Study of possibility to realize long life and low energy fusing toner predicted from highly safe Cyclic Olefin Copolymer resin

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Abstract

Cyclic Olefin Copolymer (COC) is expected to be the next generation resin for toners because of its environmentally friendly characteristics. It has fewer potential carcinogens, endocrine disrupters, and TVOC. Recently, the Print-On-Demand field has expanded its market share using the electro photographic process. In this field, non-contact fusing systems are well known; realizing both high speed printing and high print quality. The key requirements for toners are a longer life for consistent print quality, and lower energy fusing under high speed printing. In this study the durability of the toner particles in the developer was evaluated as an index of longer life property. Also, a color toner using COC resin was examined and compared to Polyester toner. At the close molecular weight distribution and thermal property, the COC toner sample showed higher durability than Polyester toner sample, and its durability was similar to that of the Polyester toner sample, which had higher thermal property and higher density cross-linking. The cyan toner samples were prepared using both COC resin and Polyester resin. The cyan color shading from the COC toner sample matched the color shading of the Polyester toner sample. The total color difference Δ E was small. However, there was a difference between the COC cyan toner sample and the Polyester cyan toner sample in the optical density curve gained by changing the mass of toner on paper.

Introduction

The Print-On-Demand field and the Digital Printing field are growing. One reason is the advantage of small lot printing with a short lead time over offset printing. The electro photographic process using toner is expanding its market share in these fields. Instead of the contact fusing system, the non-contact fusing system is well known because of its high speed process and high print quality (better resolution without pressing image). Currently, Polyester resin is typically used for toners in this field.

In non-contact fusing systems, energy reduction is being examined. Of course cutting the total energy consumption would be the main reason due to the recent concerns about the global environment. Another reason is human safety, by decreasing the VOC (Volatile Organic Compounds). Reducing energy requires toner to respond more quickly to heat energy since most of the energy is consumed in the fusing process. This can be achieved by lowering the thermal properties and molecular weight of the toner, but it could also be a disadvantage in longer life toner particles and higher printing processes.

The majority of toner formulation is a main binder resin; thus selecting a main binder resin is important to control the VOC. COC resin is polymerized from ethylene and norbornene by a metallocene catalyst [1], and the total VOC from the COC toner would be less than St/Ac toner and Polyester toner [2]. Also the olefinic properties have fewer potential carcinogens and endocrine disrupters. In previous studies, it was found that the COC toners, which were designed for contact fusing systems (heat roll), are superior to the St/Ac toners and the Polyester toners when it comes to longer life on both the mono-component developing system [3] and the dual-component developing system [4].

It is reported that COC resin is better than Polyester resin in the light transmission [5]. This property is expected to be a strong point at the color reproduction and the color mixture.

In this feasibility study, two types of COC toner samples were prepared; one was black toner designed for a non-contact fusing system, and the other one was cyan toner designed for a contact fusing system. The durability evaluation of the black toner sample with Polyester toners, and the possibility to realize longer life toner particles with lower energy fusing is discussed. Also a comparison was made between the Polyester cyan toner sample and the cyan toner using a COC resin. This, too, is discussed.

Experimental

Toner samples preparation

Black toner samples

Prior to the sample preparations, the properties of two Polyester toner products, which are commercialized for non-contact fusing systems, were studied to determine the requirements for toners. The results are in Table 1.

Table 1. Properties of commercialized Polyester products

	D50 (μm)	Tg (℃)	Tm (℃)	Mn	Mw	Mw/ Mn
Toner 1	9.1	66.4	118.8	1,720	13,500	7.87
Toner 2	9.3	56.0	105.4	2,230	12,100	5.41

D50: Volume statistics average particle size from coulter multisizer

Tg: Glass transition temperature measured from DSC of Seiko Instruments EXSTAR6000

Tm: Softening point temperature measured from CFT-500 of Shimadzu

Both Toner 1 and Toner 2 are from low molecular weight Polyester resin, but the resin for Toner 1 is assumed to have a higher density cross-linking. Regarding molecular weight distribution and thermal property, Toner 1 should be strong in longer life and Toner 2 should be strong in lower fusing.

Based on this analysis, three toner samples were prepared. The properties of these toner samples are in Table 2. And the GPC results of all toners are in Figure 1 and Figure 2.

Table 2. Properties of black toner samples

	D50 (μm)	Tg (℃)	Tm (℃)	Mn	Mw	Mw/ Mn
COC 1	8.7	55.7	107.3	2,180	5,950	2.72
PES 1	8.8	59.7	115.9	2,180	33,200	15.2
PES 2	9.5	60.1	106.3	1,850	7,020	3.80

D50: Volume statistics average particle size from coulter multisizer

Tg: Glass transition temperature measured from DSC of Seiko Instruments EXSTAR6000

Tm: Softening point temperature measured from CFT-500 of Shimadzu

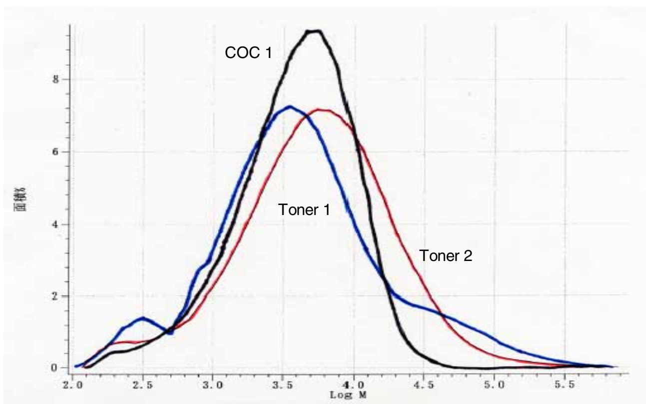

***Figure 1**. GPC result of Toner1, Toner2 and COC 1*

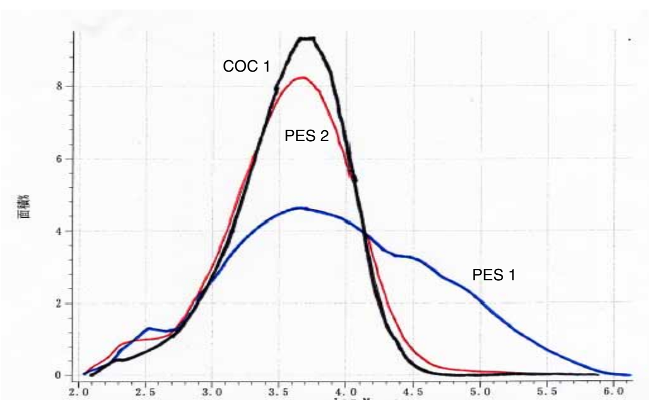

***Figure 2**. GPC result of COC 1, PES 1 and PES 2*

All three toner samples have the following same formulations, except for resin. Materials were pre-mixed, extruded, crushed and classified.

Resin: 100 parts
Carbon black: 7 parts
Charge control agent: 1 part

Each sample was mixed with the same fumed silica by 1.3%. Sample PES 2 and COC 1 have close properties with each other, and have lower molecular weights than Toner 2. The cross-linking density of sample PES 1 is assumed to be higher than Toner 1.

Cyan toner samples

The following materials were pre-mixed, extruded, crushed, and classified. The wax content was changed between these two samples to optimize fusing performance in the test condition.

COC cyan toner sample:

Resin: 100 parts
Cyan colorant: 7 parts
Charge control agent: 1 part
Wax: 7 parts

Polyester cyan toner sample:

Resin: 100 parts
Cyan colorant: 7 parts
Charge control agent: 1 part
Wax: 2 parts

Each sample was mixed with the same fumed silica by 2.6%. The properties of the toner samples are in Table 3.

Table 3. Properties of Cyan toner samples

	D50 (μm)	Tg (℃)	Tm (℃)
COC 2	7.2	49.7(63.4)	121.9
PES 3	7.3	60.9(64.1)	126.1

D50: Volume statistics average particle size from coulter multisizer

Tg: Glass transition temperature measured from DSC of Seiko Instruments EXSTAR6000 / the number in () describes Tg from resin

Tm: Softening point temperature measured from CFT-500 of Shimadzu

Durability evaluation

The durability was examined as a change of toner particle size distribution when the toner was agitated with the carrier. Each of COC 1, PES 1 and PES 2 toner samples and the carrier, which has an average particle size of 55μm, were each placed in plastic bottles. The amount of developer was 200grams and the toner concentration was 4.0%. The developers were placed in the bottles and were agitated for 20 hours using a paint shaker. The transition of the D50 particle size and the ratio of less than 5μm particles were evaluated based on the number statistics.

Possibility as color toner

Color shading and color difference

Each cyan toner sample was developed, transferred, and fixed onto paper, changing the mass of toner per square centimeter. From the dependence of optical density on the mass of toner, the color shading of the COC toner sample was compared with the Polyester toner sample. Next, the color difference between the two toner samples was evaluated.

Lightfastness

Each cyan toner sample was developed, transferred, and fixed onto paper. The pieces of paper samples were exposed to Xenon for 192 hours using a Xenon weather meter XL-75TS of Suga Shiken-ki Co., Ltd. The radiation intensity was $0.36W/m^2$ with a wavelength of 340nm. The color difference was evaluated after being exposed.

Results and Discussion

Durability

The change of toner particles in the developer is shown in Figure 3 and Figure 4. Figure 3 shows the change in number statistics D50 and Figure 4 shows the increase in number of less than 5μm particles standardized by the number at 0 hour.

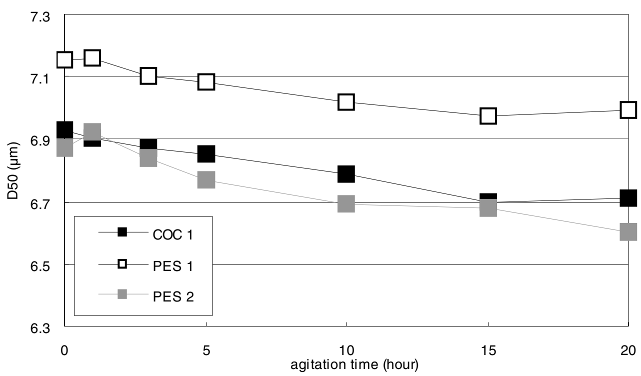

Figure 3. *Change in D50 particle size from number statistics*

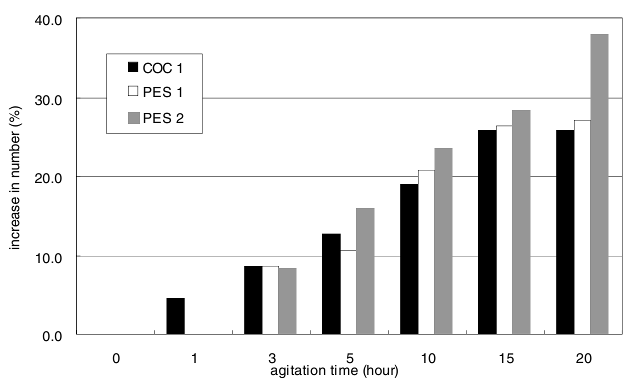

Figure 4. *Increase in number of less than 5μm particles from number statistics*

In the actual printing process, toner is consumed and replenished continuously in the developer, and each toner particle repeats the tribo-electric charging process. The change in particle size distribution is expected to cause the disturbance in tribo-electric charge distribution. Also excess fine particles could contaminate the surface of carriers and disturb proper tribo-electric charging between toners and carriers. Thus, the durability of toner is one key factor for consistent print quality and longer developer life.

The change in particle size from COC 1 is less than PES 2, and is comparable with PES 1. It is not easy to discuss about Toner 1 and Toner 2 in Table 1 since they should have different toner formulations from toner samples tested here in Table 2. Looking at the thermal property and molecular weight distribution, the order of durability is assumed as follows:

PES 1 > Toner 1 > Toner 2 > PES 2

COC 1 is similar in durability as PES 1, while its thermal property is similar to Toner 2. This means that the COC resin should maintain consistent print quality with a longer developer life and lower energy fusing.

Color shading and color difference

Figure 5 describes the dependency of optical density on the mass of toner per square centimeter, and the color coordinates at each optical density is listed in Table 4 and Table 5.

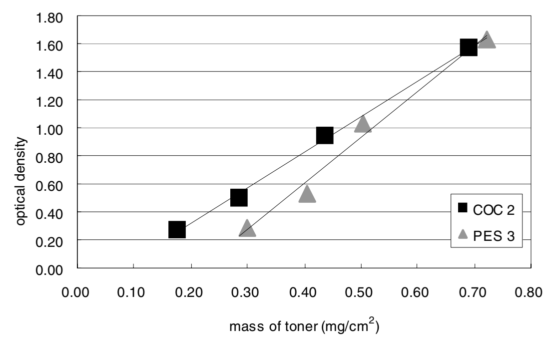

Figure 5. *The dependency of optical density on the mass of toner*

Table 4. Color coordinates at each optical density from PES 3 toner

PES 3	Optical density			
	0.285	0.534	1.032	1.633
L*	83.31	72.64	57.90	45.52
a*	-9.75	-18.17	-29.11	-31.49
b*	-16.26	-28.11	-42.79	-51.02

Table 5. Color coordinates at each optical density from COC 2 toner

COC 2	Optical density			
	0.267	0.498	0.940	1.567
L*	84.14	74.05	60.11	46.93
a*	-9.11	-17.10	-27.43	-30.77
b*	-15.27	-26.78	-41.29	-50.98

In Table 6, the color difference is evaluated between the PES 3 toner and the COC 2 toner at the nearest optical density. The numbers in the table are the differences between the PES 3 toner and the COC 2 toner.

Table 6. Color differences between PES 3 toner and COC 2 toner

	Color difference			
PES 3 Optical density	0.285	0.534	1.032	1.633
COC 2 Optical density	0.267	0.498	0.940	1.567
ΔL*	+0.83	+1.41	+2.21	+1.41
Δa*	+0.64	+1.07	+1.68	+0.72
Δb*	+0.99	+1.33	+1.50	+0.04
ΔE	1.50	2.24	3.21	1.07

In Figure 5, as the mass of toner increases, the optical density becomes higher accordingly. The slope of the COC 2 toner is more gradual than the PES 3 toner. At the nearest optical density (less than 10% difference), the total color difference ΔE between PES 3 toner and COC 2 toner is small.

COC resin has a lower specific gravity than Polyester resin. Based on the toner formula, the specific gravity of COC 2 toner and PES 3 toner are calculated as 1.04grams/cm^3 and 1.26 grams/cm^3 respectively. Theoretically, with the same number of toner particles, the mass of toner per square centimeter would be less in the COC toner than the Polyester toner.

In Figure 5, the COC 2 toner slope is more gradual than the PES 3 toner, and has a tendency of showing close optical density with PES 3 toner at less mass of toner. Toward the optical density of around 1.6, this tendency becomes less. At this optical density, the mass of toner is about 0.7grams/cm^2 and is approximated to the closest packing of a single toner layer. As it approaches the closest packing, the optical density would be saturated. As a result the slope from each toner would overlap each other.

The color shading of each COC toner particle is comparable to the Polyester toner. And, theoretically, less specific gravity could contribute to the reduction of toner consumption by a maximum of 17%.

Lightfastness

The lightfastness was evaluated under the closest packing of single toner layer, and actual mass of COC 2 toner and PES 3 toner are 0.61grams/cm^2 and 0.76grams/cm^2 respectively. Table 7 shows the color differences after 96 hours and 192 hours.

Table 7. Color difference from Xenon weather meter

	PES 3 toner		COC 2 toner	
	96hours	192hours	96hours	192hours
ΔL*	-0.12	-0.17	-0.04	+0.02
Δa*	-0.08	-0.38	-0.09	-0.34
Δb*	+0.51	+1.06	+0.06	+0.45
ΔE	0.75	1.26	0.37	0.69
change in optical density	0%	0%	0%	0%

Although there is no change in the optical density, ΔE of PES 3 toner is almost twice as great as COC 2 toner. The main change in Δb* is obvious.

This test estimates the permanency of an image under fluorescent light. The COC 2 toner is expected to be slower than the PES 3 toner in turning the image yellow.

Conclusions

Following are the findings from this study:

1. For non-contact fusing system, one COC toner sample and two Polyester toner samples were prepared. In the comparison with the commercialized products, one Polyester toner sample had the lowest molecular weight and another Polyester toner sample had the highest molecular weight. The COC toner sample had almost the lowest molecular weight and thermal property among the five toners.

The durability was evaluated as a change of toner particle size in the developer, and the COC toner sample was a match for the Polyester toner sample, which had the highest molecular weight.

2. The cyan toner samples were prepared from COC resin and Polyester resin. The cyan color shading of the COC toner sample was comparable with the Polyester toner sample, and the color differences between the two samples were small.

At the dependency of optical density on the mass of toner, the COC toner sample had the tendency of showing equivalent optical density to the Polyester toner sample with a less toner mass. This should be related to the difference of specific gravity (COC 2 toner sample: 1.04grams/cm^3, Polyester toner sample: 1.26 grams/cm^3). Theoretically, this difference would contribute to the reduction of toner consumption by as much as 17%.

After being exposed to Xenon, the COC toner sample was slower to turn yellow than the Polyester toner sample.

Therefore, it is possible to realize a longer life and a lower energy fusing toner with utilizing COC resin. Also COC resin is useful for color toners.

References

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Biography

Atsuo Miyamoto received his master degree in Physical Chemistry from the University of Hokkaido, Japan, in 1996 and then joined the Research and Development section of the Chemical Products Division of Tomoegawa Paper Co., Ltd.. He is currently working on toner development for copies and printers.