Inkjet printing as a fabrication method for hydrophobic surfaces

Liisa Hakola, Kim Eiroma, Jali Heilmann, Hannu Linna, Terho Kololuoma; VTT – Technical Research Centre of Finland, Espoo, Finland Harri Härmä; University of Turku, Turku, Finland

Abstract

Inkjet printing is an ideal manufacturing method for challenging applications. It is compatible with many kinds of fluids and substrates and it enables accurate deposition of nonconventional inks. This paper presents the use of inkjet printing to fabricate hydrophobic surfaces. Hydrophobic surfaces are needed for example in diagnostic applications for screening purposes, but also other uses can be found.

Inkjet printed hydrophobic surfaces have been demonstrated. Two different inks have been manufactured – one amorphous fluoropolymer (Teflon) and one polydimethylsiloxane (PDMS) based – and inkjet printed on a polystyrene substrate. The first ink produced a contact angle of approximately 116° and the second one 108° thus indicating a hydrophobic surface. Several methods were also tested to increase the contact angle to near 180°, but most likely the high solvent content in the inks prevented this.

Introduction

There are several reasons why digital manufacturing is believed to replace many analogical production lines in the future. Inkjet manufacturing is an additive process, where liquid drops are generated from a print head driven by computer controlled electronic signals. This is a great advantage when compared to conventional subtractive processes, because very small amounts of material can this way be added and aligned precisely and expensive materials, needed in many manufacturing applications, are not wasted. Digital manufacturing brings also extreme flexibility to the manufacturing process, which enables tailored products, shorter delivery times, decreases waste and storage costs.

So, although ink jet manufacturing has self-evidently a very bright future, implementation of inkjet printing process to replace a conventional production line, or even steps of it, is often an extremely difficult process, because substituting an analogical manufacturing line with a digital manufacturing adds complexity to an already complex process. There are questions to be solved, like how to manage the data transfer from a computer to a production printer rapidly and timely without errors, how to handle different product versions in short-run, on-demand, fast phase production and how to store tailored products, how to trace them and how to deliver them precisely and cost-efficiently – and so on. Hence, establishing a workflow for this kind of production model takes quite a lot of effort, because each interface and procedure have to be pre-arranged so that the actual work would go smoothly.

The objective of the research work presented in this paper was to fabricate hydrophobic surfaces by using inkjet printing i.e. digital manufacturing. The ultimate goal was to make structures with varying hydrophilic (substrate) and hydrophobic (printed patterns) areas. The hydrophobic areas would guide water drops to hydrophilic areas.

Materials and methods

Two materials were tested for making the hydrophobic surfaces: polydimethylsiloxane (PDMS, Sylgard 184 from Dow Corning) and amorphous fluoropolymer (Teflon, Teflon AF from DuPont). Both materials are known for producing hydrophobic surfaces when added on a substrate. In order to fabricate the surfaces these materials were made into a form of an inkjet printable ink. PDMS was mixed with 95 wt-% of mesitylene in order to lower the viscosity to the desired low level. PDMS has an inherent viscosity of almost 4000 cP and optimal viscosity for inkjet printer used was 8-20 cP. Teflon was mixed with 95 wt-% of fluorinert solvent (FC-77 from M3). Polystyrene was used as a substrate. Glass and polypropylene were also tested at first, but the inks didn't adhere on them so they were rejected from further tests.

The state-of-the-art inkjet research environment at VTT was used for printing. The research environment consists of industrial, piezo-electric printheads for two-colour printing and an Apollo II control unit both from FUJIFILM Dimatix, as well as an XY precision table with a positional repeatability of 1 μ m from iTi. Printhead with 80 pl drop size was used.



Figure 1. Inkjet printing environment used in the printing trials based on industrial printheads from FUJIFILM Dimatix (left) and XY precision table from iTi (right). The substrate is placed on the moving grey platen under the stationary printheads.

From the printed samples print quality (Scanner Based Image Analysis System, Scanner IAS from QEA), contact angle and surface profile were measured. Also SEM (Scanning Electron Microscope) and light microscope images were taken.

Results

Print quality

The line width of inkjet printed lines was measured in order to get and idea on the spreading tendency of the inks on polystyrene substrate. Ink spreading and overall print quality have an effect on how small and precise structures can be printed. The effect of amount of ink layers (1, 2 and 5 ink layers) and heated substrate (room temperature and 50 $^{\circ}$ C) was tested. The results of line width measurements are presented in Figure 2.



Figure 2. Line width of different samples as a function of amount of ink layers.

Amount of ink layers didn't have a significant effect on the line width of Teflon ink thus indicating that the different ink layers have placed themselves nicely on top of each other. Heating the substrate to 50 $^{\circ}$ C further decreased the line width with approximately 50 µm. With PDMS ink the lines were significantly wider than with Teflon ink and increase in the amount of ink layers even further increased the line width. The effect of heated substrate wasn't unambiguous.

Figure 3 presents light microscope (5 \times magnification) and SEM microscope (100 \times magnification) images of the PDMS surfaces. With light microscope it can be seen that the surface is very uneven. However, in SEM image the surface looks very smooth here and there.



Figure 3. Light microscope and SEM microscope images of the inkjet printed PDMS surface with one ink layer.

Contact angle

The amount of ink layers or heated substrate didn't have an effect on the contact angle of the printed surfaces. With Teflon the contact angle was approximately 116° and with PDMS approximately 108° . This shows that the printed surfaces were hydrophobic since a contact angle larger than 90° indicates a hydrophobic surface and a contact angle smaller than 90° a hydrophilic surface.

The initial goal was to fabricate hydrophobic surfaces for diagnostic screening and super-hydrophobic surfaces – at least a 170° contact angle – were needed. In that regard, a $108-116^{\circ}$ contact angle wasn't hydrophobic enough and several means were tried in order to achieve super-hydrophobic surfaces. However, heating the substrate during printing up to $100 \,^{\circ}$ C, exposing the printed surface to $120 \,$ W/cm² UV light for several seconds or exposing the printed surface to UV laser didn't result in increase in contact angle. Higher temperatures than $100 \,^{\circ}$ C couldn't be used since polystyrene substrate deformed in higher temperatures. UV light and UV laser might not have been powerful enough to have an effect on the structure of the printed surface.

Khorasani et al. [1] have managed to increase the contact angle of PDMS surface from 105° to 170° by exposing the surface to CO₂ laser. Unfortunately suitable CO₂ laser couldn't be found for testing for the work presented here. However, when comparing the contact angle received here by inkjet printing it falls within the same range as Khorasani et al. have achieved by other means before exposure to CO² laser. Also Oláh et al. [2] have shown hydrophobic recovery of combined UV and ozone treatment of PDMS surface. This method, however, didn't result in a superhydrophobic surface after recovery.

The effect of silica particles

Silica particles in water were tested if they have an effect on the hydrophobic nature of the PDMS surface. The assumption was that silica particles would modify the roughness of the surface which would result in more hydrophobic surface. Two approaches were used: polystyrene substrate spin coated with silica particles and inkjet printing silica particles on top of the inkjet printed PDMS surface. Spin coated substrates weren't found to have an effect on the contact angle of the PDMS surfaces. Both approaches were also tested with Teflon, but Teflon wasn't compatible with the particles resulting in surfaces with poor quality.

Five different silica particles with different diameter were used: 0.17 μ m, 0.43 μ m, 0.97 μ m, 3.14 μ m and 6.8 μ m. The silica particles were purchased from Bangs Laboratories as 10 wt-% solids in water. In order to make the particle fluids printable they were mixed with 0.5 wt-% particles, 20 wt-% water and 80 wt-% of diethylene glycol. The PDMS surface was printed first and then immediately afterwards silica layer was printed on top of it to allow particles to get mixed with PDMS. The effect of printed silica particles on the contact angle of a regular dye-based solventbased inkjet ink (Sirius Solvent Jet black ink from FUJIFILM Dimatix) was also tested with the same approach as a reference.

It was found that with PDMS the silica particles didn't have an effect on the contact angle. This might be due to the high solvent content of the PDMS ink that sort of absorbed the silica particles away from the surface of the ink layer. However, profilometer measurements showed that silica particles increased the roughness of the printed PDMS surface. In order to make super-hydrophobic surfaces nano-scale roughness should be modified, but the particles most likely had an effect only on the micro-scale roughness.



Figure 4. Surface profile of printed PDMS surface (on left) and of printed PDMS surface with printed silica layer on top of it (on right). Surface roughness is 0.83 µm and 3.68 µm, respectively.

With the regular ink the contact angle increased from 86° without particles to 120° (with 0.17 µm particles) or 95° (with other particle sizes) thus making the inherently hydrophilic ink surface hydrophobic.

Discussion

Materials like PDMS and Teflon are typically used in applications such as clear coating for optical devices, lens cover, anti-reflective, protective and/or durable coatings, semiconductor processing as well as thin films and coatings. These materials can also be moulded into mechanical parts.

For coating applications inkjet printing can offer a cheaper and simpler manufacturing method since material consumption in inkjet printing is very low and the coating process has only one process step – printing. Inkjet printing can be also used for coating even 3D surfaces and to produce very thin layers thanks to small drop size used. Furthermore, inkjet printing can be used for coating only the significant parts which also saves material. Inkjet printing can be used for making mechanical parts instead of moulding by directly depositing several layers of material on top of each other. Especially Teflon seems to have potential for this since the results in this paper showed that ink layers place themselves nicely on top of each other without increase in line width typically seen in this type of situation.

For screening purposes in diagnostics the surfaces would have to be super-hydrophobic. That wasn't achieved in this study, but with suitable exposure that might be achievable also with inkjet printed hydrophobic surfaces. One printing related application for alternating hydrophobic and hydrophilic surfaces would be manufacturing of very thin lines that are needed for example in printed electronics applications. It is usually easier to inkjet print thinner gaps between lines than to print the actual lines as very thin. Inkjet printed hydrophobic areas could be used to guide the ink into the hydrophilic gaps between them in order to fabricate finer details than can be printed directly. Usually this same approach is achieved by treating the substrate with laser or plasma [3], but the use of inkjet printing for making the hydrophobic areas could result in a simplification of the process. However, the inkjet approach is only suitable in situations where thin lines don't have to be very close to each other.

Conclusions

It has been shown that it is possible to inkjet print materials that can produce hydrophobic surfaces. It has also been shown that silica particles in a water vehicle can be inkjet printed. Furthermore, it has been found that silica particles can be used for making inherently hydrophilic ink layers hydrophobic.

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Author Biography

Liisa Hakola graduated as Master of Science from Helsinki University of Technology in 2002 and her Master's Thesis was about effect of ink composition on print quality of inkjet printing. She has studied Graphic Arts and paper technology. Since her graduation Liisa has worked at VTT as a research scientist. Her research work focuses on industrial inkjet printing, new coding methods as well as using inkjet printing as a manufacturing technology. She has published several international scientific papers as well as given conference presentations in the field of functional printing.