Complete incorporation of wax in polyester CPT using polyester-encapsulated wax emulsion

Machiko Ie, Tomohide Yoshida, Shoichi Murata, Eiji Shirai; Kao Corporation, Performance Chemicals Research Laboratories, Wakayama, Japan

Abstract

Polyester-encapsulated wax emulsions were investigated in the synthesis of polyester CPT to achieve a toner with complete incorporation of wax. The toner provided not only low-temperature fusing, but also improved durability, storage stability, and reduced contamination of print engine components. Polyester-encapsulated paraffin wax emulsions were prepared by phase-inversion emulsification with MEK as the solvent. To achieve good compatibility between the polyester resin and wax, the resin hydrophobicity was increased by grafting of hydrophobic moieties, including alkenyl succinic anhydride and styrene acrylate segments. With these resins, however, there was wax bleeding and separation of wax from the polyester emulsion. After evaluation of several resins, we found the following key conditions to achieve polyester emulsions with encapsulated wax. Firstly, the polyester was grafted with styrene acrylate segments containing long alkyl chain monomer such as stearyl methacrylate. Secondly, the wax was added internally to the hybrid polyester resin during resin synthesis. By using a resin produced under these conditions, the wax and polyester were emulsified with complete encapsulation of the wax, as confirmed by TEM. An EA toner was prepared from this emulsion and no wax was observed on toner surfaces by SEM. This means the wax stayed completely encapsulated even during coalescence, which was at a temperature above the wax melting point. In performance testing of the toner, the durability, storage stability and machine contamination levels were improved dramatically.

Introduction

In full color laser printers and copiers, the performance requirements include high speed, fine image quality, and low-energy fusing in view of the environmental friendliness [1].

To improve the performance of low-energy fusing in terms of toner production methods, the emulsion-aggregation (EA) methods have an advantage in the control of toner size, shape and the structure like core-shell structure. At NIP30, we reported on controlling the interfacial thickness between the core and shell resins by adjusting the Flory Huggins χ parameter of resins to make an "ideal" core shell toner [2-4]. The main material component of toner is the binder, which is usually polyester resin or styrene acrylic resin, and polyester resin is generally preferred to achieve the balance of low-energy fusing and good storage stability. Using EA methods, we tried to fabricate toner from polyester resins and toner functional materials, such as a wax, pigment. But wax bled out through the polyester resin during the core-shell coalescence process above the glass transition temperature (Tg) of polyester resins. Wax is a key material for toner in oil-less fusing systems and is required for good anti-offset fusing window. With styrene acrylate CPT, it is relatively easy to incorporate the wax within the toner due to the resin hydrophobicity [5]. With polyester CPT, however, the resin is relatively hydrophilic, so wax incorporation can be a challenge.

In this paper, we report on methods to keep wax from bleeding out through polyester toner. We found that wax emulsified with surfactant was not incorporated well in CPT, so we tried to fabricate polyester-encapsulated wax emulsion without surfactants.

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), and terephthalic acid (TPA). The mixture was reacted at 235°C for 10 hours, further reacted at 8kPa for 1 hour. Fumaric acid (FA) was added at 210℃, and then the mixture was reacted at 210°C for 4 hours.

PES-2; Prepared in the similar method of PES-1, except for using alkenyl succinic anhydride (AS) instead of FA.

PES-3; A 10L four-neck flask equipped with a nitrogen inlet tube, a rectifier, a stirrer, and a thermocouple was charged with BPA-PO, TPA. The mixture was reacted at 235°C for 10 hours, further reacted at 8kPa for 1 hour. The mixture was cooled to 160°C. And then styrene containing acrylic acid and di-t-butyl peroxide was dropped into the mixture at 170℃ for 1 hour. After another 1 hour, FA was added at 210℃, and then, the mixture was reacted at 210°C for 4 hours.

PES-4; Prepared in the similar method of PES-3, except for using not only styrene but also stearyl methacrylate (SMA).

PES-5; Prepared in the similar method of PES-4, except for adding paraffin wax (mp=75 ℃) to the flask before dropping styrene solution.

The composition and the glass transition temperature (Tg) of reacted polyester resins are listed in Table 1.

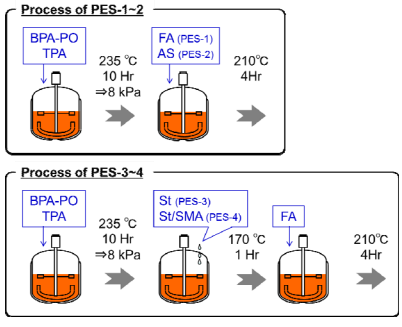

Figure 1. *The synthetic process of polyester resins (PES-1~4).*

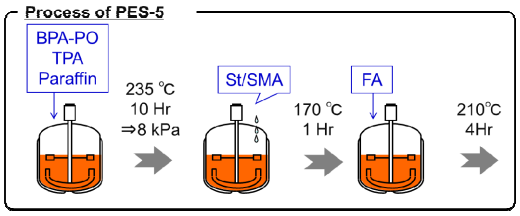

Figure 2. *The synthetic process of polyester resins (PES-5).*

Table 1. Properties of the Experimental Polyester Resin

PES	Resin composition			Tg[1)]
	Polyester Unit	PS Unit	Others	
1	BPA-PO/TPA/FA	-	-	60
2	BPA-PO/TPA/AS	-	-	55
3	BPA-PO/TPA/FA	St	-	42
4	BPA-PO/TPA/FA	St / SMA	-	42
5	BPA-PO/TPA/FA	St / SMA	Praffin Wax	42

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

Preparation of polyester-encapsulated wax emulsions

Polyester-encapsulated wax emulsions were made in neutralization process and phase inversion process with methyl ethyl ketone (MEK) as the solvent.

EM-1E; At first, a 2L four-necked flask equipped with a cooling tube, a stirrer, and a thermocouple was charged with ester wax (mp=79 ℃), PES-1 and MEK as shown in Table 2. The mixture was heated to 73℃, at which point wax is dissolve in MEK. And then, sodium hydroxide was added to neutralize carboxyl group of polyester. Next, the water was dropped to the flask to cause phase inversion. Finally, MEK was removed from the flask.

EM-2E~4E; Prepared in the similar method of EM-1E, except for using PES-2~4 instead of PES-1.

EM-4P; Prepared in the similar method of EM-4E, except for using paraffin wax instead of ester wax.

EM-5; Prepared in the similar method of EM-4P, except for not charging wax.

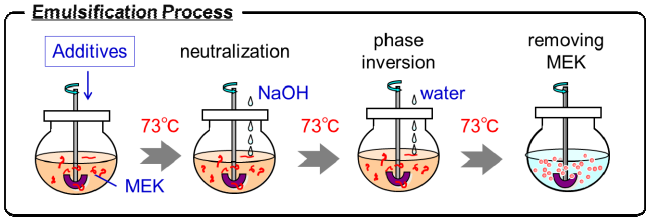

Figure 2. *The preparation of polyester-encapsulated wax emulsions*

Table 2. The composition of additives

EM	Additives	
	Resins	Wax
1E	PES-1	Ester wax
2E	PES-2	Ester wax
3E	PES-3	Ester wax
4E	PES-4	Ester wax
4P	PES-4	Paraffin wax
5	PES-5	-

Preparation of toner

TONER-5; A 2L four-necked flask equipped with a cooling tube, a stirrer, and a thermocouple was charged with EM-5 and colorant dispersion (Pigment Blue 15:3) and with common emulsification aggregation methods. Coalescence process was treated at 80ºC for 1h. And then, the prepared dispersion was cooled and 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.

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.

Transmission electron microscopy (TEM) observation

The morphological property of the EM-5 was observed by transmission electron microscopy (Hitachi 800) 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

Problem of polyester-encapsulated wax emulsion

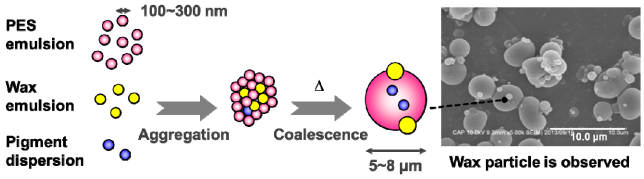

Figure 3. *The preparation of polyester toner in conventional process*

At first, we prepared CPT by a conventional process using three separate emulsions of polyester, wax and pigment. But in the coalescence process, a lot of wax appeared on toner surface as shown in Figure 3. We thought the surfactant made wax bleed out in the water. To prevent the wax bleeding, we tried to make wax emulsion without surfactant. We designed polyester resins as alternatives to surfactant, and tried to make polyester-encapsulated wax emulsion.

First, using a general polyester (PES-1) and ester wax, we tried to make EM-1E. During the solvent removal process, some centimeter-sized aggregates were generated. Upon analysis, the large aggregates were identified as wax. To better encapsulate the wax with polyester, we studied how to improve the wax affinity of polyester.

Introduction of hydrophobic group to polyester

We tried to introduce hydrophobic groups to polyester in order to improve affinity for wax. First, we introduced AS having a long alkyl chain (PES-2). When we made EM-2E, the PES-2 couldn't cause phase inversion after dropping the water in the emulsification process. The reason why PES-2 couldn't cause phase inversion was that PES-2 had decreased affinity for the water.

Then we designed the hydrophilic polyester grafted on the hydrophobic styrene to balance the emulsification ability with the affinity for wax. We made EM-3E using polyester grafted on 40wt% polystyrene in entire resin (PES-3). At that time, there is not any aggregation. With EM-3E emulsion, there were no large aggregates of wax, so we could make polyester-encapsulated wax emulsions by using PES-3.

After 2 weeks storage, however, μm-sized aggregates appeared in the EM-3E emulsion, as shown in Figure 4. The aggregates were identified as wax.

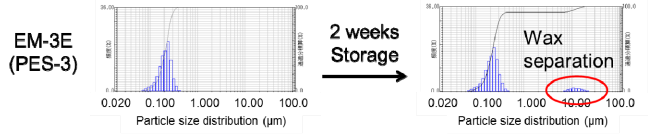

Figure 4. *The particle size distribution of EM-3E after 2 weeks storage*

After 2 weeks storage, we observed EM-3E particles using TEM. We found there were air holes on particle surfaces, so we guessed that wax was partially exposed at particle interfaces and the exposed wax was removed from emulsion particles causing wax aggregation. Next, we tried to achieve better encapsulation of wax to prevent exposure on the surface.

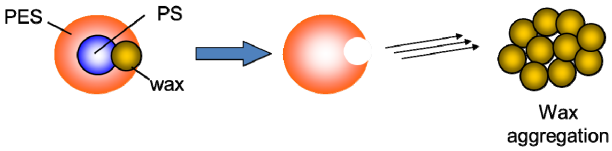

Figure 5. *The hypothesis for wax aggregation*

To improve the wax affinity of polyester resins, we grafted polyester on 80wt% polystyrene. Then we tried to prepare polyester-encapsulated wax emulsions using this resin, but phase inversion could not be completed due to low affinity of the resin for water.

Next, we tried to locally introduce more hydrophobic group to the polystyrene segments. We co-polymerized polystyrene with SMA having long alkyl-chain (PES-4). When we prepared emulsion EM-4E using PES-4, we could get emulsions having particle size distributions with single peak, like EM-3E. But furthermore, EM-4E didn't produce μm-sized aggregations after 2 weeks storage as shown in Figure 6. TEM observation showed that there was no exposed wax at the particle surface.

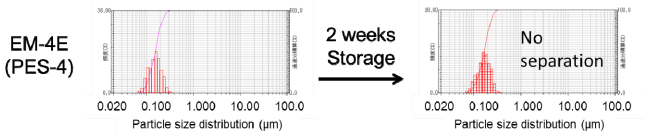

Figure 6. *The particle size distribution of EM-4E after 2 weeks storage*

According to the result of EM-1E~4E, we found that hydrophilic polyester grafted on hydrophobic polystyrene is suitable for encapsulating wax. A short summary is shown in Table 3.

Table 3. The result of emulsification in use of EM-1E~4E

EM	Could it be emulsified?	Was it single dispersion?	Was it stable after 2weeks?
1E	Yes	No	-
2E	No	-	-
3E	Yes	Yes	No
4E	Yes	Yes	Yes

Trial of encapsulating paraffin wax

Since paraffin wax is a common alternative to ester wax in toner production, as a next step, we tried to encapsulate paraffin wax.

At first, to encapsulate paraffin wax, we chose PES-4, which could successfully encapsulate ester wax. But even with PES-4, polyester-encapsulated emulsion of paraffin wax (EM-4P) was not successful. After emulsification process, the flask contained a plate-like mass of separated material which was identified as paraffin wax. In emulsification trials of PES-1 and ester wax, centimeter-sized wax aggregates were produced, but with PES-4 and paraffin wax, the wax completely separated and produced a

plate-like mass. Because the state of exposed wax in emulsification process was different between ester wax and paraffin wax, the failure mechanism for encapsulation of wax must be different.

We observed each process and found that the state of dissolving wax in MEK was different. When we dissolved PES-1 and ester wax in MEK in emulsification process, the solution was transparent. On the other hand, when we dissolved PES-4 and paraffin wax in MEK, the solution was cloudy. We confirmed that separate solutions of the two components, PES-4 and paraffin wax, in MEK were both transparent. This showed that the paraffin wax was absolutely separated from PES-4 in MEK, which is why polyester-encapsulated wax emulsion couldn't be prepared. To make polyester-encapsulated wax emulsion, the polyester resin needs to work as surfactant to provide stability to the dispersed particles of wax. When paraffin wax was separated from polyester resin in EM-4P, paraffin wax could not be dispersed.

To prevent paraffin wax and polyester from separating, we tried to pre-disperse paraffin wax in polyester resin by adding the paraffin wax in the polyester synthesis process. The paraffin wax could be pre-dispersed in the resin withμm-sized wax domains. When we used PES-5 with pre-dispersion of wax to make emulsion, we successfully produced polyester-encapsulated paraffin wax emulsion (EM-5). The emulsion was stable after 2 weeks storage with no wax aggregation. And we confirmed by TEM observation that paraffin wax was completely encapsulated as shown in Figure 7.

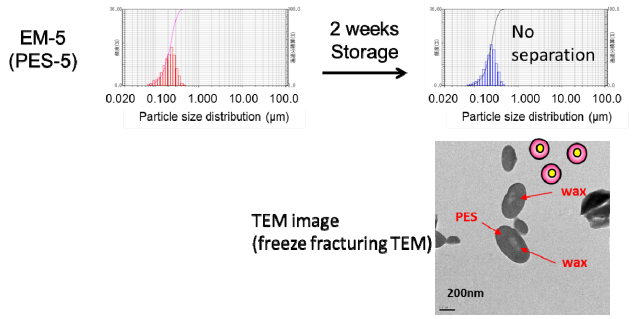

Figure 7. *The particle size distribution and image of EM-5*

EA toner fabricated by using polyester-encapsulated wax emulsions

A toner was produced by EA-method using the polyester-encapsulated paraffin wax emulsion EM-5. A 5-μm sized toner was produced without wax bleeding as shown in Figure 8.

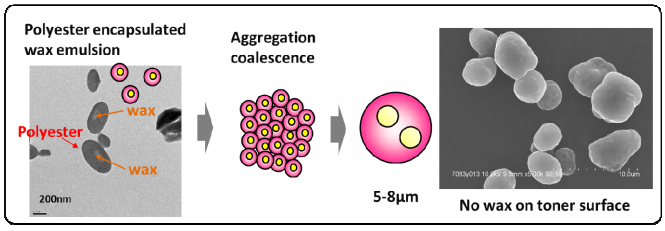

Figure 8. *Image of toner produced with emulsion EM-5*

Conclusions

1) To make polyester-encapsulated wax emulsion, the balance between emulsification and affinity for wax is important. The key of encapsulating wax is using hydrophilic polyester grafted on hydrophobic polystyrene.

2) When grafting group composed with only styrene, the affinity for wax is not enough. Co-polymerizing SMA with styrene is needed to prevent wax from exposing to surface of toner.

3) Even if we used polyester resins which could encapsulate ester wax, we couldn't encapsulate paraffin wax. To encapsulate paraffin wax, we need to finely disperse paraffin wax in polyester resins. It came true by adding wax to synthetic process of polyester resins.

Reference

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Author Biography

Ms. Machiko Ie received her master degree in science from Kobe University in 2012. Her research was based on supramolecular chemistry through the academic studies. Since 2012, she has been working for Kao Corporation in the field of toner binder and emulsion aggregation process development for chemically prepared toner based on polyesters.