

Stability of Nonaqueous Ink-jet Inks as Studied by Single-Particle Optical Sensing

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Abstract

Non-aqueous ink-jet inks and their long-time stability at different temperatures were studied using single-particle optical sensing (SPOS). Samples ground for the same period but having different amphiphilic polymer additives used for steric stabilization were prepared. SPOS characterizes the particle size distribution at the high end of the particle diameter ($> 0.5 \mu\text{m}$). In the aging at different temperatures, the high-end size distribution exhibited changes ascribed to sedimentation and aggregation. In the absence of aggregation, the decrease of the particle volume was identified as originating from sedimentation; the dependence on particle diameter and viscosity agreed with theoretical prediction. The aggregation appeared as a hump in the tail of the main peak. The hump was more clearly observed for inks aged at a higher temperature and having more loosely adsorbed polymer additives.

Introduction

Ink-jet is one of the major digital printing technologies. Ink-jet printers are used in industrial, home, office, educational, engineering and scientific, and commercial environments. Considering many different climates in which the inks are shipped and stored, the ink stability over time as well as the stability of the inks below, above, and at room temperature is important for all ink-jet inks. The stability can be characterized by the change in the particle size distribution. We used single-particle optical sensing (SPOS) to quantitatively evaluate the size distribution in non-aqueous ink-jet inks and to follow the change in the distribution with time when the ink is subject to temperatures above, below, and at room temperature. SPOS has been used in pharmaceutical, semiconductor, and beverage industries to evaluate the size distribution of large particles.¹⁻³ A stable dispersion should possess a steady particle size distribution over a long time in the whole range of temperatures recommended for storage and usage. The capability of SPOS to capture a few, but large particles among many smaller particles is essential for that purpose.

The function of the polymer used in the formulation of the ink-jet inks was also evaluated. We substituted the polymeric component in the formulation with other polymers and examined their effect on the initial particle size distribution and the long-time stability of the suspension at different temperatures. Polymer is added to a suspension to give steric stabilization. It is necessary that the polymer has a balanced lyophilic part and lyophobic part. The lyophobic part is adsorbed onto the particle surface, while the other part extends into the solvent. Three polymers different in the lyophilic part but identical in the hydrophilic part were used in the present study.

Experimental

Preparation of Ink-jet Inks

For the present study we prepared three magenta pigmented ink-jet inks in a nonpolar hydrocarbon solvent, each processed for 25 hours. All of the three inks, A25, D25 and E25, have the same formulation with the exception of the polymer component. The three polymers used were prepared by grafting alkyl chains (C_{16} to C_{20}) onto linear hydrophilic polymer. Table 1 lists the number of alkyl chains per repeat unit of the polymer. Hydrophile-lipophile balance (HLB) is also listed. The data is from the manufacture of the polymers. All of the ink samples were filtered through a 0.8 μm polypropylene capsule filter. All of these inks had 9% by mass of insoluble components.

For aging studies, we stored the three inks at room temperature, 1, 35, and 60°C using a refrigerator and ovens. A pipette was used to remove a few grams of ink from the middle portion of each vial in one, two, four, and eight weeks after the filtration to measure the particle size distribution.

Table 1: Polymers Used in the Ink Samples

Ink sample	Number of alkyl chains per repeat unit of the polymer	HLB
A25	~4	3-5
D25	~1	9-11
E25	~2	4-6

Particle Size Distribution Measurements

For measurements of the particle size distribution, we used AccuSizer 780 Automatic Particle Sizer (Particle Sizing Systems, Santa Barbara, CA) based on single-particle optical sensing (SPOS).² With simultaneous detection of light extinction and light scattering, the AccuSizer characterizes the size of each particle of diameter between 0.5 and 400 μm and reports the count of particles in each of the size bins equally spaced in logarithmic scale of the diameter. The capability of SPOS to capture a few but large particles among many smaller particles is unique. This is possible even when these large particles constitute less than 0.01% of the total particle volume.^{2,3}

We manually diluted each ink sample with solvent to 3% solids by mass and loaded it with a syringe into the sample loop. Typically we tested a given ink sample three times and took the average of the three runs.

Results and Discussion

Reproducibility of Particle Sizing

Results of the particle size distribution were reproducible. Typical results are shown in Figure 1 for three measurements of D25 immediately after filtration. The particle volume in each size bin is plotted as a function of the particle diameter d .

The three results are close to each other in the range of $d < 1.3 \mu\text{m}$ where the particle counts are high. The run-to-run variation increases with an increasing d . The solid line in the figure represents the confidence level. It was generated by assuming 10 particles per bin.

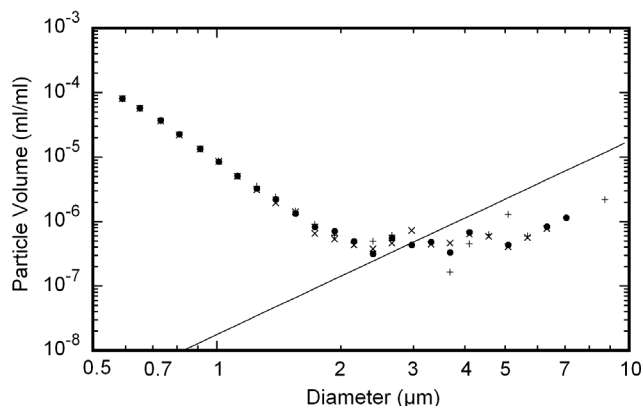


Figure 1. Particle volume distribution of filtered, fresh D25 measured using AccuSizer in three consecutive runs. The straight line represents the confidence level (10 particles per size bin).

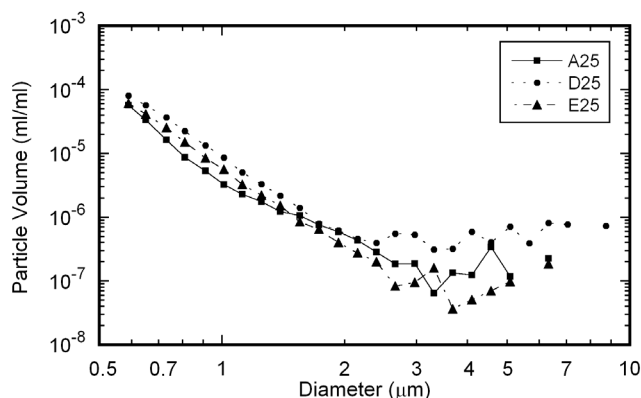


Figure 2. Particle volume distribution of fresh A25 (squares), D25 (circles), and E25 (triangles).

Particle Size Distribution of Fresh Inks

Figure 2 shows the difference in the particle size distribution of filtered A25, D25, and E25. Each data point represents the average of three measurements. For all the samples, the peak is located to the left of the measurement range of SPOS. Our dynamic light scattering results show that the average diameter is 0.24, 0.52, and 0.32 μm for the three inks. The difference in the particle size distribution is attributed to the difference of the polymer used. The high grafting density of the polymer used in A25 makes it easy to

disperse solid particles in the hydrocarbon solvent. The lower the grafting density and hence the higher the HLB, the more difficult to grind the particles, resulting in a higher particle volume in the high end of the distribution. The added polymer changes its function in the dispersion from a suspending agent to a binder with a decreasing degree of alkylation and hence with an increasing HLB.

Aging at Different Temperatures

Mechanisms for Changes of Particle Size Distribution

There are two phenomenological mechanisms for the change in the particle volume distribution. They are aggregation and sedimentation of the particles, and have distinct patterns. When the two mechanisms coexist, distinguishing them may not be easy.

In aggregation, the distribution at smaller particle diameters will be depleted, whereas the distribution at larger diameters will increase. The total particle volume will not change. Since our SPOS system looks at only the high end of the distribution, aggregation may result in an increase of the total particle volume in the range of d shown in the plot. In nonpolar media, cancellation of surface charges by adsorption of countercharges will weaken the electrostatic repulsion, leading to aggregation.

The other mechanism is sedimentation, which will cause a decrease of the particle volume over the entire range of the diameters. The decrease will be more prominent for larger particles. Precipitate of large particles will be visible as settling. The sedimentation should be more serious at a higher temperature, because of the lower viscosity of the solvent.

Changes of Particle Size Distribution

Three parts of Figure 3 show the effect of exposing D25 ink to 60°C, room temperature, and 1°C for four weeks after filtration. In part a (60°C), up to four weeks, the particle volume continues to decrease across the span of d as the sample ages, except the data below confidence level. The decrease is greater at the larger diameters. We consider that the decrease of the particle volume in the whole range of d is due to sedimentation at the elevated temperature. We do not see the effect of aggregation. In part b (room temperature), the particle volume continues to decrease across the span of d , but the decrease is less than the one at 60°C. The result at 35°C was between the results at 60°C and room temperature. The ink at 1°C (part c) shows the smallest changes of the distribution over the four week period.

The changes of E25 over the four week period at each aging temperature are similar to those observed for D25 at the temperature, but the decrease was smaller compared with D25. Apparently the E25 ink is more stable than the D25 ink.

The pattern of change was different in A25. The largest changes occurred at 35°C. The particle volume decreased by nearly the same factor for different diameters. At 60°C, a hump appeared at 0.7–1.0 μm in the two-week aged sample, indicating transfer of particle volume from the range of $d < 0.5 \mu\text{m}$ into the detection range of the AccuSizer. These results indicate that aggregation coexists with sedimentation.

The samples stored at 1°C experienced the smallest change in the particle size, common to all of the three samples. It is due to greater thermodynamic stability of ions in nonpolar media at lower temperatures and slower kinetics (aggregation, sedimentation). Unlike A25 at 60°C, there is no hump visible at 0.7 – 1.0 μm in D25 or E25 up to four weeks. It appears that D25 and E25 are more stable against aggregation than A25 is. The difference is ascribed to a greater fraction of lyophobic part in the polymer used in D25 and E25 compared with the polymer used in A25. The increased hydrophilic nature of the D25 and E25 polymers provides stronger anchoring onto the particle. In contrast, the lyophilic nature of the polymer used in A25 makes the anchoring weak. Then, most of the polymer molecules will not help stabilize the suspension.

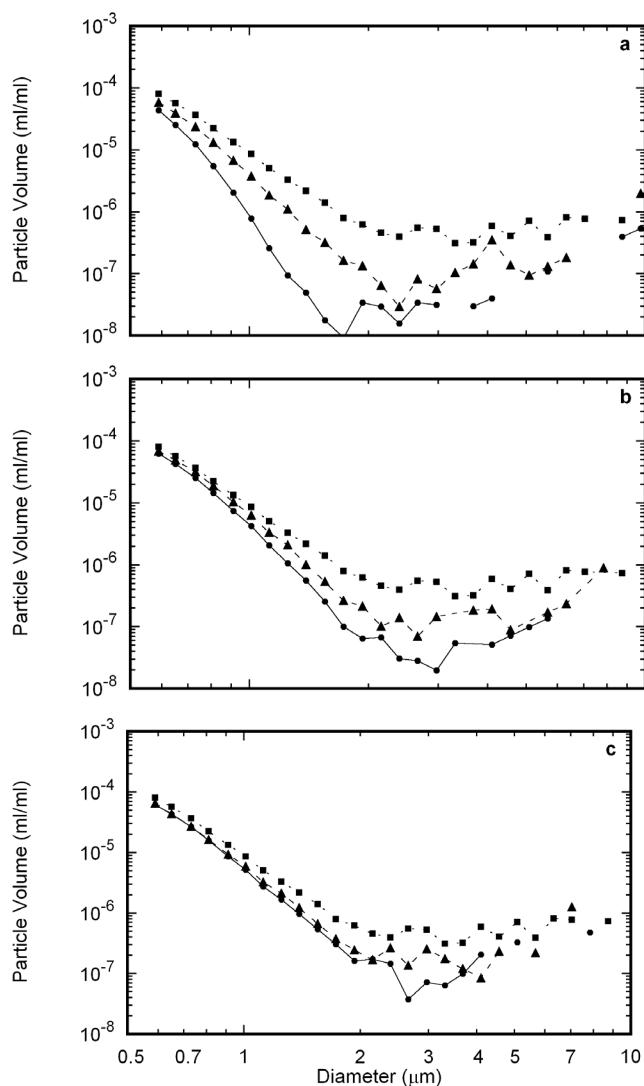


Figure 3. Particle volume distribution of fresh D25 (squares) and after exposure to different aging temperatures for two weeks (triangles) and four weeks (circles). The aging temperature is (a) 60°C, (b) room temperature, and (c) 1°C.

Sedimentation

The change of the particle volume distribution of D25 and E25 will be analyzed in light of the sedimentation mechanism. The half time $t_{1/2}$ at which the concentration of particles at depth z drops to a half of the initial value is expressed by a simple relationship:

$$t_{1/2} = z/v \quad (1)$$

where v is the sedimentation velocity. For spherical particles, $t_{1/2} \sim d^{-2}$.

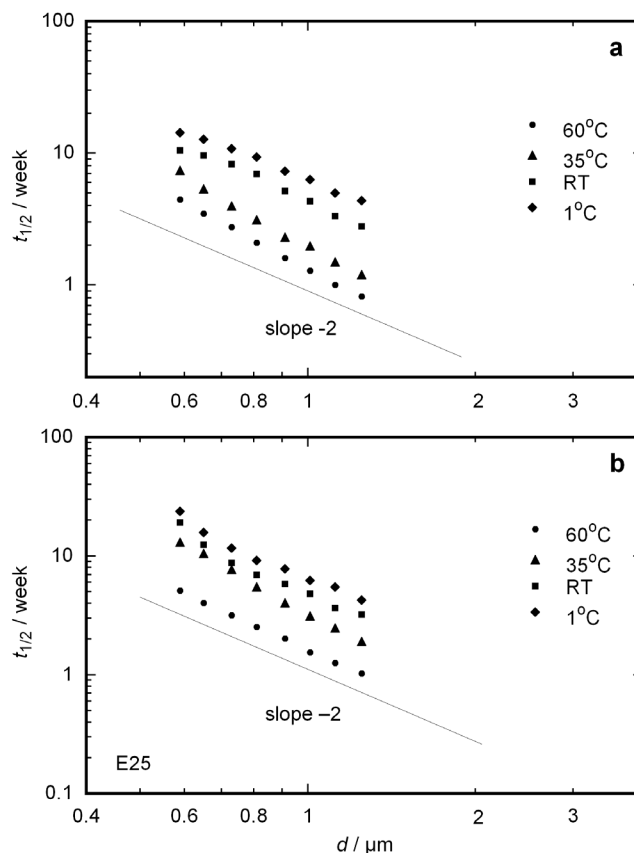


Figure 4. Half time $t_{1/2}$ of (a) D25 and (b) E25 at 60°C (circles), 35°C (triangles), room temperature (squares), and 1°C (diamonds), plotted as a function of particle diameter d . The straight line has a slope of -2 .

Figure 4 shows the plot of $t_{1/2}$ estimated as a function of the particle diameter d for D25 and E25. At each temperature, the half time becomes shorter with an increasing diameter, a reasonable result, since larger particles settle faster. The straight line in the figure has a slope of -2 , which is the exponent in the power-law relationship for solid spherical particles. The half time data at each temperature run parallel to the straight line, indicating that the particles are close to solid spheres and sedimentation is the mechanism for the particle volume change observed in Figure 3. In Figure 4, the half time data for a higher temperature is located lower. In the sedimentation, the terminal velocity is reciprocally proportional to the solvent viscosity. The different traces of the half time data at different temperatures are due to the difference of

solvent viscosity. Reducing the half time by the solvent viscosity brings the different traces close to each other. The longer half time of E25 compared with D25 is ascribed to the difference of the particle density.

Conclusions

The present study demonstrated usefulness of single-particle optical sensing (SPOS) to characterize the high end of the particle size distribution in ink-jet inks. Using SPOS to monitor the change in the high end of the particle size distribution with time for ink samples held at different storage temperatures is a viable method to test the storage stability of the ink suspensions. Exposing the inks to different temperatures changed the particle volume distribution through aggregation and sedimentation of the particles. Changing the chemistry of the amphiphilic polymer used in the ink formulations changed the particle size distribution as well as the stability.

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Author Biography

Caroline Hayes received her B.S. (1996) and M.S. (1998) in Chemical Engineering from Manhattan College. She received her Ph.D. in Materials Chemistry from Polytechnic University (2005). Her research focuses on particle size and stability of nonaqueous ink-jet inks. Dr. Iwao Teraoka was her advisor/collaborator on this project. During her research she was Manager of Process Engineering at Hilord Chemical Corporation in Hauppauge, NY. Currently she is an Ink/Materials Scientist at Cabot Corporation in Albuquerque, NM.