Behaviour of Ink Droplet Media Interactions in Model Systems

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Abstract

In this work we present a study of the characteristics of UV cure ink droplets on different media (model homogeneous and heterogeneous surfaces, PET, treated PET, etc.). By varying the magnitude of chemical heterogeneities on model surfaces, we are able to highlight the parameters that affect droplet shape. Using Lattice Boltzmann simulations of droplet spreading, we show that the location of the impact point of a droplet on patterned substrate with micron size chemical heterogeneity is an important criterion to consider with respect to the equilibrium shape of a droplet. This allows a complete understanding of the effect of chemical heterogeneity on droplet shape, and therefore on printing quality. We also report an experimental study of the morphology of ink droplets adsorbed on chemically defined substrates. This morphology appears to be related with the surface properties of the media considered.

Introduction

The study of wettability has been a matter of interest for many years. Indeed, understanding the multiple parameters governing the spreading and the wetting of a droplet on a surface is of crucial importance for applications such as inkjet printing, as well as from a fundamental and experimental point of view.[1] In the case of ideal surfaces and pure fluids, Young established a relationship between equilibrium contact angle, θ_e, surface energy of the substrate, γ_{sv}, interfacial tension between solid and fluid, γ_{sl} and the surface tension of the fluid, γ. However, for real (non-ideal) surfaces, the equilibrium state of a system may be different, mainly due to surface impurities. Cassie developed a relationship for θ_e taking into account the surface fraction of two different chemical species on the surface. In the case of very small heterogeneities as compared to the size of the droplet, this model has been verified experimentally.[2] However, for chemical heterogeneities close to the size of a spreading droplet, some deviations of the expected shape are observed.[3-5] When the size of the chemical heterogeneities are of the same order as the size of the droplet, the above models are not sufficient to explain the profiles obtained.[6,7] With the exception of a few reports,[8] there is a lack of systematic study on this subject and from a practical point of view (UV cured inkjet printing for example), it is important to understand these phenomena. Indeed, taking into account the complexity of real substrates, and the small droplets considered in inkjet printing, the magnitude of chemical heterogeneity is expected to have a major influence on print quality.

In this paper we describe some of the work undertaken within the IMAGE-IN project[9] to study fundamental aspects of the behaviour of UV cure ink droplets on both model and technologically relevant media. We consider spreading dynamics and equilibrium shapes of droplets on model surfaces, and show that our results are able to explain some printing defects on real media surfaces. Modelling of the phenomena observed experimentally is undertaken by means of lattice Boltzmann simulations. Lattice Boltzmann models are a class of numerical techniques ideally suited to probing the behaviour of fluids on mesoscopic length scales.[10] These models solve the Navier-Stokes equations of fluid flow but allow inclusion of thermodynamic information, typically either as a free energy or as effective microscopic interactions. In this paper we show that it is possible to use a lattice Boltzmann approach to model the spreading of mesoscale droplets.[11] By using this numerical modeling approach we are able to predict behaviour of ink droplet spreading on model and real media. Detailed microscopic studies on model ink behaviour has also been undertaken to reveal the complexity of the surface

Experimental Description

The inks used in this study are model UV cure inks prepared by SunJet (UK), and printed at Agfa-Gavaert (Belgium) using a test-bed ink-jet printer operating a Spectra print head. The model inks were carefully controlled fluids where the composition of the various components was varied in order to determine the role played by each. Planar images of ink droplets were taken using a scanning electron microscope (SEM) and a phase interference optical microscope (PIM). Samples for TEM imaging were prepared using cross-sections through the depth of the ink droplets on the media and achieved by careful ion beam milling using a FEI 200TEM focused ion beam (FIB) instrument utilising a gallium ion beam. Model media surfaces were prepared by treating with thiolated alkanes to produce both homogeneous and heterogeneously patterned surfaces. The chemically patterned surfaces were prepared using standard microcontact printing techniques[12,13] to give stripes which were either lyophobic ($-CH_3$ terminated) or lyophilic ($-CO_2H$ terminated) monolayers which correspond to equilibrium contact angles of 64° and 5°, respectively, for the jetted fluids. The fluids used had viscosities of 25 cP and surface tension of 24.4 mNm^{-1}.

Numerical Modelling

To numerically model the droplet behaviour we consider a one-component, two-phase fluid described by the van der Waals equation of state. The Navier-Stokes equations describing the fluid evolution were solved using a lattice Boltzmann algorithm.[11] Our aim was to reproduce the physical properties of the experimental fluid and the substrate geometry as closely as possible to obtain quantitative agreement with the experiments. We therefore used physical values for the viscosity, fluid density, surface tension and the size of the drop and the substrate stripes. The measured equilibrium wetting angles on the lyophilic and lyophobic materials was also an input parameter to the simulations.

Results and Discussion

Droplet Shape Anisotropy

Figure 1*a* shows a scanning electron microscope (SEM) image of a set of inkjet droplets that were jetted onto a model surface that has been chemically patterned. The dark and light vertical stripes are hydrophilic and the hydrophobic regions, respectively, which have been patterned onto a topographically flat gold coated silicon wafer using standard microcontact printing techniques. The droplets adopt various equilibrium shapes, and for this combination of stripe widths two general equilibrium shapes can be distinguished. A magnified droplet circled in Figure 1*a* is shown in Figure 1*b*, together with a numerical simulation obtained from Lattice Boltzmann modeling as shown in Figure 1*c*. In the latter, the thick line is the equilibrium shape of the droplet. The thin lines are droplet shape at intermediate time steps and reveal the dynamic processes of the droplet shape formation. It can be seen that the lateral wetting on the hydrophilic areas (dark vertical stripes) extends further than the equilibrium position, indicating that slight dewetting occurs. The impact point (indicated by an arrow in Figure 1*c*) has an important influence on the final droplet shape. Indeed, by varying the impact point on the stripes with the lattice Boltzmann model, we are able to generate all the shapes shown in Figure 1*a*. Due to the similarity between the model and the measured droplets the relative impact point is clearly an important parameter in determining the deviation of a droplet from a perfect spherical shape. The impact point is only important if the size of the heterogeneity is similar to the initial diameter of the droplet. It is useful, from a practical point of view, to be able to predict when this type of deviation can occur and we are now in a position to describe the evolution of droplet shape as a function of micron to millimeter size heterogeneities.

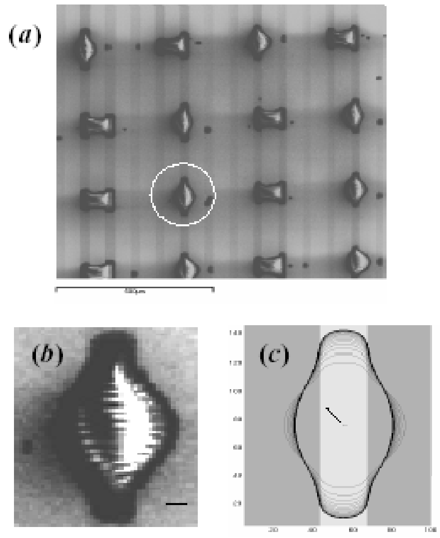

Figure 1(a). SEM image of a set of ink-jetted droplets on a chemically patterned substrate. The scale bar is 500 μm. (b) Magnified image of the droplet circles in (a). Scale bar is 10 mm. (c) Lattice Boltzmann simulation of droplet spreading, where the hydrophilic areas now shown by light grey. The point of impact of the droplet is indicated by an arrow.

Surface Modification and Ink Formulation Effects

Although the most obvious measurement to make is the equilibrium droplet shape, this does not address the issues related to the chemical interaction between the media and the multi-component UV jet inks. To tackle this issue we are also studying the internal chemical and morphological nature of droplets as a function of surface heterogeneities. This is being addressed by use of imaging (lateral resolution down to 50nm) secondary ion mass spectroscopy, AFM and advanced SEM techniques as our primary tools, coupled with lattice Boltzmann modeling.

On real surfaces, where now topography almost certainly plays a critical role, attempts are often typically made to correlate the print quality to measurable surface parameters such as surface energy and surface roughness. In fact, these parameters do not fully capture the full behaviour of ink droplets on various media. This can be illustrated by considering the behaviour of an ink droplet printed onto a polyolefin (PE) and a polyester (PET) surface either in their natural states or once treated to alter their surface energies. As anticipated by increasing the surface energy of the PE by surface treatment by 14 mN/m the droplet approximately doubles in radius, compared to the same experiment on the raw surface. However, the PET behaves anomalously in that increasing the surface energy by 5 mN/m does not increase the droplet radius as expected, but in fact the droplet radius decreases by approximately half its value compared to the raw PET. Clearly then, surface energy is not a sufficient criteria to fully judge the wetting behaviour of a media surface and other factors, such as perhaps the surface roughness, may play significant roles. This can be illustrated by inspection of Figure 2(*a*) and (*b*), where the same ink formulation has been jetted onto either a raw PET surface (Figure 2(*a*)), or a coated PET (Figure 2(*b*)). In this case a simple measurement of droplet radius is not possible because of the highly irregular shape of the contact line on the raw PET. The phase interference image in this case shows that the substrate is not flat, but has significant topography associated with it (as revealed by the variation in colour in the non-ink areas). It should be noted though that these irregular shaped ink droplets on the raw PET are not always observed for all raw PET surfaces. This may in part be due to the PET processing route, but could also be due to random variables such as surface contaminants. Although the surface roughness of the coated PET is quite different (see Figure 2(*b*)), compared to the raw PET, the surface energy is also modified. Clearly the surface coating has a dramatic effect on the ink behaviour, which produces significantly more regular droplet shapes. Unlike the raw PET for a specific surface coating the variability of droplet shape is significantly less, reflecting the uniformity in characteristics between samples. It is interesting to note from the colour differences of the droplet that the droplet shape does not appear to show the expected hemispherical profile. In this case there is a thin layer film which has formed ahead of the contact line, giving what could be described as a fried egg profile.

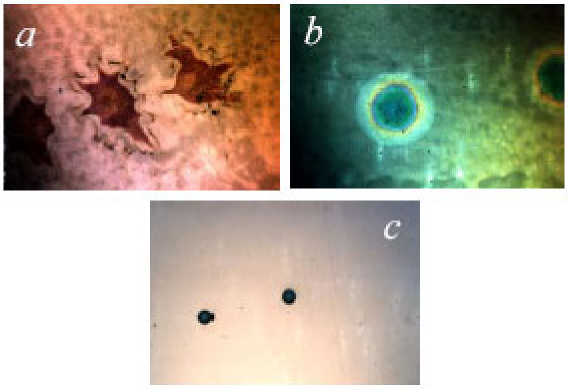

Figure 2. Phase interference optical microscope images of droplets of a model fluid ink on (a) raw PET and (b) coated PET, when the ink contains a standard surfactant. When the surfactant is modified droplet spreading on the coated PET is dramatically affected (c). These images are all taken at x10 magnification.

Also of great significance in the wetting behaviour of inks is the critical role played by the various components within the complex ink formulations. This is being investigated by a series of experiments using model fluids with varying proportions of the various components. As can be seen from Figure 2(*b*) and (*c*), by simply changing the surfactant chemistry a dramatic effect in wetting characteristics can be induced. In this case, although the surface is identical in all respects, the effect of modifying the surfactant formulations has very important implications on equilibrium wetting behaviour. This is perhaps not surprising, but as yet there is no quantitative understanding of the role played by often subtle changes in the surfactant make up. The behaviour of a variety of key surfactants are therefore being carefully investigated and the influence of their dynamic and interfacial modification properties are being compared to theoretical models and related ultimately to the observable print quality.

It is worth noting however, that care must be taken when using simplistic approaches to studying wetting because the characteristic properties needed to optimise the quality of a droplet wetting a specific surface are almost certainly not in themselves ideal for those needed to produce a solid colour fill where multiple droplets fully wet the media surface and coalesce. This apparent dichotomy in requirements in media modification and ink formulations is a challenging aspect which to date has meant that there is always a compromise in the media and ink properties to enable ink-jetting of these two extremes.

Conclusion

The evolution of droplet shape as a function of the size of surface chemical heterogeneity has been studied. It has been proved that the Lattice Boltzmann model is a power method for studying the evolution of droplet spreading on heterogeneous surfaces. For small heterogeneities, the shape of the droplet can be approximated by a spherical cap. For intermediate sizes of chemical heterogeneities that are close to the initial droplet diameter, the droplets show distinctive equilibrium shapes. In this case, the location of the impact point relative to the chemical patterning determines the final equilibrium shape. For surfaces heterogeneities much larger than the initial droplet diameter, the final shape depends mainly on the equilibrium contact angle, through Young's equation.

In addition to the droplet behaviour on model surfaces we are also looking at the factors associated with the ink characteristics and how the composition and physical properties influence wetting. By using model fluid systems we have been able to begin to assess the individual contributions of the various components to the overall behaviour.

Acknowledgements

This work forms part of the much wider IMAGE-IN project. Funding for this project is gratefully acknowledged under the EU Framework 5 Growth Programme (G1RD-CT-2002-00663). We are also grateful to all our partners in the IMAGE-IN project, in particular A Grant and H Allen (SunJet), and G Desie and D Quitens (Agfa) for supplying model fluids and technical assistance for aspects of this work.

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Biography

David Bucknall gained his PhD in polymer physics in 1991. Since this time he has specialised in studies of surfaces and interfaces, in both government research and academic institutes. He is currently a lecturer at Oxford University studying aspects of polymers and biomaterials. He is also co-ordinator of the multinational European funded IMAGE-IN research project to study and develop a better understanding of ink-media interactions for improved industrial ink-jet printing.