stability, however, appears to get worse little by little; toner containing 30% does not appear to exhibit a problem however. Storage stability degradation is considered to be the result of interaction between amorphous resin and crystalline resin. That is, when the amount of the crystalline polyester is greater, the plasticized part of the amorphous resin also becomes greater.

Thus, when considering the balance between fusing ability and storage stability, the amount of CPES may be up to 30%. When CPES content is above 30% the balance between fusing ability and storage stability becomes questionable.

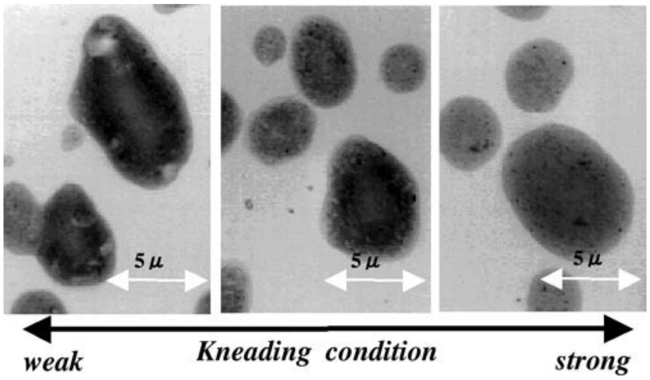

Figure 4. The effect of kneading condition on the dispersion size of crystalline polyester.

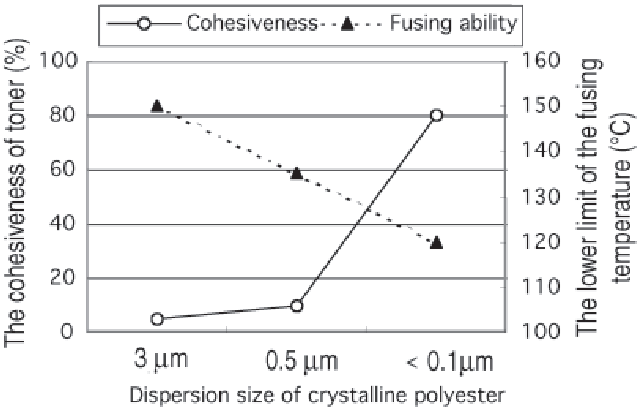

Figure 5. The dependency of storage stability and fusing ability on the dispersion size of the crystalline polyester.

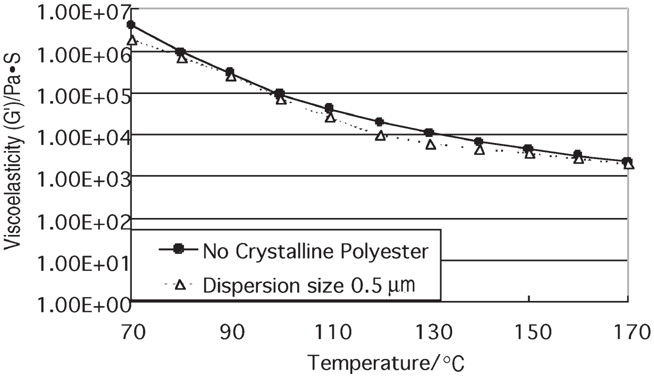

Figure 6-1. The viscoelasticity of toner with crystalline polyester.

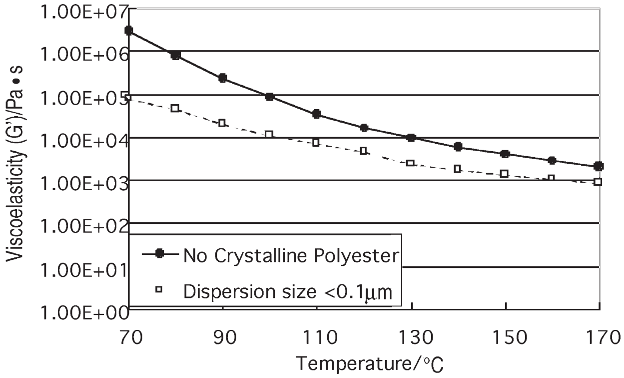

Figure 6-2. The viscoelasticity of toner with crystalline polyester.

The Influence of CPES Dispersion Size on the Fusing Ability and the Storage Stability of Toner

Second, the influence of CPES dispersion size was measured while paying an attention on the fusing ability and the storage stability. The CPES dispersion size of Toner B was controlled by the strength of kneading. As shown in Fig. 4, where CPES particles are shown as white parts, CPES behaves in the same manner as other additives. The stronger the kneading, a finer dispersion size of CPES results.

The storage stability and fusing latitude of toner at various dispersion sizes of CPES are shown in Fig. 5. This figure demonstrates how better dispersion of CPES in that the toner results in improving the lower limit of the fusing temperature. However, this figure also shows the smaller dispersion size of CPES will result in poor storage stability because of the plasticized base resin.

The dependence of the viscoelasticity of the toner on the temperature are shown in Figs. 6-1 and 6-2 (in these figures, viscoelasticity of Toner A which was kneaded under the same conditions are shown as reference data.). The viscoelasticity of CPES dispersion size of 0.5 μm toner is like that calculated from data for CPES and base resin. On the other hand, the viscoelasticity of CPES dispersion size of under 0.1 μm toner shows an anomalously low value; this proves the base resin was plasticized.

Therefore, it is extremely important to control the dispersion size of CPES. In our experimental data 0.5 μm size is the optimal balance for fusing and storage stability. From this point on, all data is based on a controlled CPES dispersion size of 0.5 μm.

The Way to Control the Melting Point of CPES

To check the effect of the melting point of the crystalline polyester for toner, different melting point of CPES were chosen. The combinations of monomers of CPES are shown in Table III. The differences in the DSC traces for these CPES are shown in Fig. 7.

The combination of 1.4-Butanediol and Fumaric acid is chosen as the base combination because of its high crystallinity from high reaction rate, as well as the rigid structure of fumaric acid. (The crystallinity is judged from the value of MP and Mpt. When the values of MP and Mpt are not very different, we say it has high crystallinity.)

Table III and Fig. 7 indicate that the melting point of CPES depends on the combination of the monomer, and just by adding small amount of 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 that crystallinity is decreased a little by adding adipic acid, but still the values of MP and Mpt are not so different.

The Influence of CPES Melting Point on the Fusing and the Storage Stability of the Toner

Then, the influence of CPES melting point on toner was measured. The fusing latitudes of Toners A, B, D, and E are shown in Fig. 8. This figure indicates that

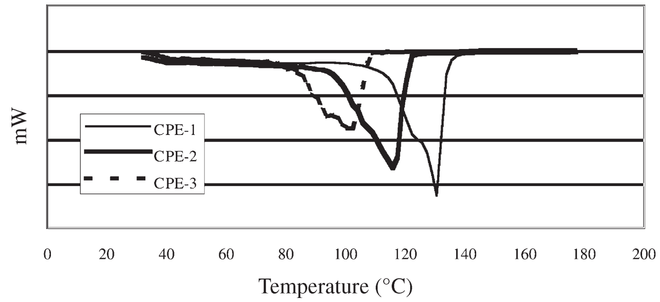

Figure 7. DSC traces of crystalline polyesters.

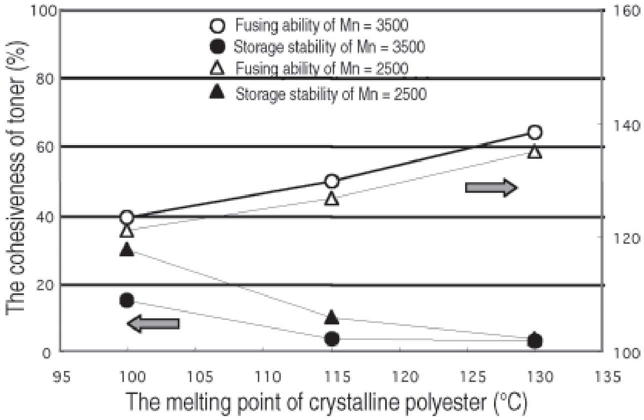

Figure 9. The dependency of the storage stability and the fusing ability on the molecular weight of the crystalline polyester.

Toners B, D, and E containing CPES show much better lower limits for the fusing temperature. The lower limit of the fusing temperature is affected by the melting point of CPES. When the toner passes through the heat roller, CPES starts melting first, followed by the melting of the other amorphous resins. The main factor controlling the lower limit of the fusing temperature appears to be how fast the CPES starts melting.

The Influence of CPES Molecular Weight on the Fusing and Storage Stability of the Toner

The fusing latitude and the storage stability of the toners containing 20% of CPES are shown in Fig. 9. Six types of CPES were prepared as in Table III. Three of them are CPES of Mn = 3500 (CPE-1, 2, 3) which are shown by circles. The melt points are 100°C, 115°C and 130°C respectively. The others are CPES of Mn = 2500 (CPE-4 ,5 ,6) which are indicated by triangles. The melt points of these three are also 100°C, 115°C and 130°C respectively. When the molecular weight of CPES is lower, the residual monomer and oligomer are larger and the viscosity after melting is lower.

Figure 9 demonstrates that fusing ability is affected by the molecular weight of CPES, but the effect is not significant. On the other hand, the storage stability is greatly affected by the melting point and molecular weight of CPES. From these results, the following are inferred.

The viscosity of molten CPES affects fusing ability, but the viscosity difference between Mn 3500 and Mn 2500 was minimal, so the effect on fusing ability was small.

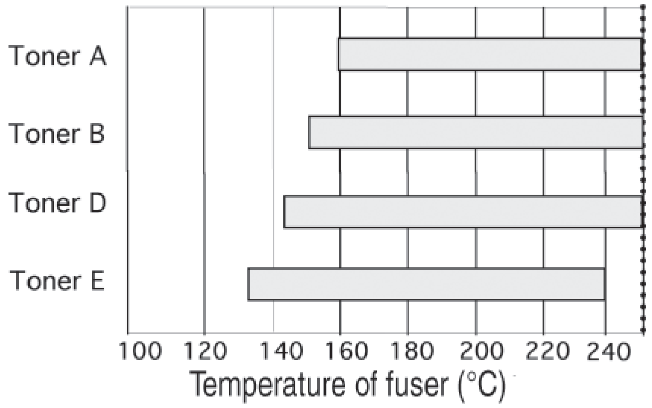

Figure 8. Fusing latitude of Toners A, B, D, and E.

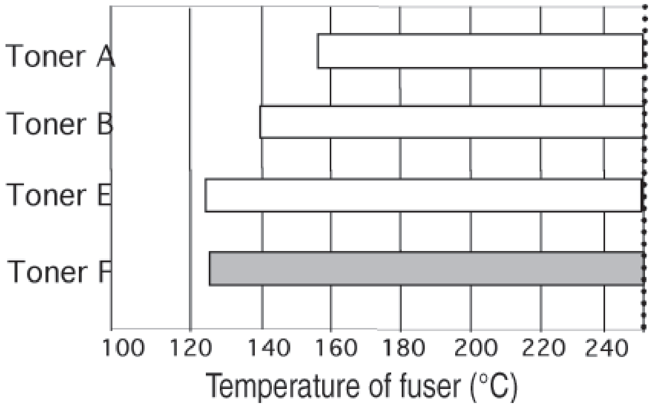

Figure 10. The fusing ability of the crystalline polyester with a small amount of stearic acid.

However the factors that affect storage stability are not only the melting point of CPES but also the levels of residual monomer and oligomer. Low melting temperature CPES used for toner places a limitation on the melting point. The residual monomer and oligomer can easily interact with the amorphous resin and make the storage stability worse.

The Challenge to Make CPES with Good Fusing Ability While Maintaining Good Storage Stability

Finally, the challenge to make CPES with good fusing ability while maintaining good storage stability was met. To improve the fusing ability of high temperature melting CPES, many types of monomers were studied, including monomers with long alkyl chains. Figure 10 shows the fusing ability of Toners A, B, E and F. Toner A is without CPES, B contains CPES with a melt point about 130°C, E contains CPES with a melt point about 100°C, and F contains a CPES combined with stearic acid with a melt point of about 130°C. Figure 11 compares the lower limit fusing ability of toner containing CPES with and without stearic acid. The toner containing CPES with stearic acid shows better fusing ability while storage stability remains acceptable. That is, with or without stearic acid, the amount of the residual monomer and oligomer does not change, so the storage stability does not change. Even with a higher melt point, CPES with a small amount of stearic acid works quite well for fusing. While it still

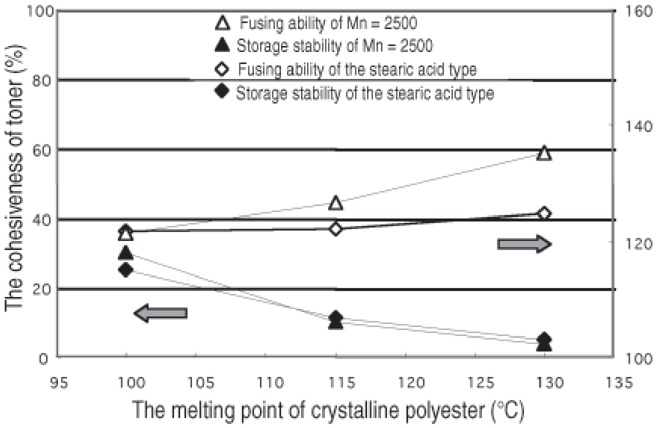

Figure 11. Storage stability and fusing ability of the crystalline polyester with a small amount of stearic acid.

is under investigation, we propose that the reason the crystalline polyester with a small amount of stearic acid works quite well (even when it has a high melting point) for the fusing ability is as follows. The polymer with mono-acid or mono-alcohol groups and with long alkyl chains interacts less with other polymers so the melt viscosity should be very low. Because of this low viscosity the fusing ability should be good.

Conclusion

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

1. CPES with adequate melting points were synthesized using fumaric acid and 1.4-butanediol for monomers.
2. The CPES greatly affects the lower limit of the fusing temperature.
3. It is extremely important to control the dispersion size of CPES, and 0.5 μm is the optimal size to balance fusing and storage stability.
4. The melting point of CPES can be controlled easily by adding small amounts of monomer, for instance, adipic acid.
5. CPES with lower melting points are more effective in achieving the desired lower limit of the fusing temperature.
6. The lower limit of the fusing temperature does not significantly depend on the molecular weight of CPES.
7. The molecular weight, and especially residual monomer and oligomer of CPES, greatly affect the storage stability of the toner.
8. CPES with a little monomer having a long alkyl side chain shows good fusing ability.

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