Fabrication of Two and Three-Dimensional Structures by Using Inkjet Printing

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Abstract

Inkjet printing is a nascent technology that is developing from only printing text and graphics into a major topic of scientific research and R&D, where it can be used as a highly reproducible non-contact patterning technique to print at high speeds either small or large areas with high quality features. Inkjet printing is an additive technique, which requires only small amounts of functional materials, which can vary from a simple polymer solution to advanced nanoparticle dispersions. The latter form of ink has been investigated more and more during the last few years, in order to produce conductive features that require a reduced amount of processing steps.

In recent years inkjet printing has been used for the production of microelectronic structures on (flexible) substrates and for the rapid production of 2D and 3D microstructures. In order to create these microstructures we present 'reactive inkjet printing' as a technology to create micron-scale polyurethane structures, such as dots, lines and pyramids. These structures were fabricated in-situ and cured within five minutes by inkjet printing successively two separate inks respectively from two separate print heads, with one ink containing isophorone diisocyanate, and the other consisting of an oligomer of poly(propylene glycol), a catalyst, and a cross-linking agent. The fast polymerisation reaction that forms polyurethane at the surface opens a new route for rapid prototyping, as well as the use of inkjet as a technique for handling moisture-sensitive reactions.

Introduction

The origin of inkjet printing goes back to the eighteenth century when Abbé Nollet published his experiments on the effect of static electricity on a stream of droplets in 1749.[1] Almost a century later, in 1833, Felix Savart discovered the basics for the technique used in modern inkjet printers: an acoustic energy can break up a laminar flow-jet into a train of droplets.[2] It was, however, only in 1858 that the first practical inkjet device was invented by William Thomson, later known as Lord Kelvin.[3] This machine was called the *Siphon recorder* and was used for automatic recordings of telegraph messages.[4]

The Belgian physicist Joseph Plateau and the English physicist Lord Rayleigh studied the break-up of liquid streams and are, therefore, seen as the founders of modern inkjet printing technology. The break-up of a liquid jet takes place because the surface energy of a liquid sphere is smaller than that of a cylinder, while having the same volume – see Figure 1.[5]

When applying an acoustic energy, the frequency of the mechanical vibrations is approximately equal to the spontaneous drop-formation rate. Subsequently, the drop-formation process is synchronised by the forced mechanical vibration and therefore produces ink drops of uniform mass. Lord Rayleigh described the instability and varicosity of jets,[6] where he calculated a characteristic wavelength λ for a fluid stream and jet orifice diameter d given by: $\lambda = 4.443\ d$

It took another 50 years before the first design of a continuous inkjet printer, based on Rayleigh's findings, was filed as a patent by Rune Elmqvist.[7] He developed the first inkjet electrocardiogram printer that was marketed under the name *Mingograf* by Elema-Schönander in Sweden and *Oscillomink* by Siemens in Germany.[8]

At the beginning of the 1970s the piezoelectric inkjet drop-on-demand (DoD) system was developed.[9] At the Philips laboratories in Hamburg printers operating on the DoD principle were the subject of investigation for several years.[10,11] In 1981 the *P2131* printhead was developed for the Philips *P2000T* microcomputer, which had a *Z80* microprocessor running at 2.5 MHz. Later the inkjet activities of Philips in Hamburg were continued under the spin-off company Microdrop Technologies.[12] The first piezoelectric DoD printer on the market was the serial character printer *Siemens PT80* in 1977.

Four different modes for droplet generation by means of a piezoelectric device were developed in the 1970s, which are summarised in Figure 2, and further explained below.[13]

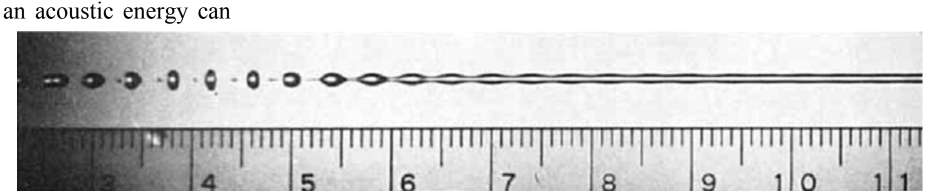

Figure 1. Break-up of a laminar flow-jet into a train of droplets, because of Rayleigh-Plateau instability. Reprinted from ref. [5].

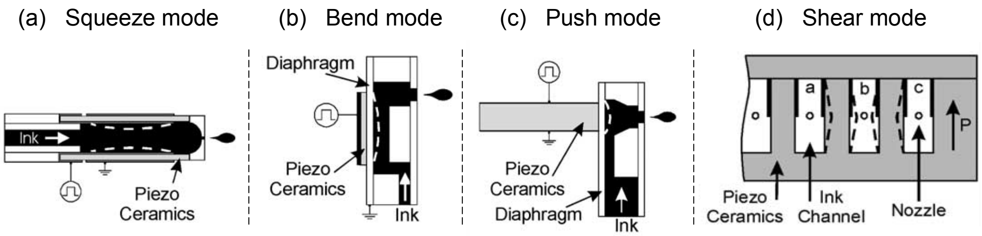

Figure 2. Different piezoelectric drop-on-demand technologies. Reprinted from ref. [13].

Firstly, the *squeeze* method, invented by Steven Zoltan,[14] uses a hollow tube of piezoelectric material, that squeezes the ink chamber upon an applied voltage (Figure 2a). The squeeze method is nowadays also used in Microdrop printing devices.[12] Secondly, the *bend-mode* (Figure 2b) uses the bending of a wall of the ink chamber as method for droplet ejection and was discovered simultaneously by Stemme[15] of the Chalmers University in Sweden and Kyser *et al.* of the Silonics company in the USA.[16] This technique is used for example in Tektronix and Epson printers. The third mode is the *pushing* method by Howkins (Figure 2c),[17] where a piezoelectric element pushes against an ink chamber wall to expel droplets, and is nowadays used in Trident, Brother and Epson printers. Finally, Fishbeck *et al.* proposed the *shear-mode* (Figure 2d),[18] where the electric field is designed to be perpendicular to the polarization of the piezo-ceramics. Typical pioneers in shear mode printheads are Xaar and Spectra.[13]

Although inkjet printing offers a simple and direct method of electronic controlled writing with many advantages, including high speed production, silent, non-impact and fully electronic operation, inkjet printers failed to be commercially successful in their beginning: print quality as well as reliability and costs were hard to combine in a single printing technique. Thermal inkjet changed the image of inkjet printing dramatically. Not only could thermal transducers be manufactured in much smaller sizes, since they require a simple resistor instead of a piezoelectric element, but also at lower costs. Therefore, thermal inkjet printers dominate the colour printing market nowadays.[19]

In scientific research piezoelectric DoD inkjet systems are mainly used because of their ability to dispense a wide variety of solvents, whereas thermal DoD printers are more compatible with aqueous solutions.[20] Furthermore, the rapid and localised heating of the ink within thermal inkjets induces thermal stress on the ink.

Although inkjet printers are widely used for graphical applications, it was only within the last decades that inkjet printing has grown to a mature patterning technique. As a consequence, it has gained specific attention in scientific research because of its high precision and its additive nature: only the necessary amount of functional material is dispensed.[21] Furthermore, the absence of physical contact between print head and substrate allows many potential applications, such as inkjet printing of labels onto rough curved surfaces, or surfaces that are sensitive to pressure. Inkjet printing is utilised to dose many different kinds of materials, such as conductive polymers and nanoparticles,[22-24] sol-gel materials,[25] cells,[26] structural polymers,[27] ceramics[28,29] and even molten metals.[30]

The impact of a droplet has a significant influence on the final printed feature, but also of great concern is a frequently observed in-homogeneous drying effect of liquid droplets on a non-absorbing substrate, the so-called "coffee drop" effect;[31,32] solute present in the solution deposits near the boundary of inkjet printed droplets – this behaviour is similar to when drops of coffee are spilt on the table. When using the technique of inkjet printing, for example for the application of OLEDs, this effect should be minimized for correct device functionality.[33] However, much research has been conducted to prevent the coffee ring effect, for example by applying an increased substrate temperature, in order to stimulate solvent evaporation, which subsequently minimises line or film bleeding,[34,35] and by combining a high and low boiling solvent, which reduces the high evaporation rate at a liquid feature's edge.[36]

Inkjet printers have also been used in several studies in order to produce a series of equal-sized droplets, which allowed the reduction of errors in the measurements and significantly increased the experimental reproducibility.[37,38]

The resolution of inkjet printed structures is comparable to the nozzle diameter, and is typically between 30 and 100 µm. While decreasing the nozzle diameter improves resolution, it also creates a smaller window of inks that can be used for printing, with respect to their viscosity and surface tension.[39]

Finally, the printability of an ink can be formulated by Fromm's *Z*-number, which is the inverse of the Ohnesorge number

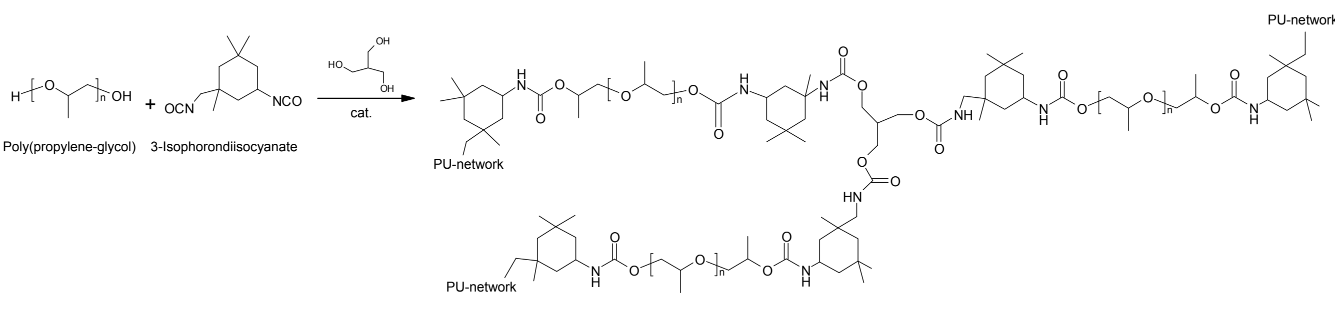

Figure 3. Schematic representation of the reaction scheme for the formation of polyurethanes from the reactants.

(Oh): $Z = \eta^{-1}(\rho D\sigma)^{1/2} = \mathrm{Oh}^{-1}$, where ρ, σ and η are the inks density, surface tension and viscosity, respectively. D is a characteristic length, which in the case of inkjet printing is the nozzle diameter. Fromm predicted that drop formation in DoD systems was possible only when the Z-number is greater than 2.[40]

Results and discussion

Many different techniques exist in rapid prototyping for fabrication of solid structures. One of the main drawbacks of rapid prototyping technologies is that only a selected range of materials can be processed directly. Some materials, like bio-ceramics, biodegradable polymers, and silicones are accessible only by post-treatment processes like pre-molding of the samples.

In order to achieve the multi-micron feature resolution typically associated with rapid prototyping techniques, inkjet printing was considered as a synthesis tool. This technique is also called reactive inkjet printing, and is a precise method for building up small structures using certain reactive materials, like polyurethanes.

Towards this aim, the synthesis of polyurethane-based materials was seen as a particularly illustrative example. The chemistry of this involves the preparation of two separate inks, one containing a diol, and the second containing a diisocyanate. The two inks are printed as successive layers on a surface, and are allowed to react to form urethane bonds. Two separate inks were subsequently inkjet printed onto each other on the substrate, illustrated by the schematic representation in Figure 3.

After printing, the reactants cured and hardened more quickly with the addition of the cross-linking agent trimethylolpropane and a catalyst. To monitor the progress of the reaction *in situ* the polymerisation kinetics in crosslinked urethane films was by FTIR spectroscopy.[41] As the isocyanate and diol functional groups are consumed, the result is an attenuation of the isocyanate peak with a maximum around 2260 cm^{-1}. By using an unchanging reference peak (*e.g.* the alkane peak at 2960 cm^{-1}), the degree of conversion can be calculated as a function of the change in the intensity of the isocyanate peak relative to the alkane peak at a particular time point, compared to the initial isocyanate/alkane peak height ratio, as depicted in Figure 4.

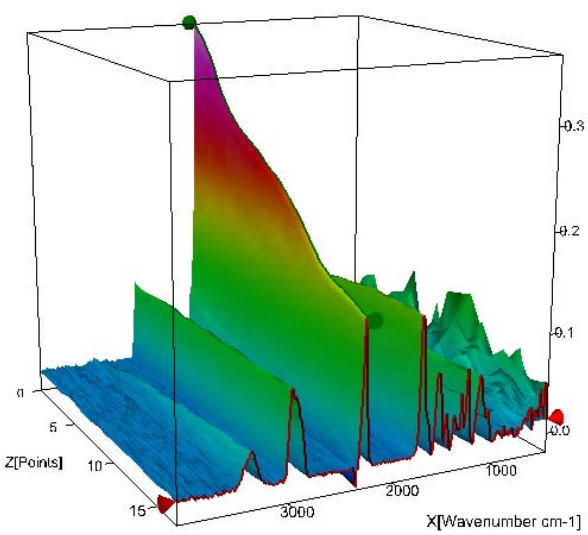

Figure 4. In-situ reaction kinetics for the formation of polyurethane by FTIR spectroscopy.

Furthermore, the substrate holder was heated to 90 °C, which resulted in conversions between 60 and 70% for a catalyst concentration between 0.1 and 2.0 wt%. Due to this relatively high conversion, solid polyurethane structures were obtained after three minutes. The resulting structures were measured using optical profilometry, as shown in Figure 5.

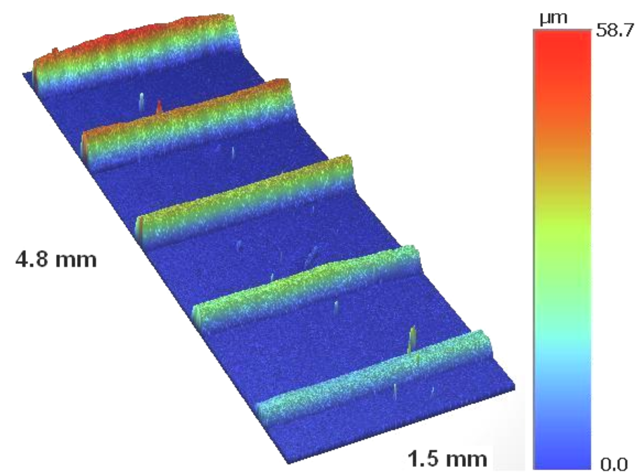

Figure 5. Five inkjet printed lines of in-situ formed polyurethane. From top to bottom, the parallel lines consist of an increased number of layers, where each layer consists of two print runs from both reactants. From top to bottom the number of layer decreases from 5 to 1, respectively.

Conclusions

We have demonstrated that defined micron-scale polyurethane-based structures can be fabricated via reactive inkjet printing starting from the corresponding monomers in a reactive, *in-situ* manner on glass substrates. This approach yields unique, cross-linked thermoset PU materials with spatial resolution in the range of tens of microns.

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Jolke Perelaer obtained his masters in chemistry at the University of Utrecht in 2004. In March 2009 he finished his PhD within the group of Prof. Schubert (Eindhoven University of Technology, the Netherlands) with the research title "microstructures prepared via inkjet printing and embossing techniques." He now continues his work with Prof. Schubert as projectleader of inkjet printing related topics at the Friedrich-Schiller-University in Jena (Germany) and the Dutch Polymer Institute (DPI). The research focuses on inkjet printing of functional materials, including conductive materials and the selective sintering thereof.