Spreading of inkjet droplet of non-Newtonian fluid on solid surface with controlled contact angle at low Weber and Reynolds numbers

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ABSTRACT

The dynamics of inkjet droplet of non-Newtonian fluid on glass substrates was investigated experimentally and compared with that of Newtonian fluid. The non-Newtonian fluids used here were 100 ppm solutions of polyethylene oxide (300k, 600k and 900k) dissolved in the 1:1 mixture of water and glycerin. Weber number (We) was 2–35 and Ohnesorge number was fixed at 0.057 ± 0.003. The wettability of solid substrate was also varied. The diameter of inkjet droplets in the present study was about 50 µm and was much smaller than the size of the previous studies on drop impact. Due to the development of a thin and long thread at the rear of the main drop the jetting window of polymer solution was much narrower than that of Newtonian fluid, and hence the experimental range of Weber number was restricted. The impact scenarios of non-Newtonian inkjet droplets were found to be qualitatively different from those of Newtonian droplets during the receding phase while they were almost the same as the Newtonian fluid case during the kinematic phase. The spreading diameter at the equilibrium was well correlated with that of Newtonian droplets during the receding phase while they were almost the same as the Newtonian fluid case during the kinematic phase. Due to the development of a thin and long thread at the rear of the main drop the jetting window of polymer solution was much narrower than that of Newtonian fluid, and hence the experimental range of Weber number was restricted. The impact scenarios of non-Newtonian inkjet droplets were found to be qualitatively different from those of Newtonian droplets during the receding phase while they were almost the same as the Newtonian fluid case during the kinematic phase. The spreading diameter at the equilibrium was well correlated with that of Newtonian droplets during the receding phase while they were almost the same as the Newtonian fluid case during the kinematic phase.

1. Introduction

Inkjet printing technology has been successfully applied to electronic and bio industries such as flat panel displays and DNA patterning as well as household or office inkjet printers. Specifically inkjet printing is being used in manufacturing color filters patterning as well as household or office inkjet printers. Specif- tronics and bio industries such as flat panel displays and DNA chips and biosensors [3–5]. Currently many researches are being performed in the field of polymer electronics and organic light emitting diods (OLED) displays [6–11]. Considering its importance in the inkjet technology as well as academic interests, in the present research we have focused on spreading of polymeric inkjet droplets on solid surfaces to give an insight into the process- ing of non-Newtonian fluids using the inkjet printing technology for various applications.

The impact of liquid drop on solid surface has been studied for almost 100 years since the pioneering work of Worthington [12,13] on the impaction of water, milk or mercury onto glass surfaces. Since then many experimental studies have been performed on the impaction of millimeter-sized drops onto solid surfaces as well as theoretical and computational studies. Recently Yarin [14] reviewed the drop impact dynamics comprehensively and delineated many interesting phenomena such as splashing, spreading, receding, bouncing and crown formation.

The various dynamic phenomena that arise during the drop impact depend on many factors: material properties such as viscosity, surface tension and density, drop velocity, drop diameter and the wettability of solid surface. To account for these factors drop impact dynamics have been investigated in terms of Weber number (We = ρDU^2/σ), Ohnesorge number (Oh = η/√Dσρ), contact angle (θ) and the maximum spreading factor (β = Dmax/D) in the previous studies, where ρ is the density of liquid, D is the diameter of droplet before impact, Dmax is the maximum diameter of droplet after impact, U is the impact velocity, σ is surface tension and η is the viscosity of liquid. Schiaffino and Sonin [15] explained the impact dynamics in terms of We, Oh, equilibrium contact angle and contact line parameter (λ/α, where λ is the slip length for relieving the stress singularity and α is the radius of droplet). Especially they classified drop impact into 4 different regimes according to Weber and Ohnesorge numbers: when We > 1 the impact pressure becomes the driving force for spreading while the capillarity becomes the driving force when We < 1; When Oh is large spreading is hindered by large viscosity and, when Oh is small spreading behavior follows that of inviscid fluid. Rioboo et al. [16] has explained that the drop
spreading consists of 4 stages: kinematic phase, spreading phase, relaxation phase and wetting/equilibrium phase. During the kinematic phase spreading is dominated by the kinetic energy of the drop. In the spreading phase the drop has a thin film or flat lamella shape. In the relaxation phase the flattened drop shows receding. In the wetting/equilibrium phase the drop takes its equilibrium shape by the contact line movement. They further investigated the impact scenario with the dimensionless time based on the drop velocity and diameter before impact for some sets of Re, We and contact angle and confirmed the four stages experimentally.

In most of the previous studies in the literature the maximum spreading diameter of the drop impacted on a solid surface was studied extensively [17–21]. Chandra and Avedisian [17], Pasandideh-Fard et al. [18] and Mao et al. [19] predicted the maximum spreading by considering the energy balance between before and after the impact and compared with the experimental results. They assumed that the drop had a shape of a circular disk at the maximum spreading condition in all of these studies. This assumption results in a large error when Weber number is small because the drop has a shape of a truncated spherical cap. To account for this problem Park et al. [20] improved the model by assuming that the drop has a spherical cap shape at the maximum spreading condition.

Until now the model predictions have been focused on millimeter-sized drops of Newtonian fluids. However most of the inks used in industries contain particles or large molecules. Also many different kinds of additives such as surfactants are added to stabilize inks. Therefore inks are basically considered to be non-Newtonian. Zhang and Basaran [22], Crooks et al. [23], Cooper–White et al. [24], Mourougou–Candini et al. [25], Bergeron et al. [26] and Bartolo et al. [27] have performed experimental studies using surfactant and polymer solutions and showed that the spreading dynamics of non-Newtonian fluids were different from those of Newtonian fluid qualitatively. In the case of non-Newtonian fluid the receding motion after reaching the maximum spreading diameter was slower and the rise at the center at the end of the receding motion was less high than in the case of Newtonian fluid. These phenomena were more distinct either in more concentrated solutions or in higher molecular weight solutions. Therefore the differences were explained in terms of dynamic surface tension, elasticity and/or first normal stress difference. Especially Bartolo et al. [27] observed that the retraction on a hydrophobic surface decreased abruptly when a small amount of polymer was added and showed that nonlinear elasticity of polymer was responsible for the reduced retraction. In other words polymer molecules contained in the impacting drop induced strong elastic normal stress and this normal stress was counter-balanced by the surface tension force near the contact line. Since the surface tension force drives the receding motion the contact line dynamics have to be influenced strongly. To support this argument Bartolo et al. [27] performed spreading experiments with 2.5 ± 0.2 mm sized drops for Weber numbers between 50 and 200. They analyzed the spreading motion by using a high frame rate camera and compared with the estimated retraction velocity based on the balance of dissipations due to the capillary force and the force due to the normal stress. They have found that the retraction velocity is independent of the impact kinetic energy and is inversely proportional to \( \Psi^{1/2} \), where \( \Psi \) is the first normal stress difference coefficient.

Despite its importance the dynamics of inkjet droplets have not been explored extensively compared to larger drop cases. This is probably due to the experimental difficulty caused by the extremely short time scale of 10 \( \mu \)s. With the recent emergence of flash videography and high performance CCD cameras, there have been attempts at investigating the spreading dynamics of inkjet droplets experimentally. In their studies on Newtonian inkjet drop dynamics Dong et al. [28] found that the initial spreading is affected by the kinetic energy of the droplet, while in the receding motion, the extent of retraction is influenced by the wettability of substrate and impact velocity and the oscillation of droplet increases with the increase in contact angle. They also found that, except the case of large contact angle, the behavior of inkjet droplet is much similar to millimeter-sized drops. They explained the difference in large contact angle cases by the larger Bond number for larger drops where the receding motion becomes smaller due to the action of gravity. van Dam and Le Clerc [29] used the flash videography technique to investigate the spreading dynamics of inkjet droplet using a frame rate of 1 \( \mu \)s. As was reported by Chandra and Avedisian [17] for millimeter-sized drops, van Dam and Le Clerc [29] observed the entrainment of small air bubbles during the impact even in the inkjet process where the width scales is 1–2 orders of magnitude smaller. They ascribe the phenomenon to the entrapment of air between the drop and substrate just before the impact. They also considered the inertial oscillation of droplets in the early stage of impact and found that \( t = \rho D^3/6\sigma (1 - \cos(\theta_{eq})) \) was better suited as the oscillation time scale than the conventional surface tension driven time scale of \( t = \rho D^3/\sigma \) when \( We \gg 1 \). Recently Son et al. suggested that a modified Weber number \( (We' = We/(1 - \cos(\theta_{eq})) \) be better suited to the prediction of the maximum spreading factor \( (P_{\text{max}}) \) for impacting Newtonian inkjet droplets on solid substrate with controlled wettability. In that the air-liquid surface tension was modified in the same form, van Dam and Le Clerc [29] and Son et al. [30] share the common idea of the importance of surface wettability, i.e., contact angle, in the spreading dynamics of inkjet droplets.

As far as the authors are aware of, until now, no study has been reported on the non-Newtonian inkjet droplet spreading. Therefore, the objective of this paper is to understand the low Weber and Reynolds number deposition of non-Newtonian liquid drops on surfaces with controlled contact angle, which has not been explored by the previous inkjet studies. We focused on the effect of added polymers on the dynamics of inkjet droplets and analyzed the experimental results by considering the time scales of polymer relaxation and droplet forming, impacting and receding processes. We have found that the dynamics of receding and oscillation of non-Newtonian droplets were quite different from the Newtonian ones while the magnitude of the maximum spreading was correlated well with the modified Weber number as in the case of Newtonian inkjet droplets.

2. Experiments

To investigate the impact dynamics of inkjet drops we set up an inkjet system as shown in Fig. 1, which is the same as the one the authors used for the previous study on Newtonian inkjet drop dynamics except for some operating conditions. The detailed experimental procedures are referred to Son et al. [30]. The system consists of an inkjet nozzle, a jetting driver (pulse generating system), a high speed camera and an illumination source. Microdrops generated from the inkjet nozzle were impinged on glass surfaces. The wettability of glass surface was controlled by adsorbing a self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS) and a subsequent treatment with UV-ozone plasma.

2.1. Inkjet system and imaging

The inkjet nozzle is a piezo-type nozzle purchased from MicroFab Co. (Model # MJ-AT). The nozzle diameter is 50 \( \mu \)m. The distance between the nozzle tip and glass surface was set at 0.8 and 1.5 mm. In generating non-Newtonian droplets, it has been found to be very important to choose a proper operating condition because, depending on operating conditions, a long ligament is attached to the rear
of the droplet and the recoil of the ligament to the nozzle results in the change of the meniscus of the nozzle tip and hence severe reproducibility problems arise. This situation is somewhat different from the Newtonian case where satellite drops can be followed by the main drop as shown in Fig. 2. To avoid such problems, a well conditioned acoustic wave has to be generated in the nozzle by choosing a proper pressure wave to the piezo element. In this research, we used the wave form shown in Fig. 3: in the figure, the rise time and decay time in the voltage pulse to the nozzle were fixed at 1 μs. The dwell and echo times were varied between 10–40 μs and the echo voltage was set at 30 V. To change the velocity of droplet we first set dwell time, echo time and echo voltage at which no satellite droplets were present, and then we changed the dwell voltage. At this set of conditions drops of 54 ± 6 μm in diameter were generated as shown in Fig. 4(a). All the experimental runs including the spreading were performed at 309 K. This higher temperature than the normal room temperature was caused by the illumination system. At this condition Ohnesorge number of the droplet was 0.055–0.060. The high speed camera (Redlake, MotionPro X-4) was triggered by the jetting driver as a droplet was ejected from the inkjet nozzle. The camera was equipped with a microscopic objective lens (Mitutuyo, M plan Apo 10×, 20×) with the magnification of 20×. As the illumination source a back lighting system (Stocker Yale, # 21AC, 180 W) was installed.

The CCD camera can capture 100,000 frames per second and some of the pictures were taken with this mode. The exposure time was 2 μs. When this fast mode was used the number of pixels per frame has to be small (512 × 20 pixels), hence the quality of picture is not satisfactorily good. One may use the flash videography method to get the better quality as demonstrated by van Dam and Le Clerc [30] and Dong et al. [31]. But, in the case of non-Newtonian drops the reproducibility of drop generation was very poor compared to the Newtonian case, hence it was virtually impossible to use the flash videography method used in the literature. So we used a modified method of the ‘flash videography’ to obtain a series of pictures with better resolution by taking 2 sets of pictures for every 13.4 μs with the time delay of 6.7 μs between the drop impingement and triggering of the shutter of CCD. Then we arranged the pictures and checked the reproducibility. In spite of the limitations in the frame rate and exposure time it was possible to track the shapes of drop within reasonable resolutions in time and space.

### 2.2. Materials

As the Newtonian liquid a 50:50 mixture in weight of distilled water (DW) and ethylene glycol (EG; Sigma Aldrich Co.) was used. As the non-Newtonian fluid polyethylene oxide (PEO; Sigma Aldrich Co.) were dissolved in the mixture of DW and EG. The molecular weights of PEO were chosen to be 300k, 600k and 900k Daltons to vary the elasticity of liquid. The concentrations of the polymer solutions were set at 100 ppm, which reflects the suitable drop generating condition for all molecular weights of PEO. To set this condition we performed drop generation experiments by varying concentrations from 10 to 500 ppm and found that 100 ppm should be the maximum concentration of PEO for our inkjet system. This is because, over 100 ppm of PEO, the ligament recoils to the nozzle tip as shown in Fig. 4(b). Even in the case of 100 ppm solution, if the operating conditions are not chosen properly, the main drop recoils...
Fig. 4. Generation patterns of inkjet drops of a PEO 900k solutions at three different conditions (a) stable generation of the main drop (100 ppm, DT (Dwell time) = 40 μs, DV (Dwell voltage) = 55 V, ET (Echo time) = 15 μs, EV (Echo voltage) = 30 V); (b) the ligament recoils to the nozzle (200 ppm, DT = 40 μs, DV = 40 V, ET = 15 μs, EV = 30 V); (c) the main drop retracted with the retraction of the tail (100 ppm, DT = 40 μs, DV = 40 V, ET = 15 μs, EV = 30 V); and (d) a long tail not detached until the head touches the substrate (100 ppm, DT = 40 μs, DV = 70 V, ET = 15 μs, EV = 30 V) (Scale bar is 50 μm and each time step is 6.7 μs.).

The viscosity of liquid was measured by a rotational rheometer (ARES, TA Instrument) and the surface tension was measure by using the Du Nouy ring method (K9 Tensiometer, Kruss GmbH). Since the polymer solutions were very dilute we consider that the viscosity is constant irrespective of shear rate. The physical properties of the liquids are listed in Table 1.

<table>
<thead>
<tr>
<th>Physical properties of the liquids.</th>
<th>Viscosity (Pas)</th>
<th>Surface tension (mN/m)</th>
<th>Density (kg/m³)</th>
<th>c/ε</th>
<th>Relaxation time (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol 50% + distilled water (base)</td>
<td>0.0032</td>
<td>56.5</td>
<td>1056</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PEO 300, 100 ppm</td>
<td>0.0034</td>
<td>58</td>
<td>1056</td>
<td>0.034</td>
<td>49</td>
</tr>
<tr>
<td>PEO 600, 100 ppm</td>
<td>0.0035</td>
<td>59.3</td>
<td>1056</td>
<td>0.073</td>
<td>105</td>
</tr>
<tr>
<td>PEO 900, 100 ppm</td>
<td>0.0037</td>
<td>58.2</td>
<td>1056</td>
<td>0.12</td>
<td>167</td>
</tr>
</tbody>
</table>
spherical shape under the action of surface tension. This observation is somewhat different from the Newtonian drop formation as compared in Fig. 2. In the case of a Newtonian drop the tail is short and thick. Sometimes satellite droplets are formed as Dong et al. [32] already observed. The time to reach the detachment from the initially stationary meniscus for polymer solution is 100–200 µs, while it was shorter than 50 µs for Newtonian fluids at similar conditions (Dong et al. [32]). In the present study the time to reach the solid substrate after the drop has a spherical shape was set to have 200–400 µs by adjusting the distance between the nozzle tip and the solid substrate. Therefore the time scale from the incipient time of jetting to the impact was 400–800 µs. This time scale for the ballistic path is much longer than the time scale of 10–30 µs for spreading on the solid surface by the inertia. The latter step was called ‘kinematic and spreading phase’ by Rioboo et al. [16] After the impacted drop spreads to the maximum wetted diameter the drop behavior changes depending on contact angle, say the drop continues to spread on a wetted surface or it recedes on a non-wetted surface by the capillary action. The time scale for this continued spreading or receding is found to be 30–100 µs in the present experiment. Finally after the kinematic and receding phase, the inkjet drop takes the equilibrium shape. Upon knowing the time scale of each phase we now consider what the conformation of polymer molecules will be at each step and how such conformation will affect the spreading dynamics. To understand the dynamic behavior of polymers in inkjet drops we next consider the coil-stretch transition of polymers.

3.2. Polymer coil-stretch transition

To predict whether polymer molecules are under the stretched or folded state we first consider the relaxation time of polyethylene oxide by the Zimm model considering that the polymer is a linear chain:

$$\lambda = 0.46 \frac{[\eta]_0 M_w T}{k_b T}$$

In the above equation $[\eta]_0$ is the zero-shear intrinsic viscosity of polymer, $M_w$ is the molecular weight of polymer, $\eta_s$ is solvent viscosity, $R$ is the gas constant and $T$ is temperature. The zero-shear intrinsic viscosity was determined by measuring the viscosities of dilute solutions by using Canon-Fenske viscometers of different capillary sizes (Schott-Geräte, Nos. 50, 100, and 150) and extrapolating to zero shear-rate. The viscosities of the dilute polymer solutions were found to be virtually not shear-thinning. From the coil overlap concentration, $c^* = 1/[\eta]_0$, the polymer solutions used in the present study were found to be in the dilute regime. In Table 1 we listed the relaxation times of PEO solutions in the 1:1 mixture of distilled water and ethylene glycol. The relaxation times are in the range 50–160 µs. From the relaxation times one may predict the conformation of polymer chains as follows: the polymer chains are stretched when a drop is generated from the nozzle experiencing high shear rate. Those parts of the polymers in the tail will remain in the stretched state during the flight in the air while the polymers in the head will be relaxed from the stretched state. Then the tail is recoiled and the whole liquid portion becomes one spherical drop. Since it takes 200–400 µs to reach the solid substrate, during this period, the polymers in the spherical drop will fully relaxed and take the self-avoiding wall conformation because PEO is a linear polymer and the solvent is a good solvent for the polymer. As the drop impacts the solid surface the liquid drop spreads and the polymers will be stretched again until it begins to recede or continues to spread by the capillary action. Since the time scale for this kinematic phase of 20–30 µs is much shorter than the relaxation times of polymers and the drop continues to deform with a sufficiently large kinetic energy, the polymers will be stretched accordingly and hence they will remain stretched. When the contact line recedes, the polymers near the contact line will experience strong shear due to the singular nature of the contact line motion which will strongly affect the capillary motion. Considering that the time scale for this motion is 30–100 µs, polymers will affect the receding or spreading motion in general. However it is expected that most of the polymer chains contained in the drop will be relaxed from the stretched state and polymers will affect the motion in the linear viscoelastic regime because the subsequent deformation will not be large. We have sketched the changes in polymer conformation in Fig. 6.

3.3. Overall spreading scenario of inkjet drop

In this research we performed experimental studies on the spreading of non-Newtonian drops and compared the characteristics with the spreading of Newtonian drops. The experimental regime was chosen for small viscosity, impact driven case, i.e., We > 1 and Oh ≪ 1. This is the ‘Region I’ according to Shi-affino and Sonin’s classification [15]. Fig. 7 shows typical drop spreading processes for Newtonian and polymeric liquids when Oh = 0.057 ± 0.003 and We = 4.0 ± 0.2 and 11.0 ± 1.1 on the solid surface of θ = 90°. Since the drop size, surface tension and viscosity are virtually the same for all the fluids Ohnesorge numbers are the same while Weber number is slightly different due to slight difference in impact velocity. In the case of the Newtonian fluid the maximum spreading factor ($\bar{R}_{\text{max}}$) and the spreading time (from the impact to the maximum spread) are 1.4 ± 0.2 and 9.2 ± 2.2 µs, respectively. In the case of polymeric liquids these are 1.4 ± 0.1 and 15.4–23.1 µs, respectively. The Newtonian fluid data are sufficiently close to Dong et al.’s results of 1.4 and 11.2 for Oh = 0.0151, We = 12.8 and θ = 88° for distilled water [28]. From this agreement we may regard that two different sets of experiments were done under the same conditions and hence we can compare our experimental results on non-Newtonian drops with Dong et al.’s results on Newtonian drops.

The overall scenario of the drop impact is as follows: as a drop impacts the solid substrate it spreads firstly by the kinetic energy; after consuming all the kinetic energy, by the capillary action, the drop may recede, continues to spread or oscillate while the contact line is pinned; finally the drop reaches the equilibrium state. In the present experiment after a drop impacts the solid substrate and spreads to the maximum diameter by kinetic energy the contact line is pinned at the position. In the experimental studies of Dong et al. [28], they reported that, when the equilibrium contact angle and Weber number were 107° and 103, respectively, the contact line receded and then the drop rebounded just after the kinematic phase and this retraction was dependent on equilibrium contact angle and impaction speed. We note that the Dong et al.’s [28] experiments on rebound were done at more hydrophobic and higher Weber number conditions than the present experiment. Mao et al. [19] has reported that such recoil and rebounding motion arises when the excess rebound energy $E_{\text{ERE}} = E_s \max \text{spreading} - E_s \text{rebound} / E_s \text{rebound}$ is greater than zero and when contact angle is less than 90°, where $E_s$ refers to the energy possessed in stage I. This observation coincides with the present experimental studies. The oscillation pattern of non-Newtonian inkjet drops was different from that of Newtonian drops. In the case of Newtonian drops, the oscillation period was short and the amplitude became smaller. However in the case of non-Newtonian drops the oscillation period was longer and as the oscillation continued the period was lengthened. As a whole it took longer time for non-Newtonian drops to reach the equilibrium.

3.4. Spreading of inkjet drop during the spreading phase

As described previously the spreading time is defined as the time to reach the maximum diameter by the kinetic energy of drop. In
the case of ideal fluid this can be written to be $t_{\text{ideal}} = D/U$. This time scale is used for defining the dimensionless spreading time, $t_{\text{max}}^{*} = t/t_{\text{ideal}}$. Chandra and Avedisian\[17\] assumed that the dimensionless spreading time was 1 and Pasandideh-Fard et al.\[18\] obtained 8/3 in their theoretical analysis based on the energy balance model. In our experimental condition of $\text{Oh} = 0.057$, $\text{We} = 10–12$ and $\theta = 90^\circ$, $t_{\text{max}}^{*}$ was very close to 1, but a slight increase was observed with increasing polymer concentration ($t_{\text{max}}^{*} = 0.94$ for Newtonian drops and 1.05–1.13 for non-Newtonian drops) as listed in Table 2. The fact that $t_{\text{max}}^{*}$ is not changing much is also reported in the literatures. Dong et al.\[28\] reported that $t_{\text{max}}^{*}$ increases with $\text{We}$ in the case of Newtonian drops, but the value remains between 0.65 and 3 and the deviation from 1 is distinct only for higher $\text{We}$ and larger contact angle than the conditions of the present experiment. Crooks et al.\[23\] also reported that spreading times and spreading factors were the same irrespective of polymer molecular weight in the case of non-Newtonian drops of mm-sizes. It appears that the polymer molecules do not strongly contribute to the spreading motion because the motion is dominated by the inertial effect. Also the strain of the initial drop spreading is not large and therefore the build-up of the extensional stress is limited. Here the maximum strain is estimated to be 1 based on the drop diameter of 50 $\mu$m and the spreading factor ($\beta$) of 1.4. Also polymer molecules are not expected to be relaxed during the short time, and hence polymers cannot contribute much to the initial spreading. A more detailed analysis on extensional deformation will be considered in a later section.

3.5. Dynamics of oscillation of inkjet drop

Fig. 8 shows the changes in the height and spreading factor of Newtonian and PEO solution of 300k from which we can compare

Table 2

<table>
<thead>
<tr>
<th>We</th>
<th>Experimental spreading time</th>
<th>Ideal spreading time</th>
<th>Dimensionless spreading time</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG + DW</td>
<td>8.9</td>
<td>10.7</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>12.1</td>
<td>9.2</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>19.9</td>
<td>7.7</td>
<td>7.8</td>
</tr>
<tr>
<td>PEO 300k</td>
<td>10.5</td>
<td>17.7</td>
<td>16.8</td>
</tr>
<tr>
<td>PEO 600k</td>
<td>5.7</td>
<td>23.1</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>12.3</td>
<td>17.7</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>19.0</td>
<td>15.4</td>
<td>13.8</td>
</tr>
<tr>
<td>PEO 900k</td>
<td>11.5</td>
<td>23.1</td>
<td>20.5</td>
</tr>
</tbody>
</table>
the oscillatory motions of drops of two different fluids. In the figure we defined dimensionless height $\delta$ as $h/D$, where $h$ is the height of spreading inkjet drop and $D$ is the diameter of drop before impact. First the dimensionless height changes show that, in the case of the Newtonian drop the oscillation period is the same while the amplitude is slowly reduced as oscillation continues. But in the case of the non-Newtonian drop both the oscillation period and the amplitude change. The spreading factor changes show that contact lines move slowly to the equilibrium state while the dimensionless height of non-Newtonian inkjet drops show oscillatory behavior. This is because the kinetic energy is not sufficiently larger than the surfaces energy during the kinetic and the spreading phases. In our experiments, kinetic energy of impacting inkjet drop is 0.44 nJ and the surface energy is 0.57 nJ. Since the contact lines are almost pinned in the present study the deformation of drop is not large enough to induce sufficiently large elastic stresses due to polymer deformation and hence the difference between Newtonian and non-Newtonian fluids will be small.

To understand the effect of added polymers on spreading dynamics in more detail we compared spreading behavior of inkjet drops in Fig. 8 and mm-sized drops in Fig. 9. Fig. 9(a) and (b) shows the changes in dimensionless height and spreading factor after the impact of a drop of 1.8 mm in diameter when Weber numbers are 153 and 6.7, respectively. The Ohnesorge numbers are the same at 0.010. The results show qualitatively the same behavior as the experimental results reported by Dong et al. [28] and Crooks et al. [23] for Newtonian and non-Newtonian mm-sized drops, respectively. At high We, the drop does not show oscillation after it is spread to its maximum diameter during the receding stage. In the case of the Newtonian drop the receding takes approximately 20 ms while the non-Newtonian drop takes longer than 50 ms. Bartolo et al. [27] argued that the longer time for receding of non-Newtonian drops was the result of the balance of the non-Newtonian normal and the shear streses of the capillary motion near the contact line. In the case of small We, it is observed that both the Newtonian and non-Newtonian drops show almost the same oscillatory behavior in the present study. This is because the kinetic energy is small compared to the surface energy and therefore the drop cannot spread appreciably by the kinetic energy and the contact line is pinned. To consume the kinetic energy the drop oscillates but the polymer molecules cannot contribute to the oscillatory motion strongly because the motion does not induce large deformation.

If we compare the oscillatory motions of inkjet drops (Fig. 8) and mm-sized drops shown in Fig. 9(b), we notice distinctly different behavior. In the case of the mm-sized drop the oscillation frequency does not change irrespectively of the presence of polymers while in the case of the non-Newtonian inkjet drop the oscillation frequency also changes. Fig. 10 shows the detailed picture of this behavior for both Newtonian and non-Newtonian inkjet drops. We note that the inkjet drop of Newtonian fluid oscillates with virtually the same period which is also observed in the case of the mm-sized drop. But in the case of the non-Newtonian drop the first oscillation takes 40 $\mu$s which is twice larger than the first oscillation of the Newtonian drop at the same condition of $We = 10.1$ and $Oh = 0.057$. At the next oscillation the non-Newtonian drop takes longer time. The difference in period between the first and the second oscillations becomes larger as Molecular weight...
increases as listed in Table 3. The increase appears to be caused by the larger relaxation time of higher molecular weight polymers during the receding stage. As explained previously the relaxation times of polymers have the same order of magnitude as the time for spreading and receding in the case of inkjet drops. But in the case of large drops the time scale for spreading and receding is millisecond which is three orders of magnitude (ms vs. μs) larger than the relaxation times of polymers. Therefore the polymers did not affect the oscillatory motion of large drops at low We. In the case of inkjet drops, however, the deformation rate becomes large enough to affect the oscillatory motion in the receding stage. But the effect appears to be still limited as described in the previous section.

3.6. The effect of extensional viscosity

During the generation of a drop a liquid thread is extended appreciably. In this stage the elongational viscosity will be of paramount importance. Since the primary concern of the present study is the impact dynamics and the elongational stress is fully relaxed during the flight to the solid surface as discussed previously, the elongational stress built during the generation of drop is not expected to affect the spreading dynamics. However, from the changes in the shape of an inkjet droplet during the impact, one may suspect that the extensional stress should affect the dynamic behavior to a large extent. This is because, if the impact motion is assumed to be purely extensional the extensional rate will be approximately 23,000 s⁻¹ during the kinetic spreading phase (This value is obtained when the initial drop radius is 25 μm, the maximum spreading diameter is 35 μm, the spreading velocity is 0.57 ms⁻¹ and the spreading time is 18 μs.) and this large extensional rate obviously exceeds the critical extensional rate for coil-stretch transition. Even though the biaxial- and uniaxial-extensional viscosities could not be measured in the present study since the solutions were too dilute we were able to conclude that extensional stress could not seriously affect the inkjet drop dynamics as discussed below.

The Brownian dynamic study revealed that to have a coil-stretch transition the required induction strain is 2.2 [33]. In the present study the total strain is approximately 1.5 assuming that the deformation is purely extensional and the shapes of the drop are cylindrical. Since the deformation in the kinematic phase will be a combination of shear and extensional deformations the net extensional component will be less than 1.5. Pasandideh-Fard et al. modeled the flow in the kinematic phase as the boundary layer flow and obtained a reasonable result on the maximum spreading factor. This means that, in the kinematic phase, the shear deformation should be dominant and the extensional deformation should be much less than 1.5. Therefore a large extensional stress cannot be developed during the kinematic phase, which in turn means that the inertial effect should be dominant. This is manifested by the experimental observation where almost no difference in the deformation is observed between Newtonian and polymeric liquids during the impact. Rozhkov et al. [34] performed a series of experiments on the impaction of drops with dissolved polymers on cylindrical surface. In this case the extensional component is dominant compared to the shear flow component but still the difference in the maximum diameter between the Newtonian and non-Newtonian fluids was not large. This latter case also demonstrates that the extensional component is not large compared to the inertia even if the extensional component is large than the planar case.

During the retraction stage the extensional deformation is even smaller than the extensional deformation during the kinetic spreading phase. In this case the extensional deformations are 0.8 and 0.87 for Newtonian and non-Newtonian droplets. These values were estimated by dividing the spreading diameter during the receding phase by the maximum diameter during the kinetic phase. We note that these values are much closer to 1 than the values of 0.14 and 0.34 for large drops studied by Crooks et al. [23], in which they found good correlation of the recoil velocity and non-dimensional height of recoil with Trouton ratio. Since the extensional deformation is close to 1 in the present case, as described in the kinetic spreading, no substantial extensional stress should be developed during the receding phase. During the oscillation the contact line is almost pinned and the height changes with time as shown Fig. 8. Also Fig. 7 shows that the foot of drop has smaller contact angle during the receding phase than the equilibrium contact angle due to the pinned contact angle. This also suggests that the shear component should be much important than the extensional component.

In both the spreading and receding phases the estimated extensional deformations are not large enough even when the deformations are assumed to be purely extensional to induce coil-stretch transition. Hence the extensional stress is expected to only a limited effect on the deformation dynamics of a non-Newtonian drop. For a quantitative estimation of the extensional flow numerical modeling studies appear to be required. But this is out of scope of the present study.

### Table 3

Comparisons of oscillation times.

<table>
<thead>
<tr>
<th></th>
<th>1st oscillation time</th>
<th>2nd oscillation time</th>
<th>Difference between 1st and 2nd oscillation times</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG + DW</td>
<td>27.3</td>
<td>24</td>
<td>–3.3</td>
</tr>
<tr>
<td>PEO 300k</td>
<td>38.8</td>
<td>41.6</td>
<td>2.8</td>
</tr>
<tr>
<td>PEO 600k</td>
<td>40.5</td>
<td>50.1</td>
<td>9.6</td>
</tr>
<tr>
<td>PEO 900k</td>
<td>46.1</td>
<td>62.3</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Fig. 11. Equilibrium spreading factors of inkjet drops. (a) Spreading factor (β) vs. Weber number (We = μL̇D/s) and (b) spreading factor (β) vs. modified Weber number (We′ = We/[1 – cos θ_0]). The spreading factor is well correlated with the modified Weber number for 2 decades.
3.7. Equilibrium spreading factor

In the previous sections we considered the spreading dynamics of inkjet drops containing polymers. Practically one of the most important factors of inkjet printing is the ability of fine patterning by controlling the size of dots. The dot size is determined by the spreading factor at the equilibrium state after spreading is finished. Therefore we have investigated the effect of added polymers in the non-Newtonian drops on the equilibrium spreading factor to find out the parameters to control the factor. Fig. 11 shows the experimentally observed spreading factors of drops of Newtonian and non-Newtonian fluids spread on surfaces of different contact angles. In Fig. 11(a) we can notice that the equilibrium spreading factors are not affected by the fluid rheology after the kinetic energy disappears even though different behavior was observed for different fluids during the receding phase. In other words after the kinetic energy disappears the polymers become fully relaxed and do not contribute to the spreading. In Fig. 11(b) we have plotted the equilibrium spreading factor as a function of modified Weber number defined as $W_e = W_e^D(1 - \cos \theta) = \frac{1}{2} \rho U^2 D (1 - \cos \theta)$ to take into account the surface energy by modifying the surface tension term with the work of adhesion as suggested in Son et al. \cite{30} based on the wide range of equilibrium contact angle and Weber number for Newtonian droplets. As in the case of Newtonian fluids the equilibrium spreading factor is well correlated with the modified Weber number. This again reveals that the equilibrium spreading factor is a strong function of surface wettability without being affected by kinetic energy under the experimental conditions chosen in the present study.

4. Conclusion

In this research we experimentally investigated the impact dynamics of non-Newtonian inkjet droplet on solid substrates for the first time. The non-Newtonian fluids used here are 100 ppm solutions of polyethylene oxide (300k, 600k and 900k) dissolved in the 1:1 mixture of water and glycerin. The experimental conditions were chosen so that Weber number was in the range of 2–35 and Ohnesorge number was fixed at 0.057 ± 0.003. The droplet diameter studied here is two orders of magnitude smaller than most of the studies reported previously. Even though the polymer solutions seem to be very weakly elastic since their relaxation times are in the order of 100 µs, due to the very short time scales of drop generation and impact dynamics, Deborah numbers for the drop generation and the impact are not small. Due to the development of a thin and long thread at the rear of the main drop or the retraction of the thread and the main drop to the inkjet nozzle by the elastic effect the jetting window of polymer solution was much narrower than that of Newtonian fluid, and hence the experimental range of Weber number was restricted. The impact scenarios of non-Newtonian inkjet droplets were found to be qualitatively different from those of Newtonian droplets during the receding phase while they were almost the same as the Newtonian fluid case during the kinematic phase. The elastic property of polymer has significant effects from the generation of drop to inertia dominates the deformation. The impact dynamics of large drops were qualitatively different from those of inkjet droplets. The difference is the result of the order of magnitude difference in the time scales of impact process hence the order of magnitude difference in Deborah numbers. The spreading diameter at the equilibrium was well correlated with the modified Weber number $(W_e = W_e^D(1 - \cos \theta_{eq}))$ as in the case of Newtonian fluid, where $\theta_{eq}$ is the equilibrium contact angle. The similarity or disparity between the Newtonian and non-Newtonian cases was discussed considering the conformation of polymer chains during each stage of drop deformation. As the inkjet printing technique begins to widen its horizon to flat panel display industries higher resolution, finer patterning techniques for narrower line width are required. To achieve the required printing resolution in the future inkjet system new methods for generating smaller and smaller droplets have to be developed. Considering that the future inkjet printing will be a low Weber process as smaller droplets are used than studied in the present research, the impact dynamics may not significantly restrict the operating windows.

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References


