Using emulsions to overcome problems associated with the inkjet printing of high-molecular-weight polymers in solution

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Abstract

Emulsions were used to overcome problems with printing high-molecular-weight polymers in solution. A polymer is dissolved in an oil and dispersed in a surfactant solution. The surface tension of the oil/water interface opposes deformation of the oil droplets and thus the polymer chains are shielded from the high extensional strain rates that occur during inkjet printing. Consequently the elasticity of polymers under strain that inhibits jetting of pure polymer solutions is circumvented. The exemplar system is a 40 %wt discontinuous phase comprising a 9.5 %wt methyl benzoate solution of polystyrene (initial M_n *= 487 kDa) dispersed in a 14.8 mM SDS solution. Drops were printed from a 50-µm nozzle and the drying process followed with a high-speed camera. The relative vapor pressure of the continuous and discontinuous phases is an important parameter in the drying process. Best results were obtained when the water evaporated first to leave a spherical cap of the polystyrene solution in oil. Limitations of the use of emulsions to print polymers are discussed.*

Introduction

The inkjet printing of text and graphics onto paper is a widespread and well-developed process in both the printing industry and personal computing. Fundamentally, the technique allows small volumes of fluid to be delivered to a substrate in a controlled and repeatable manner such that high-quality output is achieved. These characteristics have made inkjet printing a suitable candidate for depositing a broad range of materials beyond pigments onto substrates beyond paper [1]. Examples include the fabrication of three-dimensional structures from ceramic inks [2], the deposition of the photoactive layer in solar cells [3] and the printing of conductive silver tracks [4].

High-molecular-weight polymers are traditionally difficult to print by inkjet methodology because of their elastic behavior under the high strain rates experienced during printing. A Newtonian fluid rapidly necks under capillary pressure as it emerges from the nozzle until the pinch point is reached, whereupon detachment takes place [5]. A polymer solution displays the same initial jetting dynamics as a Newtonian fluid of equivalent viscosity [6], but the necking process exposes the material to high extensional strain rates [5]. If the fluid experiences a sufficient extensional rate σ, polymer chains undergo the coil-stretch transition [7]. For a linear polymer, this is expected at $\sigma = (2\tau)^{-1}$, where τ is the longest relaxation time of the polymer. The coil-stretch transition triggers a break from Newtonian dynamics and the drop does not continue rapidly to the pinch point and detach [5]. Instead, a long cylindrical filament is formed between the orifice and the main drop body, with a radius that reduces exponentially on account of the elasto-capillary regime that governs the dynamics [5, 6], The breakoff time is therefore significantly increased versus the Newtonian case and filament lifetime has been shown to correlate with polymer molecular weight and concentration [8]. The non-Newtonian dynamics exhibited by polymer solutions are problematic in inkjet formulations because filament rupture can produce satellite drops that lower printing resolution, particularly if it develops a beads-on-a-string structure [1]. The coil-stretch transition also has an impact along the filament axis. The elastic nature of the uncoiled polymer molecules acts to decelerate the main drop body and, if severe enough, is able to prevent detachment entirely [9]. This deceleration is facilitated by the long lifetime of the filament. The viscoelastic properties of polymer solutions places practical limits on their concentration before printing becomes unmanageable [9, 10]. For polystyrene with a molecular weight of the order 300 kDa, the maximum printable concentration has been reported to be less than 0.5 %wt [10].

We propose that the printing characteristics of polymers can be improved through the use of emulsions. A concentrated polymer solution is dispersed as the discontinuous phase of an oil-in-water emulsion in the presence of a surfactant stabilizer. The polymer is then shielded from extensional strain on approach to the pinch point by the elasticity of the oil–water interface. The interfacial contribution to free energy, G, of an oil droplet of area A is $G = \gamma A$ where γ is the interfacial tension. Deformation of a spherical oil droplet at constant volume increases A. Upon deformation,

$$\frac{dG}{dA} = \gamma + A\frac{d\gamma}{dA}, \qquad (1)$$

where the second term is often labelled the Gibbs elasticity. Surfactant adsorption at the oil-water interface is necessary to stabilize the emulsion against coalescence, but also reduces γ and therefore makes it easier to deform the droplet. If the interface is deformed on a time scale that is short compared to that required for surfactant to diffuse to the newly formed interface, then the number of surfactant molecules per unit area decreases and γ increases. The Gibbs elasticity thus provides an additional stabilization mechanism that opposes deformation of the droplet. If these two mechanisms prevent departure from sphericity, then the polymers contained therein do not undergo the coil-stretch transition and the fluid does not display non-Newtonian properties.

In this paper, we present results on a number of different emulsion formulations in search of a system that displays favorable inkjet printing characteristics and drying dynamics. Our goal was to formulate an emulsion containing high-molecular-weight polymer that would act as a model system and as a proof of principle.

Experimental

Emulsion formulation was varied in order to modify and improve manufacture, printing behavior and drying dynamics. The discontinuous phase comprised polystyrene that was dissolved in a good solvent and gently mechanically agitated for at least a few hours, though typically overnight. The polystyrene was kindly supplied by Dr. L. Hutchings (Durham University, UK). The

Table 1. Physical data relating to fluids used to prepare emulsions.[a] The boiling point T_b and the enthalpy of vaporization $\Delta_{vap}H$ have been used to estimate the vapor pressure p using the Clausius-Clapeyron equation.

Fluid	T_b/°C	$\Delta_{vap}H$ / kJ mol^{-1}	p/kPa
Water	100	+44.0	2.1
Toluene	111	+38.0	2.5
Anisole	154	+46.9	0.24
Methyl benzoate	199	+55.6	0.018
Diethyl phthalate	298	+77.0	2.1×10^{-5}

[a] $\Delta_{vap}H$ for diethyl phthalate from reference [11]. All other $\Delta_{vap}H$ and T_b from reference [12].

organic solvents were toluene (*Fisher, AR grade*), diethyl phthalate (DEP, *Sigma-Aldrich*, 99.5%), anisole (*Sigma-Aldrich*, 99%) and methyl benzoate (*Acros Organics*, 99%). The continuous phase was a surfactant solution in water (Milli-Q). An indication of the vapor pressures of these liquids (see Table 1) were estimated from the Clausius-Clapeyron equation,

$$p = p^* \exp\left(\frac{\Delta_{vap}H}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right) \qquad (2)$$

where p and p^* are the vapor pressures at temperatures T and T^* respectively, R is the molar gas constant and $\Delta_{vap}H$ is the enthalpy of vaporization. The vapor pressures were determined assuming that the temperature at ambient conditions was 293 K and the reference temperature, T^*, and pressure, p^*, were the normal boiling point and atmospheric pressure (101 kPa).

The surfactants used as emulsion stabilizers were SDS (*Sigma-Aldrich*, >99.0%), AOT (*Acros Organics*, 96%), $C_{12}TAB$ (*Alfa Aesar*, 99%) and Tween 80 (*Sigma-Aldrich*). The continuous and discontinuous phases were combined in a PTFE beaker and emulsification was achieved using an ultrasonic horn (*Sonics*, VC505) equipped with a 3-mm stepped microtip. Prior to emulsification, the polystyrene was found to have M_n = 487 kDa and PDI = 1.1 by gel-permeation chromatography, with calibration carried out against linear polystyrene standards. Polystyrene recovered from an emulsion subjected to the ultrasonic horn at 25% amplitude for 10 minutes displayed M_n = 310 kDa and PDI = 1.4. The degradation of polymers under ultrasound is a known phenomenon [13].

Emulsions containing high-molecular-weight polymer were ejected from a piezoelectric nozzle (MicroFab, MJ-ABP-01) with an orifice diameter of 50 μm. The printhead was actuated by a symmetrical bipolar waveform generated by the driver (MicroFab, JetDrive III Controller), with its amplitude adjusted to achieve reliable production of single drops. Drops were deposited onto a hydrophobized glass coverslip positioned in the focal plane of an objective lens (Olympus, 50x, numerical aperture 0.5) mounted directly underneath. An LED (Thorlabs, 505 nm) fixed obliquely to the substrate was focused onto the printing area, so that light was scattered at interfaces and collected by the objective. This allowed the contents of the drops to be imaged during the drying process and was particularly well-suited to revealing fine details. Light from a second LED (Thorlabs, 505 nm) was passed through the rear aperture of the objective to enable better visualization of large continuous features that were in shadow to the first LED. Footage of the drying process was captured on a high-speed camera (*Photron*, FASTCAM APX RS) and calibrated against a slide containing dots of a known spacing (*LaVision*, Micro Calibration Plate).

To prepare the hydrophobized substrates, glass coverslips were cleaned with acetone and ethanol, and then bath-sonicated in a 2 %wt alkaline detergent solution (*Decon Laboratories*, Decon90) for two hours. They were then rinsed with water (Milli-Q) and dried

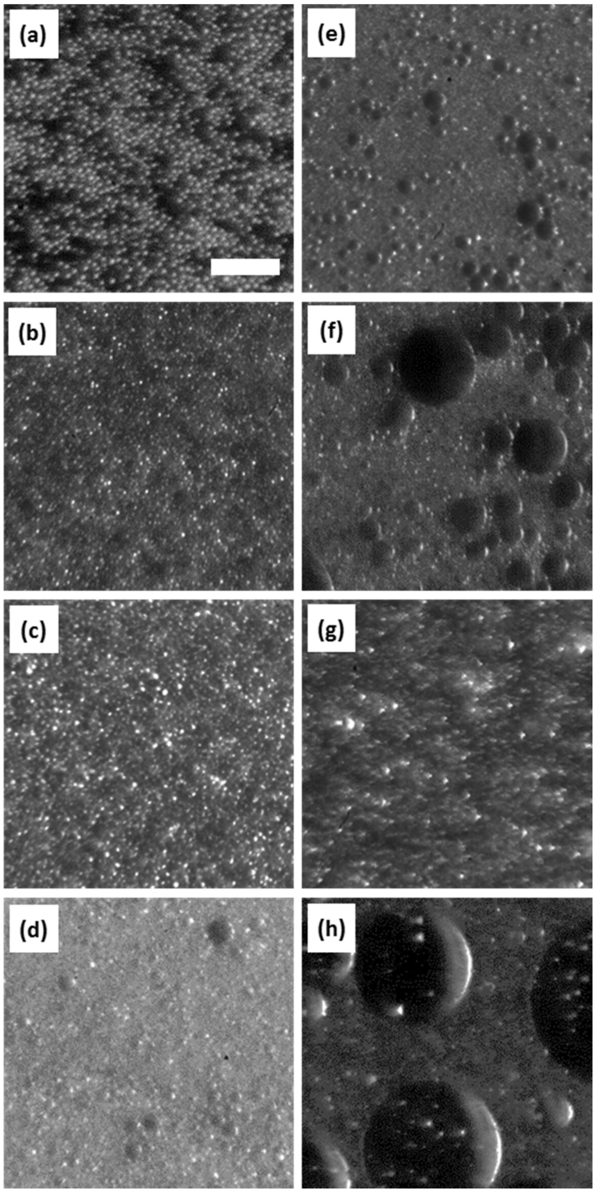

Figure 1. *Images of emulsion aliquots sandwiched between two coverslips. Four different surfactants were implemented in the absence of polymer in (a) – (d). These formulations were emulsions of 30 %wt methyl benzoate and 10 mM surfactant solutions. The surfactants were SDS (a), AOT (b), $C_{12}TAB$ (c) and Tween 80 (d). Emulsions (e) to (h) show the respective emulsions when polystyrene is included in the discontinuous phase. (e) is an emulsion of 10 %wt polystyrene in methyl benzoate (30 %wt overall) and 10 mM SDS. (f) is an emulsion of 10 %wt polystyrene in methyl benzoate (30 %wt overall) and 5 mM AOT. (g) is an emulsion of 15 %wt polystyrene in anisole (20 %wt overall) and 9 mM $C_{12}TAB$. (h) is an emulsion of 10 %wt polystyrene in methyl benzoate (35 %wt overall) and 6 mM Tween 80. Emulsification was carried out using the ultrasonic horn at 25% amplitude for 20 s for (a) – (d) and for at least a minute for (e) – (h). The scale bar is 30 μm.*

thoroughly in an oven. The substrates were hydrophobized by vapor deposition of hexamethyldisilazane (*Alfa Aesar*, >98%) under vacuum overnight. Coverslips were rinsed with water prior to printing.

Results and Discussion

Figure 1 shows how surfactant identity affects the nature of the emulsion produced, in both the absence and presence of polystyrene. Aliquots of formulations were sandwiched between two coverslips and images were captured using illumination from only the obliquely mounted LED. The emulsions generated in the absence of polymer (figure 1 a-d) show that the ultrasonic horn is a suitable means of applying energy to samples in order to break down the discontinuous phase. Visual inspection reveals that SDS (a), AOT (b) and $C_{12}TAB$ (c) facilitates production of dispersed phase drops with a radius less than 2 µm and high monodispersity. The Tween 80 (d) formulation performed less well and displayed a higher dispersed phase polydispersity with some drops exhibiting radii of up to 5 µm. Nevertheless, all of these surfactants enable emulsions to be manufactured with discontinuous phases of a much smaller scale than the 50-µm printhead orifice and would be suitable for printing. The incorporation of polystyrene into emulsions, however, has a dramatic effect on the quality of the formulations (figure 1 e-h). Under these conditions, AOT (f) and Tween 80 (h) produce emulsions that would be unsuitable for printing on account of dispersed phase features with radii of tens of micrometers. SDS (e) and $C_{12}TAB$ (g) perform much better with emulsified drops having radii sub-5 µm. All of the emulsions containing polymer show increased polydispersity versus their blank counterparts. The most likely explanation for this behavior is the manifestation of non-Newtonian properties by the polystyrene solution as the ultrasonic horn divides drops during the emulsification process. This is not unexpected since it is these characteristics that make high-molecular-weight polymers hard to print in the first place. Other methods of emulsification such as shaking by hand and bath sonication did not generate fine emulsions and were thus less successful than the ultrasonic horn. SDS formulations exhibited the best formulation characteristics, giving complete emulsification and the best dispersed phase droplet sizes. Aqueous solutions of SDS were used as the continuous phase during investigation of the dispersed phase solvent.

Figures 2–5 show how the identity of the discontinuous phase influences the dynamics of the drying process and the nature of the deposit. The key characteristics of the organic solvent that influenced overall formulation performance were density and vapor pressure relative to water. Both affect emulsion stability, likelihood of nozzle blockages and the manner in which polymer is deposited on the substrate.

Figure 2 shows images of a toluene emulsion at various times t after printing of a droplet. Initially a large number of emulsified drops can be seen, each appearing as a white spot. They are subject to outward radial migration under the so-called “coffee ring” effect commonly observed in drops with a fixed contact line [14]. Radial convection occurs at low Capillary and Bond numbers (i.e. surface tension dominates over viscosity and gravity) and with pinned contact lines, where the droplet always maintains the shape of a spherical cap during evaporation. As the drop dries, the dispersed phase collects and coalesces at the contact line, reducing overall drop brightness. Polystyrene begins to be deposited before evaporation of the continuous phase is complete and when $t = 3.8$ s a polymer ring starts to develop. The contact line recedes slightly as the polystyrene dries radially inwards. Evaporation is completed at $t = 6.4$ s and the deposit is characterized by a continuous polystyrene ring, with very little material in the center. The nature of the deposit is determined by the fact that the vapor pressures of toluene and water are similar at ambient conditions, so that there is no opportunity for the dispersed phase to coalesce before drying is completed. The tendency of the toluene ($\rho = 0.87$ g mL^{-1}) dispersed phase to cream within the feed to the printhead also presented practical challenges during jetting because the volume fraction of dispersed phase in printed drops fell over time.

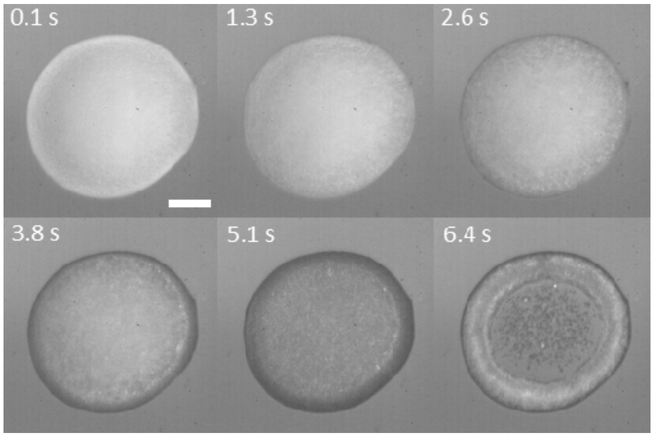

Figure 2. *Images depicting the drying process of an emulsion comprising a 10.0 %wt toluene solution of polystyrene (30 %wt overall) and 14.5 mM SDS. Emulsification was achieved using the ultrasonic horn at 25% amplitude for 120 s. Jetted with a bipolar waveform of amplitude 100 V. The scale bar is 40 µm.*

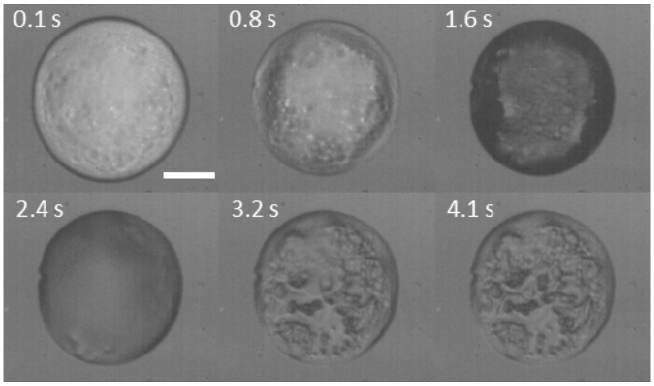

Figure 3. *Images depicting the drying process of an emulsion comprising a 9.9 %wt anisole solution of polystyrene (30 %wt overall) and 14.5 mM SDS. Emulsification was achieved using the ultrasonic horn at 25% amplitude for 120 s, then at 40% amplitude for 60s. Jetted with a bipolar waveform of amplitude 100 V. The scale bar is 40 µm.*

Formulations that used anisole as the discontinuous phase showed different drying dynamics to those when toluene was implemented (figure 3). Initially, the printed drop looks much the same with brightness corresponding to the number of dispersed phase drops. The discontinuous phase moves radially outwards under convective flow and begins to coalesce, as is visible at $t = 0.8$ s. Anisole has a vapor pressure about ten times lower than water and the evaporation of the latter is almost complete by $t = 1.6$ s. The loss of the continuous phase occurs before the discontinuous phase has dried significantly so that only polymer solution remains at $t = 2.4$ s. The result is a continuous, filled polystyrene deposit ($t = 4.1$ s) since the fully coalesced discontinuous phase dries mostly after complete water evaporation. The main advantage of anisole (ρ = 0.995 g mL^{-1}) as the discontinuous phase is that it is neutrally buoyant; the concentration of the dispersed phase remained far more consistent from drop to drop than was observed with toluene.

The printing behavior with DEP as the discontinuous phase is characteristic of organic solvents with a very low vapor pressure at ambient temperatures. Its vapor pressure is of the order 10^5 times lower than water (table 1) which means that it does not evaporate concurrently with the continuous phase in printed drops at all (figure 4). Instead, after complete loss of water at t = 2.6 s, the discontinuous phase fully coalesces to produce a continuous film of polymer solution that shows no sign of drying even after t = 5 min. Whilst this allows for greater deposit control and infrequent nozzle clogging compared to toluene and anisole, this formulation would be impractical for printing polymer films, unless a separate heating step were introduced. Additionally, in this system dispersed phase drops sediment because DEP has a density of 1.12 g mL^{-1}. Over time the discontinuous phase sinks towards the nozzle orifice so that the volume fraction of discontinuous phase in a printed drop progressively increases.

The formulation that gave the best overall printing behavior and drying dynamics contained methyl benzoate solutions of polystyrene as the discontinuous phase. Nozzle clogging was less frequent than when anisole was the dispersed phase and it was possible to print polymer at a higher overall concentration (3.8 %wt). Methyl benzoate (ρ = 1.08 g mL^{-1}) has a tendency to sediment in water, though less severely than DEP. Its vapor pressure is about 100 times smaller than water, giving printing dynamics that are intermediate between anisole and DEP. Figure 5 shows that initially the dispersed phase collects and coalesces at the contact line (t = 1.6 s). Polystyrene does not deposit before the continuous phase has fully evaporated. The discontinuous phase fully coalesces after complete loss of water and forms a uniform spherical cap by t = 3.2 s. The polystyrene solution then dries in under a minute to leave a continuous polymer deposit on the substrate. The optimized formulation contained a discontinuous phase of 9.5 %wt polystyrene solution that comprised 40 %wt of the emulsion and a continuous phase of 14.8 mM SDS. The origin of the fine features of the deposit are unknown. Surfactant makes up 0.25 %wt of this formulation, compared with 3.8 %wt polystyrene, so whilst polymer dominates the overall solids content, the irregularities could originate from surfactant phases. Alternatively, the features may arise from dewetting of the polystyrene from the substrate.

The amount of polymer that can be deposited in a single drop using the methyl benzoate formulation represents a significant improvement over that which can be achieved with a pure polymer solution. Hoath reported that the maximum printable concentration for a DEP solution of polystyrene of M_n = 290 kDa was of the order of 0.5 %wt [10], which is about eight times less than demonstrated using an emulsion here. The emulsion would, therefore, allow far more polymer to be deposited during a single printhead pass and improve manufacturing efficiency. Further, we demonstrated that it is possible to vary the discontinuous phase solvent in order to achieve a continuous deposit.

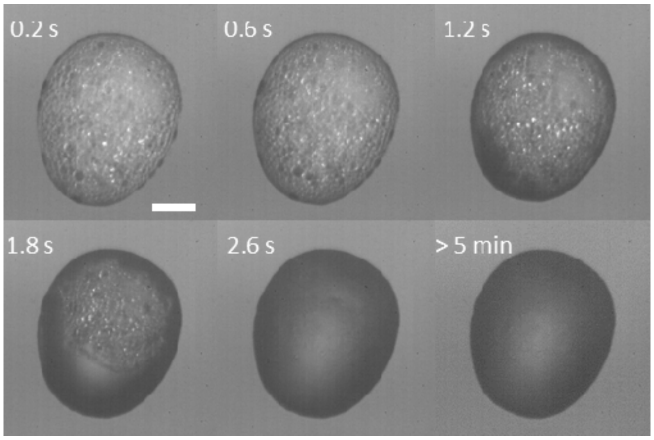

Figure 4. Images depicting the drying process of an emulsion comprising a 4.8 %wt DEP solution of polystyrene (30 %wt overall) and 14.5 mM SDS. Emulsification was achieved using the ultrasonic horn at 25% amplitude for 120 s. Jetted with a bipolar waveform of amplitude 60 V. The scale bar is 40 µm.

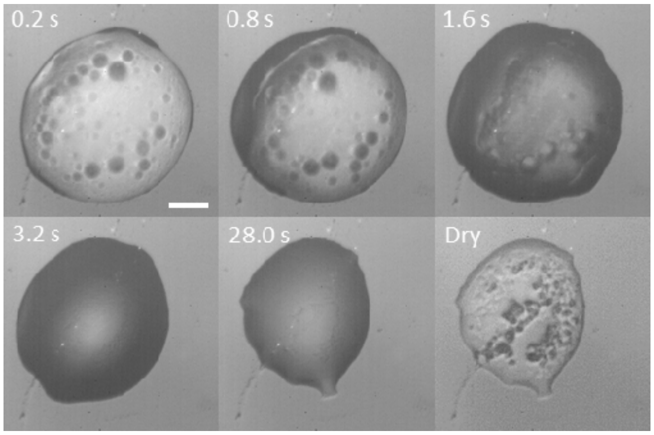

Figure 5. Images depicting the drying process of an emulsion comprising a 9.5 %wt methyl benzoate solution of polystyrene (40 %wt overall) and 14.8 mM SDS. Emulsification was achieved using the ultrasonic horn at 25% amplitude for 120 s, then at 40% amplitude for 60s. Jetted with a bipolar waveform of amplitude 100 V. The scale bar is 40 µm.

Jetting high-molecular-weight polymers via emulsions has some limitations. Sedimentation and creaming observed during printing experiments causes the amount of polymer contained within each drop to differ from that of the average of the bulk emulsion. This will tend to overstate the amount of polystyrene deposited in systems that display creaming, whilst understating the same for systems that sediment. Over the period of a day Ostwald ripening leads to an increase in the number of large droplets, exacerbating the dynamics of creaming and sedimentation in the printing head and increasing the probability of nozzle blockage. The upper limit on polymer concentration is set by our ability to manufacture a suitable emulsion. The non-Newtonian character of polymer solutions inhibits the emulsification process. We have not explored all possible emulsification methods (e.g. high-shear mixers or membrane emulsifiers), but we expect that these approaches will also suffer limitations from non-Newtonian behavior at high volume fractions of polymer. The method we employed – ultrasound – is not ideal due to the tendency to break polymer chains. Finally, the dry polymer film contains residual surfactant that might comprise the desired performance of the polymer. Judicious choice of surfactant might permit the surfactant to be removed by evaporation during a subsequent annealing step. The choice of both continuous and discontinuous phase solvents should also be made carefully for a number of reasons. First, the two should have as small a density difference as possible to minimize the effects of creaming and sedimentation. Second, the discontinuous phase must be a good solvent for the polymer. Third, the discontinuous phase fluid should have a vapor pressure that is significantly lower than the continuous phase fluid to allow complete coalescence of emulsified drops before the polymer gels or reaches its solubility limit.

Conclusion

We have demonstrated that emulsions can overcome the limitations of printing high-molecular-weight polymers in solution. The systems trialed comprised a polymer solution as the discontinuous phase and a surfactant solution as the continuous phase. The aim of constructing the fluid in this manner was to shield the polymer from the high extensional strain rates encountered just before drop detachment and hence prevent the manifestation of non-Newtonian properties. The formulation that gave the best printing behavior and drying dynamics contained 3.8 %wt polystyrene overall. It was manufactured by emulsifying a 9.5 %wt methyl benzoate solution of polystyrene with a 14.8 mM SDS solution, with the discontinuous phase making up 40 %wt of the emulsion. This fluid was printed from a nozzle with a 50-μm orifice and footage of the drying process was captured on a high-speed camera. The formulation is designed so that the continuous phase evaporates rapidly relative to the discontinuous phase so that the polymer solution fully coalesces after complete water loss. This polymer solution then dries in under a minute to leave a continuous polymer deposit. This system allows about an order of magnitude increase in the amount of polymer that can be jetted in a single drop compared to a pure polymer solution. We varied the identity of the discontinuous phase and found the deposit morphology can be changed by doing so. A dispersed phase solvent like toluene had a vapor pressure similar to water which led to a polymer ring, since the dispersed phase was carried to the contact line under coffee-ring flow and was deposited in the absence of opportunity for polymer solution coalescence. DEP had too low a vapor pressure for the fully coalesced discontinuous phase to dry at room temperature, but could be used with a heated drying stage. Anisole formulations produced filled deposits since its vapor pressure was low enough to allow for complete coalescence after loss of the continuous phase. Methyl benzoate dries more slowly than anisole so that polymer was deposited over 30 s, as opposed to the 2 s observed with anisole.

Acknowledgements

The authors are grateful to O. W. J. Burnham for his assistance in collecting gel-permeation chromatography data. This work was supported financially by EPSRC under grant number EP/H018913/1.

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