

Polyester Resin for High-Speed Printer Toner

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Abstract

The market share of Print On-Demand (POD) is increasing year by year because POD can give many benefits such as reducing the printing costs and the delivery time, or decreasing the waste of excess quantities of printed materials. The toner marking technologies for POD printer have been improved rapidly over the last several years. Then, process speed of the printer is increasing and the print quality is improved to higher resolution. Concerning the consumables of the printer, polyester resin is often used as a toner binder resin in high-speed printer because the polyester toner shows the low temperature fusing and the long developer life. This paper will describe the advantages of the polyester resin and the design of the molecular structure of the polyester for high-speed printer.

Introduction

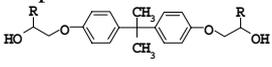
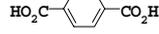
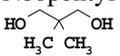
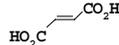
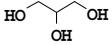
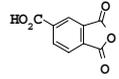
Recently, polyester resins are used for the several categories of electrophotographic toners of copier, printer or fax, because the polyester toner has many advantages such as low temperature fusing, high durability, quick chargeable property and uniform dispersion of pigments in the toner¹. Especially in high-speed printer for POD, it is necessary for the toner to have high durability because the toners suffer from high mechanical impact in the developer station. Furthermore, the toner should have the lower temperature fusing ability because it is fused at a high speed fusing conditions. From the point of view of the energy saving and the ease of machine maintenance, the low temperature fusing ability is strongly expected. In case of the styrene-acrylic toner, it is difficult to accomplish both the low temperature fusing ability and the high durability. The highly cross-linked structure is necessary in the styrene-acrylic toner in order to overcome the damage from the mechanical impact. Therefore it is difficult to avoid increasing the fusing energy. On the other hand, the polyester toner can achieve not only the low temperature fusing ability but also the high durability because the polyester resin has originally many polar functional groups such as carboxylic groups, hydroxyl groups and ester bonds. Those groups bring the higher cohesive force to the resin², so that the polyester resin shows the higher mechanical strength than styrene-acrylic.

Molecular Structure Design of Polyester Resin

Monomers of Polyester Resin

It is very important to select the monomer combinations and to adjust the monomer ratio for controlling the resin characteristics.

Table 1. Typical Monomers of Polyester Resin

Alcohol monomers	Acid monomers
Bisphenol A derivatives 	Terephthalic acid (TPA) 
Neopentyl glycol 	Fumaric acid 
Ethylene glycol 	Alkenyl succinic anhydride (ASA) 
Glycerin 	Trimellitic anhydride (TMA) 

The ratio of rigid monomers and flexible monomers is one of the important factors to control the thermal properties of the polyester resin, such as softening point (T_m) or glass transition temperature (T_g). Bisphenol A derivatives, terephthalic acid and trimellitic anhydride are more rigid structure monomer than other monomers because they have the benzene ring in their structure. Therefore if these monomers are used, T_m and T_g become higher. On the other hand, the aliphatic alcohol or the aliphatic acid decreases T_m and T_g of the polymer due to their flexible structure.

Using a polyvalent monomer such as trimellitic anhydride or glycerin that works as a cross-linking monomer can not only expand the molecular weight distribution but also increase the molecular weight of polymer. Regarding the heat roller fusing system, the lower temperature fusing and the wide offset resistance can be achieved by using the polyester having wide molecular distribution. The lower molecular weight parts give the lower temperature fusing and the high molecular weight parts give the higher hot offset temperature.

Improving the Durability of the Toner

For improving the durability of the toner, it is necessary to increase the mechanical toughness of the binder resin. Then, the crushing index (CI) is mentioned as one of the parameter to check the resin toughness. The CI shows the crushing level of the resins, so the resin that has higher CI value is not easily crushed as compared to the resin having lower value. The CI is measured by the following procedure. The resin was classified to the size of 16-mesh pass and 20-mesh on. And 20g of the classified resin were crushed by the coffee mill for 10 seconds. The crushed resin was classified by 30-mesh sieve, and the residual resin on the sieve was weighed accurately. As a result, the CI was calculated from the weight of residuals by the following equation.

$$CI (%) = R / W * 100 \tag{1}$$

R: Weight of residuals on the mesh (g)

W: Sample weight (g)

Therefore the toner based on the resin having higher CI value is expected to show a higher durability.

Experiments

Preparation of Polyester Resin

The polyester resins were prepared from propoxylated bisphenol A, ethoxylated bisphenol A, TPA, ASA and TMA. The polymerization degree of the resins is respectively changed by adjusting reaction temperature and reaction time. Table 2 shows the characteristics of the prepared resins.

Table 2. The Characteristics of Polyester Resins

Resin Name	AV	Tm	Tg	CI	Gel content
PES-1	3	134	62	18	2
PES-2	4	148	68	23	4

AV: Acid value (KOHmg/g)

Tm: Softening point measured by Shimazu Flow Tester (°C)

Tg: Glass transition temperature

CI: Crushing index (%)

Gel content: Insoluble parts in chloroform (%)

The CI of PES-2 became higher than that of PES-1 by increasing the molecular weight. Furthermore Tm and gel content increased as well.

Durability of the Toner

Before the toner was tested with the printer, the accelerated durability test of the toner was done.

The toners were prepared according to the following process. Binder resin, carbon black, charge control agent and other additives were pre-mixed in a batch mixer, and the mixtures were kneaded in the twin extruder and were pulverized to 10micron diameter by the jet mill.

The developer that consisted of the toner and the carrier was mixed with the steel beads whose diameter was 2mm, and stirred at 50rpm for 6hours in order to increase the stress between the toner and the carrier. Then, the toner impaction volume (TIV) on the carrier

was obtained by the volume of the total organic carbon. The results are shown in Table 3.

Table 3. The Results of the Accelerated Durability Test

Toner	Toner impaction volume (TIV) (%)
Toner-1 (based on PES-1)	2.1
Toner-2 (based on PES-2)	1.5
Toner-SA (based on highly cross-linked styrene-acrylic)	1.5

The TIV of Toner-2 became low as compared to that of Toner-1. The good result must depend on the higher CI of PES-2. Though the optical density of the images decreased in Toner-1 after 300K pages, Toner-2 still showed a stable performance at the image quality in the printing test after 2,000K pages.

On the other hand, the TIV of Toner-SA based on styrene-acrylic was low because the resin was highly cross-linked. Therefore, the toner also showed good durability in the printing test. However the fusing performance of the toner was not enough. The details are described below.

Fusing Performance

For improving the low temperature fusing performance of Toner-2, the amount of ASA that is a flexible monomer was increased in PES-3. The characteristics of PES-3 and the results of the fusing test are shown in Table 4 and 5.

Table 4. The Characteristics of Polyester Resin

Resin Name	AV	Tm	Tg	CI	Gel content
PES-3	7	149	64	25	30

Table 5. The Results of the Fusing Test

Toner	LFT	HFT
Toner-2	210	260<
Toner-3 (based on PES-3)	190	260<
Toner-SA	220	260<

LFT: The lowest fusing temperature (°C)

HFT: Hot offset temperature (°C)

Process speed: 140ppm, Heat roller fusing system

The CI of PES-3 was controlled as same level as that of PES-2, so that the image quality of Toner-3 was also stable after 2,000K pages in the printing test. Furthermore, the LFT of the toner became 20°C lower than that of Toner-2 thanks to increasing the amount of ASA. By the way, the LFT of Toner-SA was 30°C higher than that of Toner-3, so that it was difficult to accomplish both the low temperature fusing and the high durability in the styrene-acrylic toner.

For further lower temperature fusing, introducing crystalline polyester or wax-incorporated hybrid resin were recently proposed.^{4,6} These technologies can be also applied to the high-speed printer toner.

Conclusion

1. By increasing the molecular weight, the crushing index (CI) of the polyester increased. Consequently, the toner impaction volume (TIV) on the carrier decreased in the accelerated durability test, so that the toner showed a stable performance at image quality in the long-run printing test.
2. By increasing the amount of flexible monomer (ASA), the toner was fused at 30°C lower temperature than the styrene-acrylic toner.

As a result, the low temperature fusing and the high durability were achieved in the polyester-based toner.

References

1. Masayuki Maruta, The Material Design of the Polyester Color Toners, IS&T's NIP 12, San Antonio, TX, 1996, pg. 488-492.

2. Yoshihiro Ueno, Recent Progress in Polyester Resin Technology, IS&T's NIP 16, Vancouver, Canada, 2000, pg. 614-617.
3. USP 5,607,805.
4. Kawaji Hiroyuki, Full color toner for oil free fuser, IS&T's NIP 13, Seattle WA, 1997, pg.109-111.
5. Eiji Shirai, The toner for low energy fusing by using crystalline polyester, IS&T's NIP 17, Fort Lauderdale, FL, 2001, pg.354-357.
6. Eiji Shirai, The toner for low energy fusing by using crystalline polyester, IS&T's NIP 18, San Diego, CA, 2002, pg.258-261.

Biography

Hiroyuki Kawaji received his master degree in chemistry from Waseda University at Tokyo in 1991. Since 1991 he has worked in the Performance Chemicals Research Laboratories at Kao Corporation in Wakayama, Japan. His work has focused on the development of polyester resin and polyester/styrene-acrylic grafted resin for B/W or full color toner. He is a member of the IS&T.