The Improvement of Core-Shell Toner by Controlling the Interfacial Thickness Between Core and Shell Polyesters

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Abstract

The fabrication of polyester core-shell toner by emulsion aggregation method was investigated to realize better balance of low-energy fusing and good storage stability. In core-shell toners which use high Tg shell resin and low Tg core resin, the storage stability can be significantly worse than expected from shell Tg. It was thought that the core moiety diffused into the shell by interfacial polymer diffusion in the heating coalescing process. From this viewpoint, the control of the interfacial diffusion (interfacial thickness: λ) between the core and shell was examined based on the χ parameter of the polyester resin combinations which was calculated by monomer composition. After examinations of several polyester combinations based on calculated χ parameters, it was found that 1,2-propanediol (1,2PD)/isophthalic acid (IPA) polyester and 1,2PD/alkenyl succinic anhydride (AS) polyester showed a strong phase separation. The ellipsometry measurement revealed that the interfacial thickness of this combination was only 10nm, which was too small for sufficient adhesion between the core and shell. Therefore larger interfacial thicknesses were tested by incrementally decreasing the χ parameter by changing monomer composition. A strong relationship between actual λ and the χ parameter was found. The λ could be controlled at 80nm by using a resin combination based on 1,2PD/IPA and 1,2PD/IPA/AS, and a core-shell toner was produced using this combination of polyester resins. The adhesion between core and shell was found to be sufficiently strong, and the relationship between low temperature fusing and storage stability became significantly better compared with the toner having miscible core and shell.

Introduction

In full color laser printers and copiers, the performance requirements include high speed, fine image quality, and environmental friendliness. Specially designed toners are needed to meet these requirements. Binder resins having low thermal properties (like Tg and melt viscosity) can provide low-energy fusing, however the toner storage stability becomes worse. To develop a toner with both low-energy fusing and good storage stability, many players have used the technology of chemically prepared core-shell type toner in which the shell has high thermal properties and the core has low thermal properties. Most of these toners were produced with styrene acrylic resin, and only a few toners were produced with polyester resin which provides superior fusing with lower energy consumption.

During recent years, we have investigated the fabrication of core-shell toner by emulsion-aggregation method using all polyester resins rather than styrene acrylic resins to realize a better balance of low-energy fusing and good storage stability [1, 2]. However, even with the use of high-Tg shell and low-Tg core, the toner storage stability was significantly worse than expected from shell Tg. For this reason, it was thought that the core moiety diffused into the shell by interfacial polymer diffusion in the heating coalescing process which reduced the Tg of the shell surface. In fact, it was found by optical micrograph observations of melt blends that the common core and shell resins were totally miscible.

In this paper, in order to design an ideal core-shell toner, we have examined the interfacial polymer diffusion between the core and the shell resins in terms of the interfacial thickness (λ). The magnitude of this interfacial thickness was controlled by the χ parameter of the polyester resin combinations based on the Flory Huggins theory [3].

Experimental

Preparation of experimental polyester (PES) resins

PES-1; A 10L four-neck flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with bisphenol A propylene oxide adduct (BPA-PO), isophthalic acid (IPA), and dibutyltin oxide. The mixture was reacted at 230°C for 10 hours, further reacted at 8kPa for 1 hour, and then quenched by cooling. PES-2; Prepared in a similar method, except for using alkenyl succinic anhydride (AS) as acid monomer. PES-3; A 10L four-neck flask equipped with a nitrogen inlet tube, a rectifier, a stirrer, and a thermocouple was charged with 1,2-propanediol (1,2PD), IPA, and dibutyltin oxide. The mixture was reacted at 180-220°C for 15 hours, further reacted at 8kPa for 1 hour, and quenched by cooling. PES-4; Prepared in a similar method, except for using AS as acid monomer. PES-5; prepared in a similar method, except for using IPA and AS as acid monomer.

In this study, in order to remove resin molecular weight as a factor, the molecular weights and distributions were made uniform by gel permeation chromatography fractionation of the resins. The glass transition temperature (Tg) and molecular weight of polyester resins are listed in Table 1.

Table 1. Properties of the Experimental Polyester Resin

PES	composition	Tg 1)	Mn2)	Mw 2)
1	BPA-PO/IPA (shell)	70	4300	5000
2	BPA-PO/AS (core)	35	4500	5900
3	1,2PD/IPA (shell)	65	4700	5300
4	1,2PD/AS (core)	26	4500	5300
5	1,2PD/IPA/AS (core)	35	4400	5400

1) The glass transition temperature (Tg: °C) was measured by a differential scanning calorimeter (DSC). Tg was read by the tangential way.

2) The molecular weight was measured by gel permeation chromatography (GPC) with THF.

Optical micrograph observation of PES/PES blend

A thin film of polyester blend was cast from MEK solution onto the slide glass and dried by natural evaporation at room temperature for at least 24 hr. A cover glass was placed on top of the film and observed using optical micrograph, KEYENCE NHX-100.

The Flory Huggins χ parameter calculation

The Flory Huggins χ parameter between PES/PES was calculated by COSMO method.

Measurement of PES/PES interfacial thickness by ellipsometry

The PES/PES bilayer specimens were prepared by mounting a thin film of PES-3 (~0.5 um) on the surface of a thick PES-4 substrate (~0.5 mm) by a common procedure [4], and treating at 80°C for 1h based on actual coalescence condition. Ellipsometric measurements were carried out using an auto ellipsometer EL-8, Optec Co. The wavelength of the laser was 632.8 nm, and the incident light beam had an angle of 70° to the bilayer specimen at 80°C. The interfacial thickness λ between PES-3 and PES-4 was calculated by four-layer model [5]. The λ between PES-3 and PES-5 was also determined by a similar procedure.

Preparation of PES emulsion

Polyester emulsions used for core and shell were made by mechanical emulsification with methyl ethyl ketone (MEK) as the solvent.

Em-1; At first, a 2L four-necked flask equipped with a cooling tube, a stirrer, and a thermocouple was charged with PES-1, MEK, and Sodium polyoxyethylene alkyl ethers sulfates as a surfactant. Then PES-1 and surfactant were dissolved in MEK by stirring at 30°C for 3 hours. Secondly, emulsification was achieved by adding ion-exchanged water over 30 minutes with mechanical agitation. Finally, an emulsion of PES-1 was obtained by removing MEK under reduced pressure at 60°C. Then the emulsion of PES-1 was filtered through a wire mesh after cooling. Em-2, -3, and -5; Prepared in a similar method using PES-2, PES-3 and PES-5 instead of PES-1.

The average particle sizes of the resulting polyester emulsions were all 200-210 nm as determined by a laser scattering particle size analyzer. The solid content concentration were adjusted to 20 wt% for all emulsion samples.

Preparation of toner

TONER-A (core: PES-2/shell: PES-1); A core ingredient was prepared from Em-2, colorant dispersion (Pigment Blue 15:3) and wax emulsion (paraffin wax) with common emulsification aggregation methods. Next, a shell ingredient was prepared from Em-1 using the methods similar to the core, and the system was treated at 80°C for 1h for coalescence. Thirdly, the prepared dispersion was subjected to a suction filtration step, a rinsing step, and drying step, to give a fine colored resin particle powder with particle size of 5.0μm. The colored resin particle powder was blended with fumed silica as a fluidizing agent.

TONER-B (core: PES-5/shell: PES-3); In a similar method, a core was prepared from Em-5 and shell was prepared from Em-3.

Measurement of the particle size distribution of emulsions and toners

The particle size distribution of PES emulsions was measured using a laser scattering particle size analyzer (LA-920, HORIBA Co., Ltd.). The particle size distribution of toners was measured using a Multisizer II (Beckman Coulter, Inc.) with the 100μm size aperture.

Measurement of fusing property

Fusing performance was evaluated using off-line oil-free fusers (hot roll & pressure roll types.)

At first, each toner sample was developed and transferred on the paper so that the mass per area was 0.45mg/cm2. The paper was J-paper by Xerox Corporation. Then the paper was passed through the fuser. The line speed was 160mm/sec.

The fusing temperature was defined as the lower temperature limit at which the cold-offset was not observed and the fusing ratio of the toner exceeded 80%. The fusing ratio of toner was calculated as the change in image density before and after Scotch tape (3M) stripping.

Measurement of heat storage stability

Each toner sample (20 g) was placed in a polyethylene bottle and was allowed to stand at 55°C for 8 hours. Heat storage stability was determined by the amount of blocked and aggregated toner observed in the sample. In the case of good storage stability, blocking and aggregating of toner was not observed.

Transmission electron microscopy (TEM) observation

The morphological property of the TONER-B was observed by transmission electron microscopy (Hitachi 800, Japan) with microtomed samples. A powder toner sample was dispersed into an epoxy resin and then solidified. After quenching with liquid nitrogen, it was sliced with a microtome.

Results and discussions

Control of interfacial thickness λ between core and shell resin for ideal core shell toner

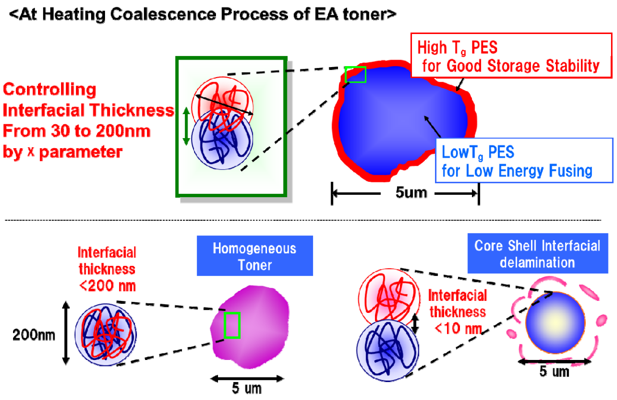

Figure 1. *The interfacial thickness target between core and shell resin at heating coalescence process.*

In core shell type toner produced by emulsion aggregation process, it was considered that the core and shell resin diffused into each other by interfacial polymer diffusion in the heating coalescing process which made the toner morphology homogeneous. Because of the homogeneous morphology, the toner storage stability was significantly worse than expected from shell Tg. Based on this hypothesis, we have examined the control of interfacial diffusion (interfacial thickness: λ) between core and shell polyester by χ parameter adjustment.

The target of the λ between core and shell resin was determined by the following two demands. Firstly, based on the emulsion particle size (200nm), the interfacial thickness must be less than 200nm. Secondly, for sufficient adhesion of the shell layer on the core surface, the interfacial thickness must be above 30nm [5]. Therefore, the target of the λ was decided from 30 to 200nm. In order to produce the ideal core shell toner, precise control of the λ was examined.

A miscibility prediction for binary resin system based on the Flory-Huggins theory

Miscibility of a binary resin system is explained by the following Flory-Huggins theory. Based on this theory, $\Delta G_{mix}>0$ means resin 1 and 2 become miscible, and $\Delta G_{mix}<0$ means they become immiscible [3].

$$\frac{\Delta G_{mix}}{NRT} = \underline{\left(\frac{\phi_1}{m_1}\ln\phi_1 + \frac{\phi_2}{m_2}\ln\phi_2\right)} + \underline{\boxed{\chi_{12}}\cdot\overset{(\phi_1=\phi_2=0.5)}{\phi_1\cdot\phi_2}}$$

Molecular weight = const.
(by fractionation GPC)

ΔG_{mix}: free energy change of mixing
N, R: const. T: temperature
ϕ_1, ϕ_2: volume fraction of resin1,2
m_1, m_2: molecular weight of resin1,2

Figure 2. Compatibility prediction of between two resins based on Flory-Huggins theory

In this study, ΔG_{mix} was adjusted to generate an immiscible resin system only by controlling the χ parameter. Other variables in the equation for ΔG_{mix} were held constant by fixing the number average molecular weight at 5000 using fractionated gel permeation chromatography, and by fixing the volume fraction φ at 0.5. As a result of the χ parameter calculation between various kinds of common polyester in our laboratory by the COSMO method, the combination of PES-1/PES-2 had the largest χ, 0.15. However, the PES-1/PES-2 blend still was totally miscible as shown by optical microscope observation (Figure 3).

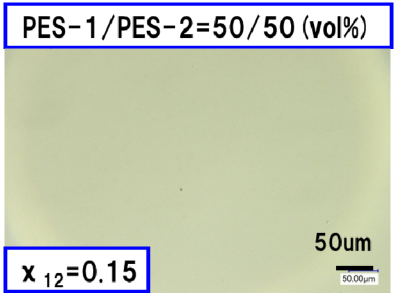

Figure 3. Optical micrograph observation of PES-1/PES-2=50/50 (vol%) blend.

On the basis of this result, the χ parameter value above 0.15 was examined. In this system, IPA and AS moiety act to increase the χ parameter. However, in the PES-1/PES-2 system, a big volume fraction in the resin was occupied by the BPA based monomer (Figure. 4). Therefore IPA and AS, which occupy a small volume fraction, are not effective for increasing the χ parameter. On the basis of this hypothesis, we examined the χ parameter increase by replacing the relatively large BPA monomer with a smaller di-alcohol molecule, 1,2-PD.

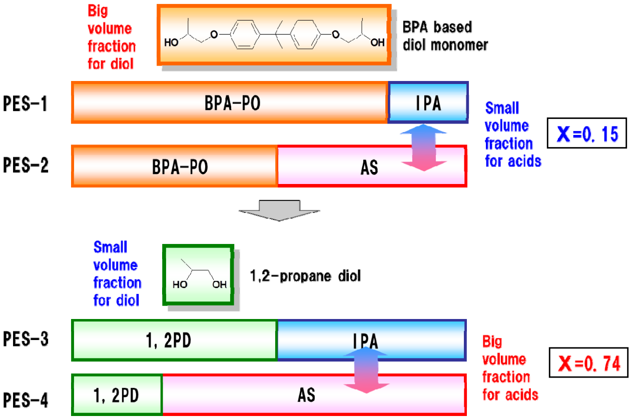

Figure 4. Increment of χ by using small volume fraction diol monomer, 1,2-PD.

From the COSMO calculation, the χ parameter increased dramatically from 0.15 to 0.74 for the PES-3/PES-4 system. This binary system was immiscible as confirmed by the optical microscope observation (Figure 5).

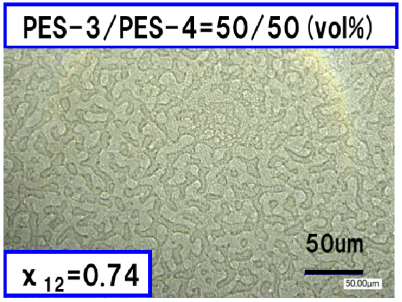

Figure 5. Optical micrograph observation of PES-3/PES-4=50/50 (vol%) blend.

Determination and control of interfacial thickness of binary resin system

An interfacial thickness λ was estimated by ellipsometry for PES-3/PES-4 binary system. According to a result, the λ was only 10nm, less than 30nm which is required for sufficient adhesion between the core and shell. There was a concern that the shell layer would peel from the core surface, so we examined a resin system with lower χ parameter based on PES-4.

As a result of trying various polyesters combinations, the χ parameter could be reduced to 0.17 by decreasing AS amount based on PES-4 which was attained by partial replacement of AS by IPA (PES-5: Figure 6). The λ between PES-3 and PES-5 became 80nm. This λ is in a preferred range in the view of the controlled interfacial diffusion and adhesion. The strong relationship between χ parameter and λ is shown in figure 7.

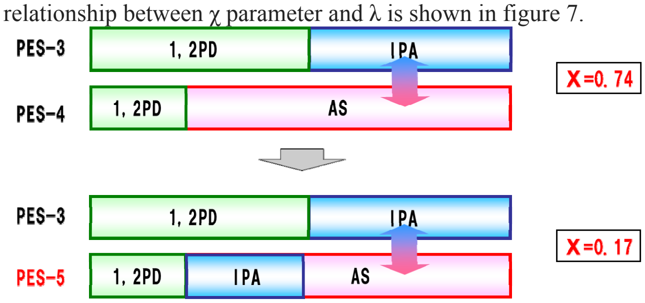

Figure 6. Precision control of χ parameter by AS volume fraction.

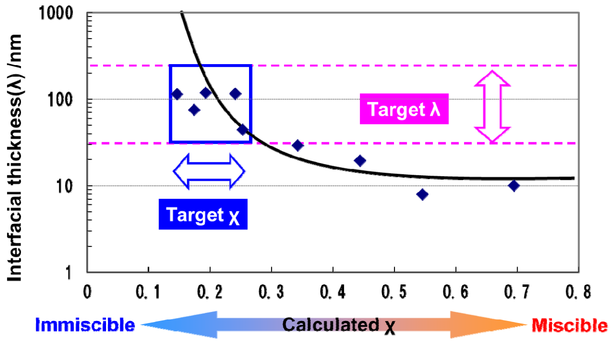

Figure 7. Calculated χ parameter and Interfacial thickness λ relationship

Properties of toner with controlled interfacial thickness λ between core and shell resin

The fusing temperature and storage temperature of the toner were investigated and the results are shown in Figure 8. The toner with miscible core and shell combination (TONER-A; PES-2 for core/PES-1 for shell) was on the common trade-off line in the relationship between fusing and storage because it was thought the toner was homogeneous. On the other hand, the toner with controlled λ between core and shell resin (TONER-B; PES-5 for core/PES-3 for shell) achieved the combination of lower fusing temperatures and better storage stability. It is believed that the reason the toner shifted away from the common trade-off between fusing and storage stability was that the toner formed ideal core shell morphology as shown in Figure 9.

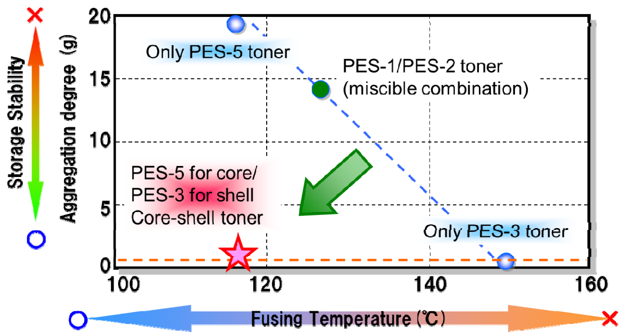

Figure 8. Fusing temperature and storage stability relationship

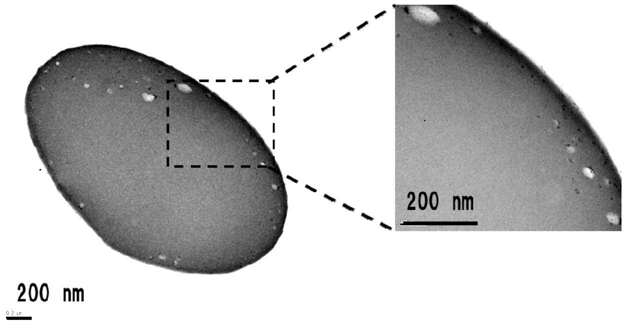

Figure 9. TEM image for morphological observation of TONER-B.

Conclusions

The study of the improvement of core-shell toner by controlling the interfacial thickness between core and shell polyesters has led to the following conclusions:

1) Flory-Huggins χ parameter was controlled by the monomer composition, and the monomer volume fraction in a continuous fashion.

2) A strong relationship between calculated χ parameter and interfacial thickness λ of polyester/polyester binary interface was observed.

3) By carefully controlling the interfacial thickness λ, a core shell toner was designed that provided the combination of low temperature fusing and good storage stability.

Reference

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Author Biography

Dr. Tomohide Yoshida received his PhD in polymer chemistry from Osaka University in 2005. And he moved to University of Minnesota as a post-doctoral researcher. His research was based on the development of living polymerization system through the academic studies. Since 2009, he has been working for Kao Corporation in the field of toner binder development for chemically prepared toner based on polyesters.