Eco-Friendly Prepared Chemical Toner with Mixed Polyester Resin

Eui-Hyun Ryu, Sung-Yul Kim, Il-Hyuk Kim, Kyung-Yol Yon, IT Material R&D Team, R&D Center, Samsung Fine Chemicals, LTD. Daejeon, South KOREA

Abstract

Mixed polyester resins are fascinating materials in toner development because of the possibility to tune the toner properties by the simple mixing of different resin components. But the miscibility of two different components with quite different properties is still a challenge in both pulverized and chemical toners. For chemical toners, one alternative is to use organic media to dissolve both components, but this still generates environmental problems because of the increasing level of volatile organic compounds (VOCs) used on during production and released during usage.

We have developed an eco-friendly process to reduce the amount of VOCs in toner. Every process was performed in a water-based condition. This technology was also applied to mixed polyester resins to cover a wide range of properties of M_w, T_g, $T_{1/2}$, and gloss. The resulting eco-friendly prepared toner is tunable in its basic properties according to the balance of polyester resin components and has a low level of VOCs.

Introduction

Environmental Issues

Environmental issues have received considerable attention in all areas from global warming to personal health care. Because the environmental problems make a huge impact on our environment and human body, manufacturers must make an effort to minimize these problems.

A printer, as an electrophotographic device, is ubiquitous in our life and a part of the everyday environment for many people. It is important that the environmental impact of digital printer must be minimized during usage and component manufacture. The following environmental issues that need to be addressed during the mass-production of printer components and end-user usage includes energy consumption, organic vapor emission, toxic chemical exposure, waste reduction, water utilization, excessive noise & electromagnetic wave generation, and air-borne particulate (toner dust) contamination.

Environmental regulations and standards define many of the development specifications for printer components. For example, the German Blue Angel eco-label, established in 1978 and amended in 2004, recommends not using heavy metals, azo-dyes, other hazardous substances, and specifies the maximum emission levels that are defined for volatile organic compounds (VOCs) and toner dust. The maximum level of total volatile organic components (TVOCs) contaminates allowed for a product to achieve environmental certificates from the Landesgewerbeanstalt (LGA) or Hauptverband der gewerblichen Berufsgenossenschaften (HVBG) are 300 mg/kg and 1000 mg/kg, respectively [1].

Polyester-based Chemical Toners

The choice of polymers as toner binder and the appropriate process are important to develop superior toners. The polyester-based chemical toner, produced by bottom-up approach, has achieved successful results in 1) saving energy by using less energy during the manufacturing process than pulverized toner, 2) reducing fuser power consumption by lowering the fixing temperature, 3) obtaining higher image quality and lower toner consumption by controlling toner size & narrow particle size distribution and shape. The next attempt is to tune basic properties of toners by resin modification or using a simple mixture of polyester binder resins. The modification of polyester resin is a chemical process which takes a relatively longer time, but the simple mixing of a series of polyester resins, as a physical method, is an easier approach. So mixed polyester resins are fascinating materials in toner development because of the possibility to tune the toner properties by the simple mixing of different resin components. But the miscibility of two different structures is still a challenge. In chemical toner preparation, one solution is to use organic media to dissolve both components, but this still generates environmental problems because of the increasing level of VOCs during production and usage [2, 3].

Samsung Fine Chemicals' ACE toner [6]

Samsung Fine Chemicals developed polyester chemical toners using a water-based polyester chemical toner process as the next generation of chemical toners [4]. In this process, every raw-material including dispersion solutions of colorant, lubricant, and binder resins, was prepared so as to obtain a low level of TVOCs. Next, every ingredient in aqueous phase was mixed to make fine toner particles with controllable small diameter, a narrow size distribution, and circular shape. The level of TVOCs of final toners was lower than 300 ppm which is compliant to the LGA criteria.

Experiment

Binary polyester dispersion solution was prepared by two methods. In method A, two different kinds of polyester resins were mixed and then dispersed in water to make a mixed polyester dispersion solution. In this preparation, one dispersed particle can include mixtures of polyester resins. In method B, each polyester resin dispersion solution was prepared separately, and then each dispersion solution was mixed to produce mixed polyester dispersion solution. In this method, one dispersed particle only includes one polyester resin type.

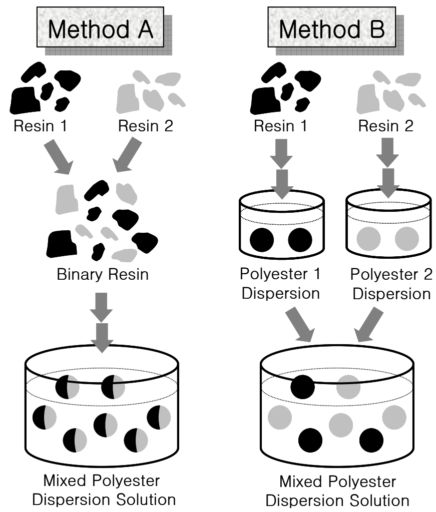

***Figure 1.** Schematic diagrams of the preparation of binary polyester resin dispersion solution with method A & B*

Result

Polyester dispersion solution

The thermal properties of binary polymers, such as T_g or $T_{1/2}$, are dependent on the miscibility of binary polymer [5]. The polyester dispersion solutions for polyester resins with different miscibility were prepared by different preparation methods. In method A, a binary mixture of polyester resins formed a homogeneously dispersed particle. In method B, each dispersed particle contains only one resin type and then the 2 types of dispersed particles were mixed together to form a binary dispersion (Figure 1).

Table 1. Properties of a series of polyester resins and their dispersion solutions

Resin	M_w [a]	T_g [b]	$T_{1/2}$ [c]	AV [d]	Resin dispersion	D_{50} [e]
P-1	22.8	69	126	12	**D-1**	160
P-2	54.0	60	117	12	**D-2**	190
P-3	28.6	65	121	13	**D-3**	160
P-4	49.6	67	130	12	**D-4**	160
P-5	26.3	72	142	20	**D-5**	160
P-6	8.6	67	120	25	**D-6**	190
P-m	mixture of **P-1** & **P-2** with 1/1 ratio				**D-m**	160

a. × 10^3; *b*. Glass transition temperature (°C); *c*. Softening point measured by CFT 500; *d*. Acid value; *e*. Average particle diameter (μm)

Table 1 lists the properties of a series of polyester resins (P-1 to P-m) and polyester resin dispersion solutions (D-1 to D-6). The average particle size of polyester dispersion solutions was controlled within a 150~200 nm particle size range.

Polyester chemical toners

The basic properties of core toner were measured without the addition of external additives. Each polyester chemical toner sample contained 5 wt% of black pigment and 5 wt% of lubricant. The average particle size of toners was 6.4 μm with spherical shape (Figure 2). The percentage of small particles which are smaller than 3μm in diameter averaged about 3.0%. Table 2 lists the properties of the 13 polyester chemical toner samples evaluated in this study.

The thermal behavior of toners C & D were compared to understand the effect of miscibility of two different types of polyester resins in the toners. Both polyester toners C & D contained polyester resins P-1 & P-2 in a 1 to 1 ratio. Polyester resin dispersion solution for toner C was prepared by method A (toner D by method B). It is difficult to predict the relationship between polyester resin miscibility and the thermal rheological properties of the final toner because other components, eg lubricant & colorant, were added to the final toner. A comparison was made using toners prepared from one-polyester resin, the binary mixture of polyester resins (by method A), and the binary dispersion of polyester particles (by method B).

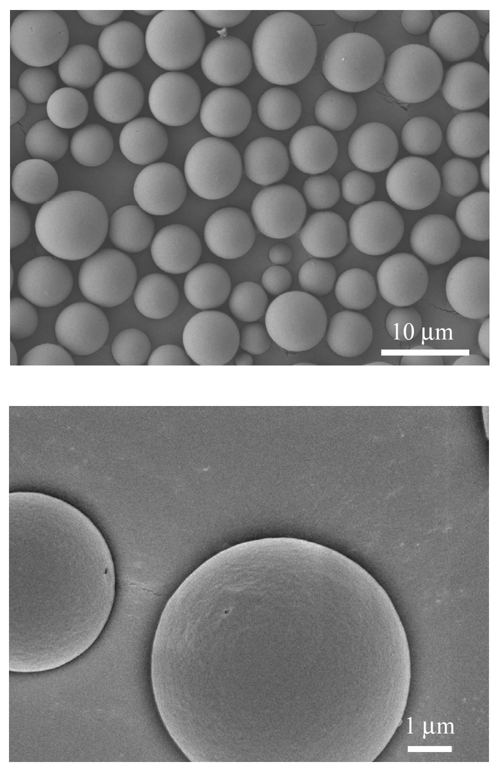

***Figure 2.** SEM images of SFC's ACE toner*

Table 2. Properties of a series of mono & binary polyester chemical toners

Toner[a]	Conditions			Properties				
	Resin 1	Resin 2	Ratio	D_{50}[b]	<3μm[c]	Circularity[d]	T_g[e]	$T_{1/2}$[f]
A	**P-1**	-	1/0	5.84	3.0	0.99	67	141
B	**P-2**	-	1/0	6.36	2.9	0.99	65	139
C	**P-m**		1/1	6.45	2.5	0.99	65	143
D	**P-1**	**P-2**	1/1	6.14	3.8	0.99	63	130
E	**P-3**	-	1/0	6.33	3.8	0.99	69	139
F	**P-4**	-	1/0	5.85	4.5	0.99	66	157
G	**P-3**	**P-4**	9/1	6.18	2.4	0.99	67	139
H	**P-3**	**P-4**	8/2	6.44	2.2	0.99	68	146
I	**P-3**	**P-4**	7/3	6.44	4.1	0.99	68	147
J	**P-3**	**P-4**	6/4	6.31	2.0	0.99	68	148
K	**P-5**	-	1/0	6.50	3.4	0.99	73	142
L	**P-6**	-	1/0	7.63	2.9	0.99	69	133
M	**P-5**	**P-6**	1/1	6.49	2.7	0.98	67	130

a. All binary polyester dispersions for chemical toners, except toner C, were prepared by method B; *b*. Average particle diameter (μm); *c*. percentage o f number of particles whose diameter is smaller than 3μm; *d*. Measured by Sysmex FPIA 300; *e*. Glass transition temperature (°C); *f*. Softening point m easured by CFT 500

The glass transition temperature (T_g) and softening temperature ($T_{1/2}$) of binary polyester toner C (prepared by method A) were higher than those obtained for toner D (prepared by method B). We think that the higher temperature of both T_g and $T_{1/2}$ of toner C was induced by the better miscibility of polyester resins, P-1 and P-2. Further research will be performed for better understanding of these behaviors.

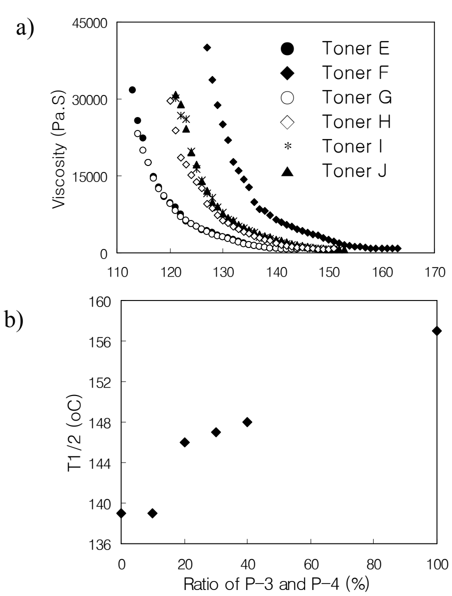

Figure 3. *Relationship of $T_{1/2}$ and ratio of P-3 and P-4 of toner E to J*

A series of binary dispersions of polyester particles at ratios from 9:1 to 6:4 of resins P-3 and P-4 were prepared to study the influence of resin type properties on final toner properties. As the percentage of polyester resin P-4 increased from 10 to 40 wt% in the binary chemical toners G to J, the T_g and $T_{1/2}$ values gradually increased in the range between the minimum and maximum temperatures of the E and F polyester toners that contained only one polyester resin as a binder. Therefore thermal behavior of chemical toners was tuned by changing the ratio of binary polyester resins in chemical toners (Figure 3).

The molecular weight of the polyester resins also had a huge impact on fine-tuning of toner properties. Toner M has polyester P-5 and P-6 of a 1:1 ratio. The Mw difference of P-5 and P-6 is almost 3:1. Mono polyester toner K had a higher fusing temperature with lower gloss level than mono polyester toner L which was not measurable in this temperature region. In case of binary polyester toner M, the fusing temperature range shifted to a lower region with higher gloss, which reached a gloss value of 13 at 165 °C (Figure 4).

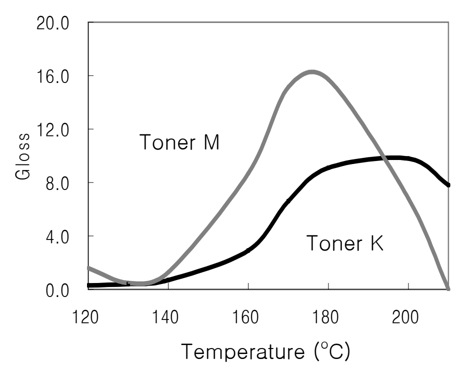

Figure 4. *Gloss of toner K & M*

Total volatile organic compounds (TVOCs)

The quantitative analyses of total VOCs of OEM, ACE, and aftermarket (A/M) toners were performed by using thermal desorption GC-MS. The TVOCs level of ACE toner was lower than 300ppm (LGA criteria of VOC for toner is 300ppm). It was compared with OEM chemical toner and A/M refill toners. TVOCs level of SFC chemical toner were 2 times lower than those of OEM chemical toner and 5 or 8 times lower than those of A/M refill toners (Figure 5).

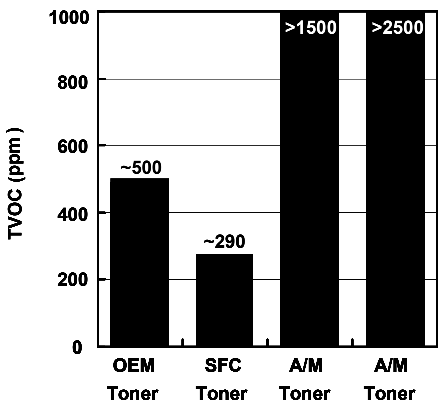

Figure 5. *The level of TVOC in OEM, SFC's ACE, and A/M toners*

Conclusion

Mixed polyester chemical toners were prepared by using the SFC's proprietary method. As the next generation of chemical toner preparation, SFC's ACE toner technology was very useful for toner development because the toner properties could be tunable by using polyester resin mixtures. In addition, SFC's ACE toners had a low level of TVOC because toner formation process was performed in a water-based condition.

References

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Author's biography

Dr. Eui-Hyun Ryu received his Ph.D. degree from Iowa State University in 2006 from the Department of Chemistry with a thesis entitled "Conformationally Controllable Amphiphiles for Hosts and Catalysts". After two years of post-docotral period in Northwestern University, he joined Samsung Fine Chemicals as a senior researcher where he started working in the toner development area.