Drop on Demand Inkjet Drop Formation of Poly Ethylene Oxide (PEO) Aqueous Solutions

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Abstract

Research on drop on demand (DOD) inkjet drop formation of polyethylene oxide (PEO) aqueous solutions was conducted. Based on the technique developed by our group, the whole inkjet printing process from ejection to formation of drop(s) was studied. An imaging system with an interframe time of 1 μs and a spatial resolution of 0.81 μm/pixel was used to visualize the DOD drop formation process for a series of poly ethylene oxide (PEO) aqueous solutions with molecular weight ranging from 14,000 g/mol to 1,000,000 g/mol and concentration ranging from 0.005 wt% to 10 wt% jetting from a nozzle orifice with a diameter of 53 μm The dynamics of DOD drop formation was analyzed in detail based on the experimental results.

The addition of a small amount of PEO to fluids may have a significant effect on the DOD drop formation process, depending on PEO molecular weight and concentration. The effects are ascribed to fluid elasticity associated with the addition of polymer.

Introduction

Patterning of polymers on a small scale is of great importance in many areas of modern science and technology, with the applications ranging from the production of integrated circuits, information storage devices, and display units to the fabrication of micro-electromechanical systems (MEMS), miniaturized sensors, microfluidic devices, biochips, photonic bandgap crystals, micro-optical components, and diffractive optical elements [1]. Depending on the requirements of applications, various patterning methodologies, such as writing [2], self-assembly [3] and replication [4], are used. Inkjet printing is a type of writing. Compared to other methods of patterning, inkjet printing has many advantages such as the high flexibility in deposition area, materials and substrates. Inkjet printing has become one of the ideal choices in many cases of polymer patterning. Although inkjet printing technology has been successfully used into a variety of polymer patterning applications [5], the effect of polymers on Drop-On-Demand (DOD) drop formation is still not yet fully understood.

Previous research has been focused on the drop formation of polymer solutions in continuous jetting and dripping mode. Christanti et al. [6, 7] investigated the influence of polymer (PEO) on jet stream break up for continuous jetting. They found that both the polymer molecular weight and polymer concentration affect the breakup dynamics, and showed that solutions with higher extensional viscosity and relaxation time are more effective at retarding break up. Tirtaatmadja, Mckinley and Cooper-White [8] investigated the dynamics of drop formation and pinch-off for a similar series of PEO solutions in the dripping mode. Tirtaatmadja, Mckinley and Cooper-White [8] investigated the dynamics of drop formation and pinch-off for a similar series of PEO solutions in the dripping mode. Low viscosity elastic fluids had similar shear viscosity and surface tensions, but differed substantially in viscoelastic properties. The viscous and elastic stresses were irrelevant prior to the rapid formation of the pinch region, during which the dynamics were controlled by an inertial-capillary balance. However, the rapid decrease in the radius on approach to break-off produced large increased in the extension rate and elastic effects became important. They demonstrated that even at very dilute concentrations, the polymer molecules can be highly extended during the approach to the pinch region. As a result, the elastic stress grew to match the capillary pressure, preventing the neck from breaking off.

The results of the investigation discussed in paper provide information on the drop formation process of PEO aqueous solutions and are useful in formulating inkjet ink containing polymer, which may lead to improvement in inkjet printing quality and polymer patterning control.

Experimental

Visualization System

The method used for visualizing on the DOD drop formation is based on flash photography, and the setup developed by Dong el al. [9] was utilized. The camera, laser system and print head (nozzle orifices having a diameter of 53 μm) are fastened on an optical table to minimize vibration. By synchronizing the pulsed laser, CCD camera with the inkjet print head, sharp images (interframe time of 1 μs and a spatial resolution of 0.81 μm/pixel) of drop formation can be obtained.

Materials

The inkjet inks used for the experiments were dilute aqueous polymeric solutions. The polymer primarily used was poly (ethylene oxide)/PEO which were purchased from Sigma-Aldrich with viscosity molecular weights of 14k, 35k, 100k, 300k, 1000k g/mol.

The solutions (weight concentration, c, ranging from 0.005% to 10%) were prepared by mixing distilled water with PEO at room temperature and were held for at least 48 hours before using. The composition and basic properties of some of the PEO aqueous solution are given in Table 1. The addition of PEO increased the shear viscosity at all molecular weights, but the change was small for the dilute solutions.

Table 1 Composition and basic properties of PEO aqueous solutions

M_w (g/mol)	c (wt%)	[η]	c/c*	η_s (mPa•s)	η (mPa•s)	σ (mN/m)
100,000	0.01	128.0	0.013	1.06	1.12	66.6
300,000	0.01	261.5	0.026	1.06	1.13	69.2
300,000	0.02	261.5	0.052	1.06	1.16	65.9
300,000	0.05	261.5	0.13	1.06	1.26	65.8
300,000	0.10	261.5	0.26	1.06	1.30	65.9
1000,000	0.01	571.9	0.057	1.06	1.13	72.7

The critical overlap concentration, c*, is defined as the concentration at which the polymer coils start to overlap with each other. For c/c* < 1, the solution is considered to be in the dilute regime and the viscoelastic properties of the solution are assumed to be governed by the behavior of a single polymer molecule. In order to determine c* of the polymer solutions studied, the theory of Flory for flexible polymer solutions was used:

$$c^* = 1/[\eta] \qquad (1)$$

where [η] is intrinsic viscosity with units of cm^3/g.

For the polymer solutions, [η] was calculated using the Mark-Houwink-Sakurada (MHS) equation:

$$[\eta] = AM_w^{\alpha} \qquad (2)$$

where M_w is molecular weight with units of g/mol. A and α were assume to be 0.0063 and 0.65, respectively, as recommended by Tirtaatmadja et al. [10] for PEO solutions.

The properties of the inks were characterized using available equipment at Georgia Tech. The static surface tension was measured using a Kruss bubble pressure tensiometer BP21was used to measure the static surface tension. The shear viscosity of the liquids was measured using a Brookfield DI-V+ Viscometer with LV spindle set.

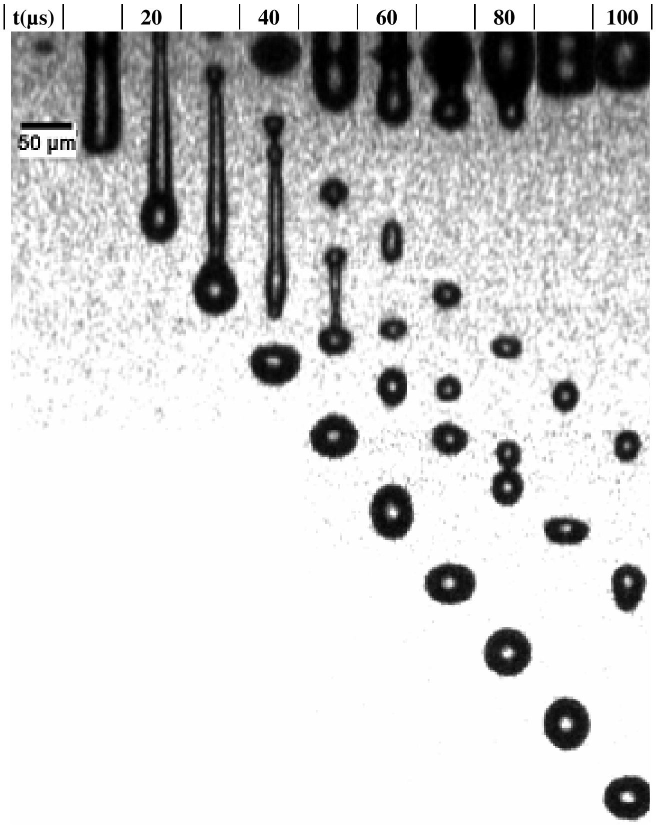

Figure 1 Images of DOD drop formation of distilled water. Driving voltage = 44.2 V, frequency = 20 Hz. Images begin at 0 µs when liquid emerges from the nozzle and are shown for every 10 µs through 100 µs.

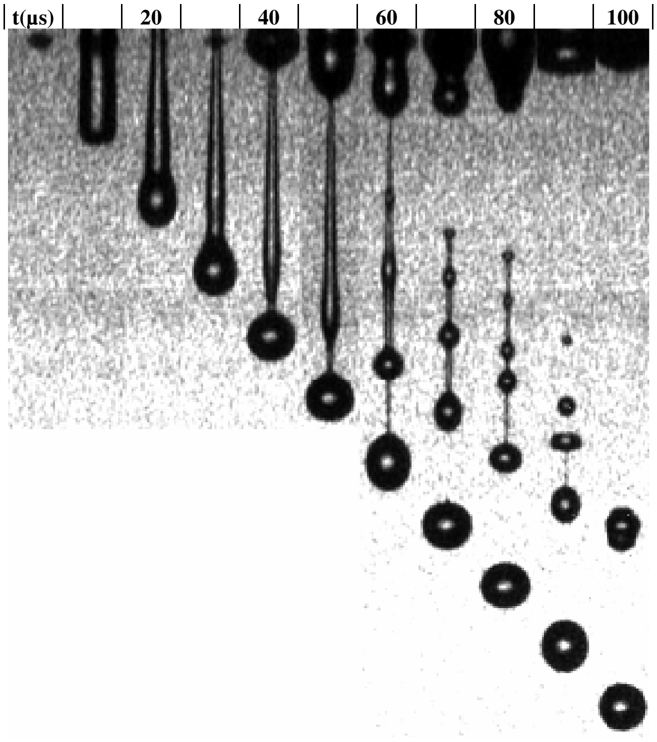

Figure 2 Images of DOD drop formation of aqueous solution containing PEO with molecular weight of 300,000 g/mol, concentration of 0.01wt% and c/c = 0.03. Driving voltage = 44.2 V, frequency = 20 Hz. Images begin at 0 µs when liquid emerges from the nozzle and are shown for every 10 µs through 100 µs.*

Results and Discussion

The effect of the addition of PEO depends on both molecular weight and concentration. For the 14,000 and 35,000 g/mole PEO, the effects are much smaller than those of the larger molecular weight polymers. For example, even for c/c* ~ 1, the changes in breakup time, t_b, and drop speed, v, were small (t_b increased from 31 µs to 32 µs, and v decreased from 6.9 m/s to 6.8 m/s).

Data for PEO having molecular weights of 100k, 300k and 1000k g/mol revealed that the effects of polymer increases significantly with PEO molecular weight. At low concentration, the effects of 100k g/mol PEO were small compared to those of 300k and 1000k g/mol PEO. The effects of the PEO with molecular weight of 1000k g/mol were so large that the ejected liquid did not pinch off from the nozzle for concentrations of 0.02 and 0.05 wt%, and thus no drop was generated.

Image sequences of drop formation for distilled water and an aqueous solution of 300k g/mol PEO at a concentration of 0.01 wt% are shown in Figures 1 and 2. The breakup time for PEO aqueous solution was about 63 µs, compared to a breakup time of 28 µs for distilled water. Satellite formations are also different. For distilled water, the free liquid thread exhibited a clear and quick breakup, which led to four satellites. For PEO aqueous solution, capillary breakup of liquid threads slowed down due to the existence of polymer and bead-like structures were generated along the thread, which were connected by secondary threads. These were connected by secondary threads that eventually broke up, and four or more satellites were formed. After the satellites were generated due to the capillarity, they recombined into one major satellite at about 100 µs, compared to two major satellites which were generated during the DOD drop formation of distilled water.

The leading point, which is the leading edge of the material ejected from the nozzle which eventually becomes the leading edge of the primary drop, is plotted versus time for distilled water and PEO aqueous solution in Figure 3. The two leading point curves were almost identical for times up to about 30 µs. Thus the velocities of the leading points were almost the same during the ejection stage of drop formation. As the liquid was stretched, the velocity of the leading point of PEO aqueous solution decreased. As a result, the primary drop speed of PEO aqueous solution was much smaller than that of distilled water (7.5 and 6.2 m/s, for distilled water and PEO aqueous solution, respectively). Apparently the polymer chains are not appreciably oriented and stretched during the ejection stage of drop formation. Once the ejection stage is over, the ligament attached to the nozzle is stretched due to the momentum of the liquid. The stretching causes the polymer molecules to become oriented and stretched in the flow direction, creating an elastic stress which reduces the speed of the leading point. The elastic stress in the ligament resists the capillary force tending to pinch off the ligament, delaying pinchoff. When PEO concentration is sufficiently high, pinchoff does not occur. If pinchoff occurs, the primary drop size is insignificantly affected by polymer concentration and/or molecular weight. Apparently primary drop size, for a given voltage and surface tension, is determined by nozzle pressure in the initial phase where elasticity effects are small.

Hoyt et al. [10] suggested that the addition of polymer to the ink can reduce the number and size of satellites. The PEO data reported here support their observations; however, breakup time is increased and drop speed is decreased. Also, a longer breakup time lowers the maximum rate of jetting frequency. When the weight concentration of 300k g/mol PEO reached 0.05%, there were no obvious satellites formed, but drop speed was reduced to 1.1 m/s.

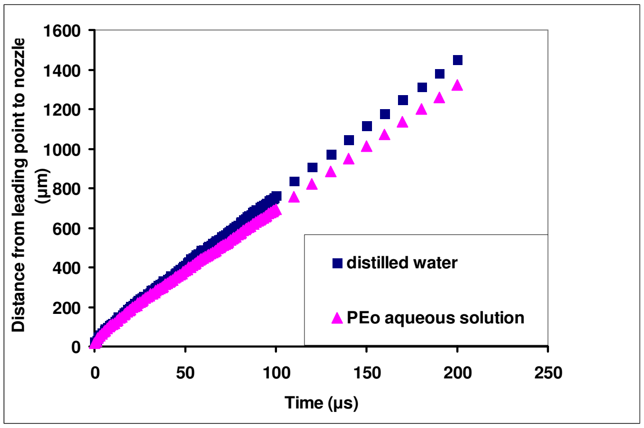

Figure 3 Leading point curves of drop formation process for water and PEO aqueous solution containing PEO with Mw of 300k g/mol and concentration of 0.01wt%. Driving voltage=44.2 V and frequency=20 Hz.

During the stretching of the liquid, the relative rates at which two opposing phenomena occur are important in determining the degree to which the polymer affects DOD drop formation. The elongation of the liquid column causes the polymer chains to be stretched and oriented. At the same time, Brownian motion disorients the polymer chains. After the liquid is ejected from the nozzle and before pinchoff occurs, the polymer chains are stretched and oriented. As a result, an elastic stress develops in the liquid column and resists capillarity-driven pinching off from the nozzle and is responsible for the decrease in drop speed and longer breakup time.

Conclusions

The addition of PEO increases the shear viscosity at all molecular weights, but the change is small for dilute solutions. However, the addition of a small amount of PEO can have a significant effect on the DOD drop formation process, increasing breakup time and decreasing primary drop speed and the number of satellites. The effects of polymer depend on both molecular weight and concentration. At lower molecular weights, the effect of PEO over the dilute solution regime was small when the drop formation process for the dilute solution was compared with that of a Newtonian liquid having similar shear viscosity, and the effect of PEO was small even at concentrations large enough that the solution does not fall in the dilute regime.

As molecular weight is increased, the effects of PEO on the DOD drop formation process increase significantly, and the effects depend on concentration. These effects are explained by the fluid elasticity which increases with increasing in molecular weight and concentration. When the liquid jets out of the nozzle, the polymer chains are stretched and oriented. As a result, an elastic stress develops in the liquid column and resists capillarity-driven pinching off from the nozzle and is responsible for the decrease in drop speed and longer breakup time.

Inks having the similar properties including shear viscosity, which is widely measured by ink jet industry, can behave quite differently in DOD drop formation. In addition to the parameters normally used to characterize inkjet inks, viscoelastic properties that correlate with DOD inkjet drop formation are needed when polymers are added to the ink.

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Author Biography

Xuejia Yan is a Ph D candidate in School of Polymer, Textile and Fiber Engineering in Georgia Institute of technology. He received his master and bachelor's degrees on polymer science in Tsinghua University where he worked on projects of organic solar cell fabrication and thin photoelectric films. He is now working on the project of inkjet printing of polymer solutions to improve the formulation and optimize printing quality of commercialized print heads on different substrates.