

## Fabrication of Black Printing Toner through in situ Polymerization: An Effective Way to Increase Conversion

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### ABSTRACT

**S**tyrene- acrylate copolymer was synthesized in the presence of carbon black through heterogeneous polymerization. The percentage of monomer conversion was measured by gravimetric method. Moreover, PSA, SEM, DSC and GPC were used for studying the particle size, particle size distribution, morphology, thermal properties and molecular weight, respectively.

Color properties were then characterized by spectrophotometric method. The average size of achieving spherical particles was 3.32 with a span of 4.41. The  $T_g$  of the polymeric particles was 66 °C. The results showed that the copolymer was appropriate to be applied as a printing toner. In this study, a redox initiator system was applied so as to improve the monomer conversion, therefore the conversion increased from 20% to 75%. Although other properties such as particle size and distribution, morphology, thermal behavior, molecular weight and color properties were affected by this change, they were in the acceptable range. Prog. Color Colorants Coat. 8 (2015), 115-121 © Institute for Color Science and Technology.

### 1. Introduction

Powder form composite which can create an image or text in photocopy machines and digital printers working based on electrophotography as well as other applications such as microfluidic devices [1-4], is called toner. Image-producing process in electrophotographic systems includes the following

steps: (1) forming an electronic image on a photoconductor drum by applying laser or LEDs, (2) developing an image on the photoconductor drum by transferring the toner on it through electrostatic force, (3) transferring the toner to the substrate, (4) fixing, (5) fusing and (6) cleaning [4]. In order to obtain a

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homogenous mixture, the produced toner should undergo cooling, grinding and pulverizing as well as classifying, all in a step-by-step method [5].

In general, there are physical and chemical methods for toner production. The physical process is time- and energy-consuming and expensive. The product, moreover, will have a low proficiency and quality because of the broad particle size distribution and the non-spherical particle shape. For these reasons, chemical methods such as *in-situ* polymerization have been recently developed to produce toner. Through *in-situ* polymerization method, toner is prepared in a one-step process via polymerization of monomers in the presence of pigment and other additives. Suspension polymerization is the most common method among other chemical methods. In suspension polymerization, because of droplet nucleation, perfect spherical shape particles with appropriate size and distribution with homogeneous components can be obtained [5-7].

Benzoyl peroxide, as a prevalent oil soluble initiator, causes droplet nucleation in suspension polymerization. This initiator reacts with carbon black pigment in black toner production through *in-situ* suspension polymerization [8, 9]. Hayashi et al. [10] and Hayashi and Tsubokawa [11] used the well-known fact that carbon black acts as a strong radical trap to prepare polymer-grafted carbon black via trapping polymer radicals formed by the thermal decomposition of azo- and peroxide-containing initiators. Furthermore, Kiatkamjornwong et al. [8] and Liu et al. discussed the inhibitory effect of carbon black in polymerization reaction in the presence of benzoyl peroxide initiator. As a result of this effect, the conversion of polymerization decreases intensely and it makes product precipitation too difficult [8, 9].

It is obvious that conversion enhancement reduces the production costs through the consumption of residual monomers that are conventionally abundant in such systems. The population of untreated monomers poses harmful environmental impacts. It is to be emphasized that the removal of these monomers is associated with serious difficulties and requires applying expensive methods [8]. Thus, it would be indispensable to lessen the inhibition effect of carbon black, keeping other properties of toner sufficiently

high for versatile applications.

To our knowledge, the conversion of monomer in a toner polymerization media is conventionally low as a consequence of carbon black incorporation. Liu et al. [9] suggest simultaneous addition of azobisisobutyronitrile and benzoyl peroxide as initiators of *in situ* polymerization to reduce carbon black inhibition effect. We hereby intend to justify the fact that an effective way to achieve conversion increment would be applying a *redox* system as an initiator to compensate the inhibition caused by carbon black to meet higher conversions. This water soluble initiator system can create very high active radicals. The reactivity of radicals initiated by *redox* precursor in the presence of carbon black is indeed lower than that of oil soluble radicals. The electrophotographic toner is synthesized through the copolymerization of styrene and butylacrylate. The products are then compared with the purpose of increasing the conversion.

## 2. Experimental

### 2.1. Materials

Styrene (St) and n-butylacrylate (BA) monomers were obtained from Urmia petrochemical (Iran) and Merck (Germany), respectively. Benzoyl peroxide (BPO) was provided by Merck (Germany) and served as initiator. A *redox* precursor composed of sodium formaldehyde sulfoxylate (SFS) reducing agent and tert-butyl hydroperoxide (TBHP) oxidant, sodium dodecyl sulfate (SDS) surfactant and 1, 4-butanediol diacrylate (BDDA) crosslink agent were all purchased from Merck (Germany), while polyvinylalcohol (PVA) stabilizer was obtained from Air products (China). The carbon black (CB) [8, 9] colorant, under the trade name of printex U, was provided by Degussa (Germany). Noticeably, the above mentioned chemicals were all used as received, except for St which was washed with a 10 wt% NaOH solution to remove the hydroquinone inhibitor. The ingredients of polymerization are listed in Table 1.

**Table 1:** Recipe for polymerization reaction.

Materials	Function	Content (phm*)		Reference
		A	B	
Water	Continuous Phase	600	600	
Sodium dodecyl sulfate (SDS)	Surfactant	1	1	[8, 12, 13]
Polyvinyl alcohol (PVA)	Stabilizer	3	3	[8, 9, 14]
Styrene (St)	Monomer	80	80	[8, 12, 15]
Butylacrylate (BA)	Monomer	20	20	[8, 12, 15]
1,4-Butanediol diacrylate (BDDA)	Crosslink Agent	6	6	
Benzoyl peroxide (BPO)	Initiator	1	1	[8, 9]

\* Parts by weight based on 100 parts of monomers

## 2.2. Preparation of polymer particles

In method "A", the disperse phase components are: monomers, an oil-soluble initiator, a crosslink agent and a pigment. The continuous phase included distilled water, surfactant and stabilizer. Continuous and disperse phases were mixed together for 15 min with a homogenizer (HG-15D, WiseTise) at the speed of 7000 rpm. Polymerization was carried out for six hours, at 70 °C under nitrogen purge and agitation speed of 200 rpm by a mechanical mixer (RZR 2020, Heidolph). Precipitation of the product was carried out by centrifuging (VS-550, VISION Scientific) with distilled water. The product was dried for 24 hours in a vacuum oven [8, 9]. To increase the conversion in method "B", the reaction was done similar to method "A" except that the *redox* system was introduced 4 hours after polymerization. The reaction resumed for 2 hours at 70 °C. Adding the *redox* system made the product precipitation so easier merely with repeated filtering and rinsing without centrifugation.

## 2.3. Characterization

The degree of each polymerization scheme after centrifuging and drying was determined by employing gravimetric method. The resultant toners were dispersed in water followed by sonication for about 2 min. The dispersions were prepared for particle size and particle size distribution measurements on a particle size analyzer (PSA, Malvern Mastersizer 2000,

England) in the range of 0.02-2000  $\mu$ m. The

morphology of the polymerized toner composites was observed by scanning electron microscopy (SEM, KYKY-EM3200, China) and the shape factor of toners was determined utilizing image J software. Thermal behavior of the toner was conducted on a differential scanning calorimeter (DSC, PerkinElmer USA). Approximately 5 mg of each sample was loaded on a pan and sealed with a covering lid. Measurements were carried out over a temperature range of 0-150 °C at a heating rate of 10 °C/min in a nitrogenous atmosphere. A high-performance liquid chromatography (HPLC) apparatus with pump and RI-detector, equipped with a PL OligoPore column from Agilent Technologies was employed to determine the average molecular weight, wherein polystyrene standards were used for calibration and chloroform as an eluent. Color characterization was conducted using Ihara SpectroCam (Japan). The spectral reflectance factor of each sample was determined and then transformed into CIELAB colorimetric coordinates ( $L^*$ ,  $a^*$  and  $b^*$ ) using the CIE standard illuminant D65 and the CIE 1964 standard colorimetric observer.

## 3. Results and discussion

### 3.1. Conversion and product precipitation

The presence of carbon black during polymerization process inactivates the primary and propagating

radicals, hence reduces the conversion. This phenomenon is intensified by applying peroxy radical initiators such as benzoyl peroxide which act as strong oxidant for carbon black [8, 9, 16]. So the conversion of polymerization in method "A" is very low (~ 20%) according to Table 2. Precipitation process in this method includes centrifugation which is a time and energy consuming method.

Using SFS-TBHP initiator can increase the conversion from 20% to 75% in method "B", (Table 2). It shows that *redox* initiator system is very effective in conversion increment. *redox* system's production of radicals with high activity can excite a high percentage of monomers to get involved in polymerization [17] and reduce the intensity of carbon black inhibitory. In this method, the density of toner particles is higher than method "A" and the formed particles settled at the bottom of the residual liquid. Therefore, the precipitation process is carried out through filtering and rinsing only. These aggregates are loose and get broken easily.

### 3.2. Morphology, particle size and particle size distribution

The shape of toner particles, also particle size and distribution, have significant roles in the quality of printed images. Because of its uniform charge distribution and high flowability, a toner with a spherical shape is theoretically an ideal toner but spherical toner has some disadvantages such as reducing adhesion to the substrate and reducing the blade cleaning efficiency. These two points are very important in obtaining a toner with the best morphology. The sphericity quantity of the particles can be measured by Equation 1 [7, 18].

$$SF = \left( \frac{(ML)^2}{A} \right) \times (\pi/4) \times 100 \quad (1)$$

Where *SF* is the shape factor, *ML* the maximum length of a particle in  $\mu\text{m}$  and "A" the maximum projected area ( $\mu\text{m}^2$ ) all of which were obtained from SEM images, by "Image J" software in this paper. According to Equation 1, an ideal sphere has the

*SF*=100 and shape factor in the range of 120-140 is desirable for toner particles [7].

In suspension polymerization, because of the high stability of spherical monomer droplets and the creation of polymer particles in these droplets, a spherical morphology is obtained [8, 12, 15]. So according to Figure 1, spherical toner particles can be produced by method "A", where *SF* is 105 in this case. Using SFS-TBHP in polymerization systems in some research studies indicates that produced particles have lumped shapes [19].

As it is shown in Figure 1, the shape factor of synthesized toner increases from 105 to 136 and particles with irregular shapes are obtained with the addition of *redox* system in method "B". So adding *redox* system not only leads to the creation of particles with irregular morphology through emulsion polymerization with homogeneous nucleation, but also destroys the spherical shape of particles produced by suspension polymerization with droplet nucleation. Also, particle size and particle size distribution can affect the image quality. Theoretically, in order to create images with higher resolutions, it is necessary to use toner particles with smaller average diameter size. Moreover, narrow particle size distribution is essential for printing a great quality image because it leads to uniformity in toner particles' charge distribution [7, 8, 12].

The size of polymer particles which are prepared by suspension polymerization is predictable and controllable, there is a direct relationship between monomer droplet size and final polymer particle size, so it is possible to obtain particles with small diameter size and narrow size distribution by controlling the parameters of suspension polymerization [6].

The average particle size ( $d(50)$ ) and particle size distribution ( $\text{span} = d(90) - d(10) / d(50)$ ) of produced toners are presented in Table 2. Toners synthesized by methods "A" and "B" have an appropriate particle size in the acceptable toner range. SFS-TBHP initiator system applied in method "B" leads to the creation of fairly big aggregates which increase the average particle size from 3.3 to 5.6  $\mu\text{m}$ , but the span changes little from 4.4 to 4.7.

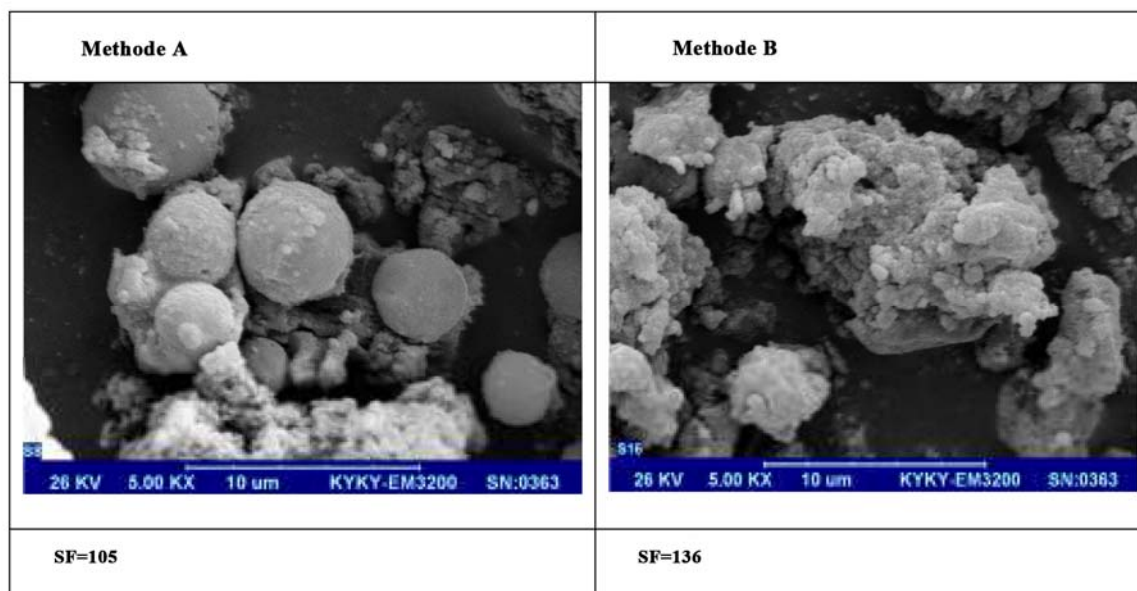


Figure 1: SEM Images of toners.

Table 2: Particle size and particle size distribution and conversion in method A & B.

Method \ Parameter	Particle size (µm)	Particle size distribution (span)	Conversion
Method A	3.3	4.4	20%
Method B	5.6	4.7	75%

### 3.3. Thermal behavior and molecular weight

After the deposition of toner on the substrate, it is fused to form a solid layer, typically through having a contact with a heated roller. The fusing temperature has a direct relationship with glass transition temperature ( $T_g$ ), Therefore  $T_g$  is the best representative for the evaluation of toner thermal behavior. Generally, toners should have a  $T_g$  of about 50–70 °C [2, 8].

DSC results show that the  $T_g$  value of toner synthesized with method "A" is higher than method "B" (Table 3). According to the results of molecular weight measurement (Table 3), it seems that the addition of *redox* system leads to the creation of shorter

polymer chains so the average molecular weight decreases, followed by reducing the  $T_g$  [20].

### 3.4. Color characterization

Investigation of colorimetric values by spectrophotometry method shows that the blackness of toner synthesized through method "A" is more than method "B", because the larger amount of monomer, in polymerization, contributes to the same amount of carbon black, so in order to obtain a better color efficiency, we need to use the larger amount of carbon black in method "B". Table 4 shows the colorimetric values of synthesized toners.

**Table 3:** Molecular weight and  $T_g$  of toners.

Method \ Parameter	Method A	Method B
$T_g$ (°C)	66	61
$M_n$	71200	51900
$M_w$	284600	243400

**Table 4:** Colorimetric values of produced toner.

Colorimetric values	Method A	Method B
$L^*$	11.44	22.63
$a^*$	0.0166	-0.5677
$b^*$	-1.9586	-2.3449

#### 4. Conclusions

Spherical toner particles with a particle size of 3.3  $\mu\text{m}$  and a span of 4.4 were synthesized via suspension polymerization. Applying a *redox* system which has the ability to create high active radicals led to conversion increase from 20% to 75% through reducing the inhibitory effect of carbon black. The

conversion improvement followed by the reduction in the monomer residual also facilitates product precipitation. Besides the conversion, other properties of toner were affected by adding the *redox* system; the particle size and the span changed to 5.59 and 4.69, respectively. Furthermore, the spherical particles changed to particles with lumped shapes.

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