

A Hybrid Resin for Toner II

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Abstract

Recently, we have reported new type resin "Hybrid Resin" for toner.¹ This resin contains micro-domain structure was prepared by hybridizing polyester and styrene-acrylic using bi-reactive monomer such as fumaric acid to utilize advantages of both resins for toner binder. This paper describes the development of new hybrid resin has no domain by using higher reactivity of bi-reactive monomer such as acrylic acid, and improved fixing property with charge stability of the toner using the resin compared to those of the micro-domain type.

Introduction

There are many technological requirements for electrophotographic toner: i.e., low temperature fixing ability, long life of developer, quick chargeability and charge stability at various environmental conditions. Especially, low temperature fixing ability is one of the most important requirements in the field of low end as well as high speed copier or printer, because it brings minimization of consumed energy of the overall machines and less trouble in paper feed or paper burning, and so on.

Recently, we have reported a new type resin prepared by hybridizing polyester and styrene-acrylic using bi-reactive monomer such as fumaric acid.¹ To disperse styrene-acrylic in polyester uniformly, we have developed a technique that both monomers are concurrently polymerized in the same vessel. By controlling dielectric constant (ϵ) of the resin, we can minimize the difference in triboelectric charge of the corresponding toner among three different environmental conditions. By decreasing molecular weight of styrene-acrylic part, we can lower energy for fixing

of the corresponding toner. In addition, the uniformity of the resin is obtained by using a bi-reactive monomer that has both C = C double bond and carboxylic groups such as fumaric acid or maleic anhydride.

Fumaric acid and maleic anhydride are not so reactive in addition polymerization. Therefore there exists only styrene-acrylic addition product in the resin. As a result the resin has island and sea structure (micro-domain structure).

In this study, we have synthesized a new hybridized polyester with styrene-acrylic using another reactive bi-reactive monomer such as acrylic acid or methacrylic acid. If we use adequate amount of bi-reactive monomer, we can synthesized homogeneous resin which is confirmed by transmission scanning electron microscope (TEM). We call it Non-domain type Hybrid Resin which shows lower fixing temperature than that of Micro-domain type Hybrid resin. The result is considered, in view point of cohesive energy, in other word, surface tension.

Experimental

Preparation of Resins

To take advantage of low temperature fixing of polyester, large amount of polyester monomers is used compared to those of styrene-acrylic.

Polyester monomers are put in a vessel. Styrene-acrylic monomers including bi-reactive monomer such as acrylic acid or methacrylic acid with radical initiator are mixed and put into a dropping funnel. After the mixture of polyester monomers is heated to the temperature at which addition polymerization starts, the styrene-acrylic monomer mixture is added dropwise from the dropping funnel to the vessel. After by completing addition polymerization reaction, the reaction temperature is elevated to polymerize other

Table 1. Monomer Compositions of Resins

Entry	Monomers		
	Polyester	Styrene-acrylic	Bi-reactive monomer Substance name
Hybrid Resin A	BPA-PO, TPA, TMA OSA (large amount)	St,2-EHA	Fumaric acid
Hybrid Resin B	BPA-PO, TPA, TMA OSA (large amount)	St,2-EHA	Acrylic acid
Polyester A	BPA-PO, BPA-EO TPA, TMA OSA (large amount)	—	—
Styrene-acrylic	—	St,2-EHA DVB	—

monomers. In order to monitor the degree of polymerization a Ball & Ring softening point (Tsp) is measured (ASTM E28-67) by commercially available instrument measurement machine is ASP-MGK2 (MEI-TEC Corporation). Polymerization reaction is stopped at desired Tsp.

The monomer compositions are listed in Table 1. Physical properties of Hybrid Resins with reference resins are listed in Table 2. Pure polyester is prepared by condensation polymerization, and pure styrene-acrylic is prepared by addition polymerization in *o*-xylene. Flow tester softening point (Tm) of resin is measured by a Flow Tester (Model CFT 500, Shimazu), and glass transition temperature (Tg) is obtained by DSC (DSC Model 200; Seiko Instruments, Inc.) (ASTM D3418-75). Acid value (AV) is also measured (ASTM D1980-67).

Table 2. Physical Properties of Resins

Entry	Domain particle size	TM (C°)	TG (C°)	AV (KOhmg/g)
Hybrid Resin A	1.5 μ m	136.0	59.5	9.5
Hybrid Resin B	None	133.8	59.5	12.0
Polyester A	—	134.0	62.0	8.9
Styrene-acrylic	—	133.0	62.5	—

Measurement of Average Domain Size of Resin

The resin block is sliced to a thickness of 150 nm using a microtome. Thin samples obtained are observed using a transmission scanning electron microscope (TEM) (“JEM-2000” manufactured by JOEL (Nihon denki Co Ltd)). The areal proportion of the dispersed domain is calculated by analyzing photographic images.

Measurement by Gel Permeation Chromatography

The molecular weight of resin is measured by Gel Permeation Chromatography (GPC). The resin is dissolved at room temperature in chloroform in concentration from 0.05 to 0.5 wt%. The solution is filtrated through membrane filter with pore sizes of 0.5 μ m to remove insoluble part.

Preparation of Toners

Mixture of 91.5 wt% of resins, 5.5 wt% of a carbon black, 1.8 wt% of a polypropylene wax, and 0.9 wt% of charge control agent (CCA) is compounded by twin-extruder, crushed, pulverized and size-classified to 11 μ m in volume median diameter. All toners for test are treated with 0.3 wt% of hydrophobic silica to get efficient flow for actual operation.

Preparation of Developers

Mixture of 97.0 wt% of toners, 3.0 wt% of a ferrite coating carrier is mixed by V-blender.

Measurement of the Critical Surface Tension (γ_c) of Resin

Resins are melted and formed thin pellets. After heating at 150°C for 5min., they are cooled to room temperature. The size of pellet obtained is about 40mm \times 10mm \times 1mm. The Critical surface tension (γ_c) of each sample is measured with Wilhelmy method using dynamic contact angle meter (model “ST-1S” Shimazu).

Evaluation of Fixing Ability

Fixing ability is evaluated by determining the lowest fusing temperature. The lowest fixing temperature used herein means the temperature of the fusing roller at which the fixing ratio of the toner exceeds 70%. This fixing ratio of the toner is calculated from the image density change before and after rubbing by sand-rubber eraser. The image density is measured with Macbeth Densitometer. Heat-roller diameter was 40 mm. Nip width and nip pressure is set 2 mm and 2.0 kg/cm², respectively. Process speed is at 160 mm/sec.

Measurement of the Dielectric Constant of Resin and Toner

The resin or toner is melted and pressed to the form of thin pellet. After heating at 135 °C for 5 min., they are cooled to room temperature by degree applying the pressure. The thickness of pellet obtained is about 2 mm. The dielectric constant (ϵ) of sample is measured according to JIS K6911 5.14 at several temperatures.

Measurement of the Triboelectric Charge (q/m) of Resin and Toner

The triboelectric charge is measured with a blow-off method. For the test, resin/developer or toner/developer mass ratio (T/D) is set at 3%. After roll-milled at 250rpm for appropriate time, 0.5 grams of the mixture is transferred into a pre-weighed Faraday cage and the toner particles are blown off from the carrier by air jet (2 sec. at 1.5kgf/cm²) through a wire screen with 36 μ m opening. The q/m values of the powders are calculated from the charge measured with Kawaguchi Universal Electrometer (Model MMA2-17A).

Results and Discussion

In general it is said that the lower fixing ability is increased with increasing cohesive energy of binder. Then we tried to increase cohesive energy of hybrid resin for the lower temperature fixing ability. The micro domain type hybrid resin we discussed last year¹ is considered to have lower cohesive energy than that of pure polyester, because of low cohesive energy of island part: styrene-acrylic. Therefore we develop a homogeneous hybrid resin using another bi-reactive monomer. We chose acrylic acid and methacrylic acid for bi-reactive monomer, because they have higher reactivity to addition polymerization than that of fumaric acid or maleic anhydride.

Relation Between Reactivity of Bi-Reactive Monomer and Average Domain Size

At first the average domain size is observed by changing the species and the contents of bi-reactive monomer. Average domain size decreases with increasing bi-reactive monomer content. We can not get the average domain size under 0.2 μ m in the case of using fumaric acid as a bi-reactive monomer. On the other hand increasing acrylic acid content caused homogenous structure by TEM observation. It is, we consider, due to high reactivity of acrylic acid to styrene or acrylic monomer. We measured number average of molecular weight and acid value of styrene-acrylic after completing addition polymerization and found that almost

one fumaric acid monomer is introduced in two styrene-acrylic chains, and almost two acrylic acid monomers are introduced in one styrene-acrylic chain.

Relation Between Average Domain Size and Cohesive Energy (Critical Surface Tension(γ_c))

Since surface tension is considered to be in proportion to cohesive energy as shown in Formula 1². We evaluate cohesive energy level by the critical surface tension.

$$\gamma_c/V^{1/3}/D = \text{const} \quad (\text{Formula 1}^2)$$

γ_c ; Surface tension
 D ; Density of cohesive energy
 V ; Molecular volume

Table 3. Critical Surface Tension (CSF) of Resins

Entry	ADS*(μm)	CSF(dyn/cm^2)
Hybrid Resin A	1.5	36.1
Hybrid Resin B	Non	37.9
Polyester A	Non	41.2
Styrene-acrylic	Non	32.0

* ADS: Avg. domain size

As shown in Table 3, critical surface tension is in the following order, "Polyester A" > "Hybrid Resin B" > "Hybrid Resin A" > "Styrene-acrylic". Non-domain "Hybrid Resin B" shows a larger critical surface tension, i.e. larger cohesive energy, compared to that of micro-domain "Hybrid Resin A".

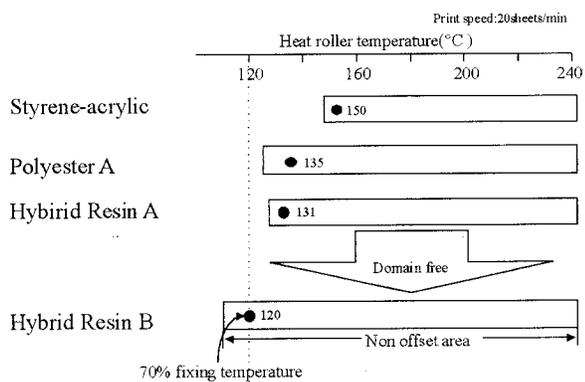


Figure 1. Fixing properties of toners.

Fixing Ability

Under similar thermal properties between two different kind of resins larger cohesive energy of resin or toner, we think, causes lower energy of fixing to paper because of large critical surface tension of paper surface.³ Fixing property is investigated. As shown in Figure 1, the toner using non-domain "Hybrid Resin B" fixes at lower temperature than that of the toner using micro-domain "Hybrid Resin A".

The toner using hybrid resin fixed at low temperature compared to polyester based toner. It should be noted that the molecular design was to get wide molecular weight distribution of hybrid resin.

Electric Properties of Non-Domain Hybrid Resin

We have reported the environmental stability of triboelectric charge of the toner using micro-domain hybrid resin.¹ In case of non-domain hybrid resin, at first, temperature dependence of dielectric constant (ϵ) is investigated as shown in Figure 2, non-domain "Hybrid Resin B" shows slightly higher ϵ value and similar temperature dependence of ϵ value compared to those of micro-domain "Hybrid Resin A". Styrene-acrylic introduction might inhibit the dipole orientation brought by polyester part, also in non-domain hybrid resin. Secondary, temperature dependence of triboelectric charge of the toners was investigated. Similar to the temperature dependence of ϵ , triboelectric charge of non-domain hybrid resin increases slightly at 50°C compared to that at 40°C. Then the triboelectric charge is measured at different environmental conditions. As shown in Figure 3, the toner using non-domain "Hybrid Resin B" shows smaller difference in triboelectric charge among three different environmental conditions.

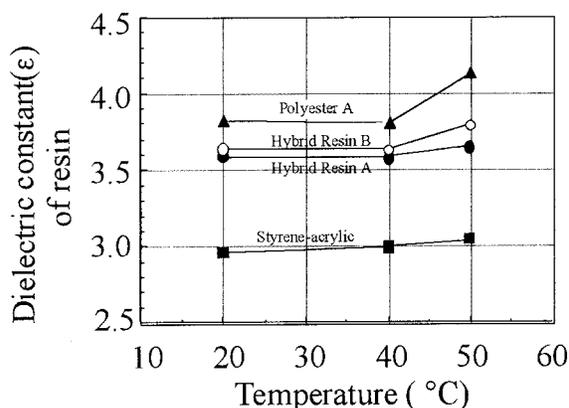


Figure 2. Temperature dependence of dielectric constant (ϵ) of resins.

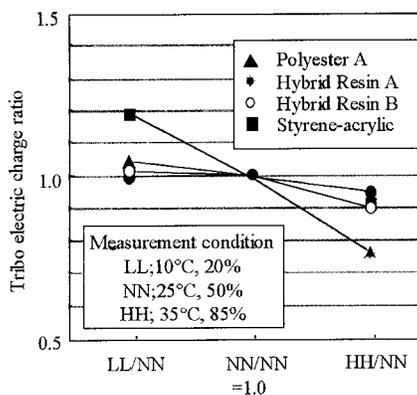


Figure 3. Triboelectric charge ratio of the toner.

Conclusion

Non-domain hybrid resin is obtained by using a bi-reactive monomer such as acrylic acid or methacrylic acid which has higher reactivity toward additional polymerization. The toner using the non-domain hybrid resin fixed at a lower

temperature compared to that of the toner using micro-domain hybrid resin. It is also confirmed that the triboelectric charge properties are similar to that of micro-domain hybrid resin under three different environmental conditions.

References

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