Manufacturing of micro-scale polyurethane foams by reactive inkjet printing

Fabian Schuster,[1] Fabrice Ngako Ngamgoue,[2] Thomas Hirth,[3] Achim Weber[1,2*]
[1] Institute of Interfacial Process Engineering and Plasma Technology IGVP, University of Stuttgart, Stuttgart, Germany
[2] Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB, Stuttgart, Germany
[3] Karlsruhe Institute of Technology KIT, Karlsruhe, Germany

Abstract

Reactive inkjet printing (RIJ) was used as an additive manufacturing (AM) tool. Combined with polyurethane (PU) chemistry, it is shown that RIJ can be used to build micro-scale foams. Waterblown polyurethane foams (PUF) based on polyethylene glycol 200 (PEG200), glycerol ethoxylate (Star-PEG) and 1,6-hexamethylene diisocyanate (HDI) were used to prepare the foams. The system was catalyzed using iron(III) chloride, dibutyltin dilaurate (DBTL), diazabicyclo octane (DABCO) and bis(2-dimethylaminoethyl) ether. The influence of iron(III) chloride and DBTL were investigated by means of temperature profile measurements. The stability of the catalyst system was tested for 32 hours within the ink formulation. The ink formulations were then printed with a Dimatix DMP3000 (Fujifilm, USA) printer using a 16 nozzle printhead with a nominal 10 pL drop volume. The reaction of the inks and the building of PUF after printing were investigated by light microscopy and SEM. It seems favorable to use high amounts of catalyst in order to obtain a more porous structure.

Introduction

Building three-dimensional objects using additive manufacturing (AM) methods is currently a popular field in research. Additive manufacturing is an appropriate name to describe the technologies that build three dimensional objects by adding layer-upon-layer of material, whether the material is plastic[1], metal[2], concrete[3] or tissue related[4]. For polymers, a variation of techniques can be applied to build up the structure of choice. Only to name the most essential, fused deposition modeling (FDM®)[5] uses polymer filaments that are melted and deposited through a nozzle in layers to form a three-dimensional design. Selective laser melting (SLM)[6] processes metallic powders by melting and fusing the particles. Stereolithography (SLA)[7] is a very high end technology, utilizing laser technology to cure layer-upon-layer of a photopolymer resin (a polymer that changes properties when exposed to light) to form multi-layered objects. Polyjet® printing[8] is based on inkjet printing technology primarily using UV-light curable inks to form an object layer-by-layer. One very specific printing technique is reactive inkjet printing. Here, the three-dimensional structures are formed by placing accurately liquid droplets on top of each other.[9] The fluids will either react with the substrate[10], are forced to react subsequently by an external source[11] or will react with a second fluid that was either deposited simultaneously or subsequently.[12]

In the latter case, it has been shown that PU's are suitable materials for building 3D-structures via reactive inkjet printing.[13], [14] Due to the versatility of PU materials, it is possible to formulate numerous inks, yielding diverse material properties. *Kroeber et al.* demonstrated the ability to print polyols and isocyanates subsequently forming polyurethane structures *in situ* on a glass substrate.[13] *Mueller et al.* have shown that structures with gradient mechanical properties using two polyols and one isocyanate were successfully achieved by inkjet printing.[14] Besides solid and non-porous polyurethane structures, polyurethane foams (PUF) are well-known e.g. in the fields of insulation, light-weight materials or cushioning.[15] Further on, PUF materials are of specific interest as scaffolds for tissue engineering[16], [17], as adsorber materials[18] or as 3D-carriers for cells.[19] In addition, the possibility of obtaining micro-scale PUF using the reactive inkjet printing approach was previously mentioned.[13] Aiming towards the manufacturing of PUF via inkjet printing, two different inks have to be developed as otherwise the foaming reaction would take place inside the printer cartridge. One ink contains the hydroxyl-terminated polyol and water as the chemical blowing agent. The second ink contains the isocyanate compound. Another important ink component is the catalyst. They play a key role in the production of PUF.[18–22] In particular organo-tin compounds are widely used as gelling catalysts in PU and PUF production.[24]

Dibutyltin dilaurate (DBTL) is one of the most applied organo-tin catalysts in the production of polyurethanes as it shows strong catalytic activity towards diisocyanates and polyols.[25] Furthermore, 1,4-diazabicyclo[2.2.2]octane (DABCO) is used to catalyze the reaction between water and isocyante.[26] In addition to organo tin compounds, the use of iron(III) chloride as an alternative to DBTL was tested. *Britain et al.* showed that iron(III) chloride is a very strong catalyst towards the reaction of 1,6-hexamethylene diisocyanate (HDI) with a secondary hydroxyl-containing polyoxypropylene triol.[20] The focus on this study is towards the reactive inkjet printing of porous polyurethane materials.

We investigate the formulation requirements for manufacturing of micro-scale polyurethane foams by reactive inkjet printing. We used a mixture of PEG200, Star-PEG and water combined with HDI in order to achieve polyurethane foams. The materials were selected due to their low viscosities and in case of HDI additionally due to its reactivity. The effect of the catalysts DBTL and iron(III) chloride in combination with DABCO was examined by means of temperature profile measurements of the appointed ink formulations. Furtherly, the storage stability for high catalyst concentrations was evaluated by the mixtures temperature profiles. The obtained results were then transferred towards inkjet printing and the printability of the ink formulations were tested in a Dimatix DMP3000 (Fujifilm, USA) printer using a 16 nozzle printhead with nominal 10 pL drop volume. The reaction of the inks and the building of PUF were investigated by light microscopy and SEM.

Materials and Methods

Materials

Polyethylene glycol 200 (PEG200, Mn = 200 g/mol) was purchased by Merck Millipore (Germany). 1,6-hexamethylene diisocyanate (HDI, Desmodur® H) was provided by Covestro AG (Germany). Glycerol ethoxylate (Star-PEG, Mn = 1000 g/mol), iron(III) chloride hexahydrate and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased by Sigma-Aldrich (USA). A PEG-12 dimethicone surfactant Xiamater®-OFX 0193 Fluid was purchased from Dow Corning (USA). Deionized water was used as the chemical blowing agent. Dibutyltin dilaurate (DBTL, DABCO® T12-SL) as well as bis(2-dimethylaminoethyl) ether (DABCO® BL-11) were obtained from Air Products (USA).

Instrumentation and methods

The physical properties of the polyol and the isocyanate compound were determined by means of viscosity, dynamic surface tension and density measurements. The inks viscosity was determined by rotary concentric cylinder rheometry using a Physica Modular Compact MCR301 Rheometer (Anton Paar, Germany) with a shear rate of 100 s^{-1} at 60 °C. The inks dynamic surface tension was determined using a bubble pressure tensiometer BP50 (Kruss, Germany). The surface age was recorded at 15 ms with a temperature of 60 °C ± 2 °C. The samples were heated in a controlled water bath. Density measurements were carried out at 60 °C using a Kruss K12 tensiometer equipped with the density setup DE0601 (Kruss, Germany). Temperature profiles were recorded using a thermocouple data acquisition system TC-08 (Omega, Germany) with a thermocouple type T (Cu-CuNi).

Printing was done using a drop on demand (DOD) Dimatix DMP3000 (Fujifilm, USA) printer. As the printhead a 16 nozzle DMC11610 (Fujifilm, USA) cartridge with 10 pL drop volume was selected.

Foam preparation and temperature measurement

The detailed preparation of the foams has been described elsewhere [27]. The used ink composition is shown in Table 1.

Table 1: Formulation recipe of the prepared PUF with an isocyanate index of 110.

Polyol component	**Weight (g)**
PEG200	92
Star-PEG	8
Deionized Water	2
Xiameter® OFX-0193 Fluid	2
DBTL or iron(III) chloride hexahydrate	varies
DABCO	0.4
BL-11	0.4
Desmodur® H (HDI)	108

For the temperature recordings the thermocouple was connected to the bottom of the reaction vessel (60 mL PP-plastic cup, Roth, Germany) with adhesive tape. To assure good connection between the thermocouple and the reaction vessel, heat paste was applied. Thirty seconds prior to mixing, the recording was started and the temperature profile was logged for 550 seconds.

Results and Discussion

In order to investigate the influence of different catalyst concentrations used in the ink formulation, the heat evolution during the foaming reaction was recorded (Figure 1 and Figure 2). The graphs show the temperature evolution with time. Note that 30 seconds prior to mixing the polyol and the isocyanate the recording was started. The foam mixtures show a steep rise in temperature up to a maximum between 90 °C and 100 °C for DBTL and between 85 °C and 110 °C for iron chloride. The maximum temperature that is reached seems not dependent on the catalyst concentration. The time elapsed until the maximum is reached is shifted in dependence of the catalyst concentration used. Lower concentrations take longer time to reach the heat plateau before cooling down.

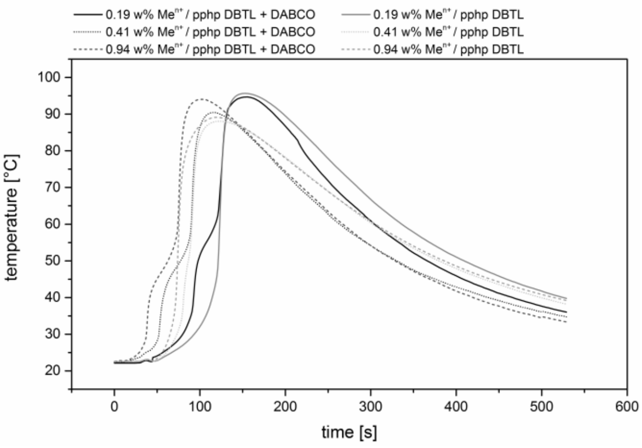

Figure 1: Temperature profile of the foaming reaction using DBTL at different concentrations. The concentration of DABCO was held constant at 0.4 pphp.

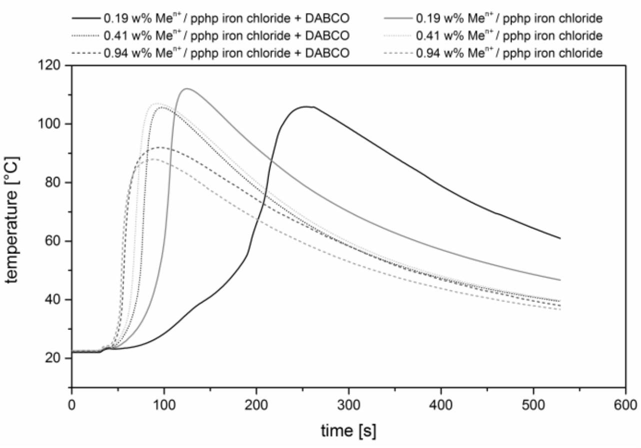

Figure 2: Temperature profile of the foaming reaction using iron chloride at different concentrations. The concentration of DABCO was held constant at 0.4 pphp.

In Figure 3 the time to reach maximum heat is displayed in dependence of catalyst and catalyst concentration. For all mixtures the largest decrease in time comes with roughly doubling the catalyst concentration from 0.19 w% Me^{n+}/pphp (weight of metal ion e.g. Sn, per hundred parts polyol) to 0.41 w% Me^{n+}/pphp. Adding more catalyst to the mixture does not show significant faster reactions. Furthermore, for DBTL it shows that DABCO slightly enhances the reaction rate compared to DBTL alone. For iron chloride this effect is reversed.

Adding 0.40 pphp of DABCO to the mixture increases the time until the maximum is reached. Especially at 0.19 Me^{n+}/pphp the negative effect of DABCO in the iron chloride ink is visible. Moreover, it is known in the literature that organo-tin compounds hydrolyze with water to form catalytic inactive oxides.[28]

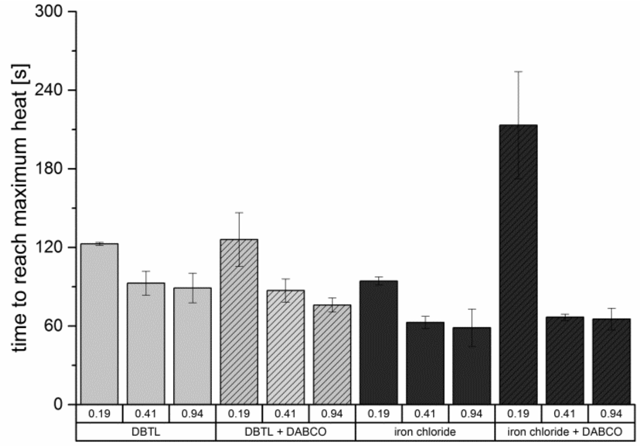

Figure 3: *Determination of the time [s] until the reaction mixture reaches maximum heat evolution at different catalyst concentrations. Each concentration is given in w% metal ion per hundred parts polyol.*

Therefore, it was investigated if a reaction mixture containing 0.94 w% Me^{n+}/pphp gives stable temperature profiles over the course of 32 hours. This threshold was chosen as it would allow one to use the ink formulation for two working days. The obtained results are shown in Figure 4. Starting point of the ink containing DBTL was roughly at 90 seconds. The mixture containing iron chloride started roughly at 60 seconds. The values are in good accordance to the ones shown in Figure 3. During the course of 32 hours, recordings were taken after 8 hours, 24 hours and 32 hours. The values obtained for DBTL were slightly lower than the starting point. However, this should be appointed to the measurement method and can be seen within the tolerance of error. Hence, the ink containing 0.94 w% Me^{n+}/pphp gives constant temperature profiles during foam reaction. The ink containing iron chloride did not show any significant changes during the time period of 32 hours and therefore gives stable inks at 0.94 w% Me^{n+}/pphp as well.

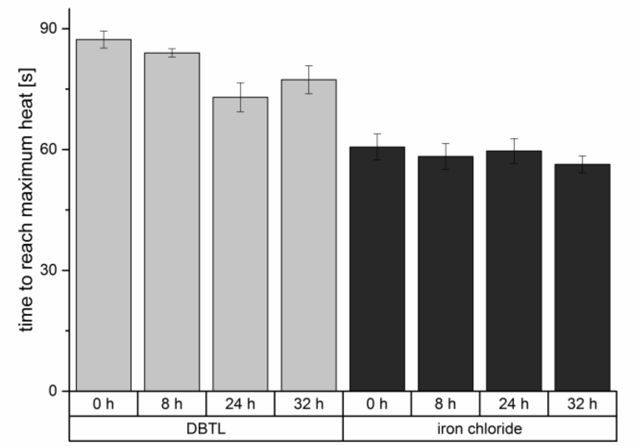

Figure 4: *Stability tests using a catalyst concentration of 0.94 w% Me^{n+}/pphp at different ages of the solution. The time until the reaction mixture reached maximum heat was evaluated.*

To investigate the film formation and the printing of the inks a reactive inkjet printing approach was selected. The inverse Ohnesorge number (Z) for the polyol ink was found to be in the range of Z = 2, while the HDI ink was found to be in the range of Z = 10. According to *Reis and Derby* both inks should be suitable for DOD inkjet printing.[29] The polyol ink was able to jet at 65 °C with a droplet velocity of 6 m/s, whereas the HDI ink was jetted at room temperature with an average droplet velocity of 3 m/s to 4 m/s. Faster droplet velocities were accompanied with satellite formation. The film formation was achieved by printing

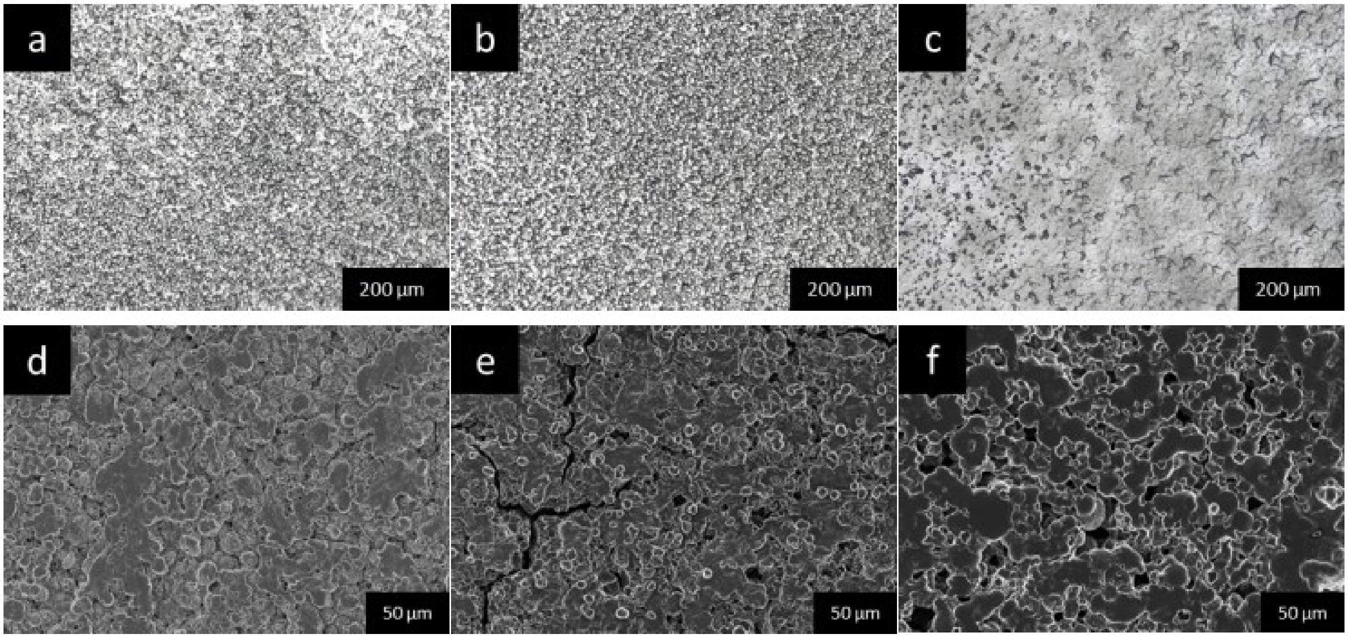

Figure 5: *Microscopic images (a-c) and scanning electron images (d-f) of printed PUF layers using different concentrations of DBTL. a,d = 0.19, b,e = 0.41, and c,f = 0.94 w% Me^{n+}/pphp.*

two layers of the polyol ink followed by two layers of the HDI ink subsequently. Figure 5 shows light microscopic as well as the corresponding scanning electron microscopic images of the samples surface. The catalyst content increases from image a (0.19) to b (0.41) to c (0.94). The light microscopic images show solid and uneven surfaces after the reaction of HDI and polyol took place. The displayed structure is caused by the CO_2 gas formation that takes place when the isocyanate compound reacts with the containing water in the polyol ink. Image c in Figure 5, comprising the largest amount of catalyst, shows a slightly different surface character. The surface seems denser with small voids being distributed statistically over the surface. The SEM image (f) confirms this impression. Regarding the SEM images (d,e,f) it seems favorable to use high amounts of catalyst in order to obtain a more porous structure.

Conclusion

We showed that the catalyst concentration within reactive ink formulations for waterblown polyurethane foams has significant influence on the reaction rate of the mixture. In order to use inkjet printing as the manufacturing tool, low viscous PEG inks as the polyol component and low viscous monomeric HDI as the isocyanate component meet the criteria to jet them in a DOD printhead. Higher contents of catalyst seem favorable obtaining porous structures using reactive inkjet printing of PU ink formulations.

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Author Biography

Fabian Schuster *received his bachelor degree in chemical engineering for colors and coatings from the University of Applied Sciences in Esslingen, Germany, where he focused on UV-coating materials for flexible substrates. He continued his studies as a master student in the field of applied material and surface sciences at the University of Applied Sciences Esslingen & Aalen, Germany. During his Master's he focused on the pigmentation of polyurethanes for inkjet applications. Since 2015 he is working as a PhD-student at the Institute of Interfacial Process Engineering and Plasma Technology in Stuttgart, Germany in the field of inkjet applications.*

Fabrice Ngako Ngamgoue *received his bachelor degree in chemical engineering for colors and coatings from the University of Applied Sciences in Esslingen, Germany. His thesis focused on the catalysis of polyurethane foams with reference to reactive inkjet printing.*

Prof. Dr. Thomas Hirth *studied chemistry at University Karlsruhe, Germany where he received his PhD at the Institute of Physical Chemistry and Electrochemistry. From 1992 to 2007, Thomas Hirth worked at Fraunhofer Institute for Chemical Technology ICT in Pfinztal, holding different positions from postdoctoral research fellow to product manager for environmental engineering. In December 2007, he moved to Stuttgart to become the Director of Fraunhofer Institute for Interfacial Engineering and Biotechnology. Since 2008, he in addition has been professor at the University of Stuttgart and head of the Institute of Interfacial Process Engineering and Plasma Technology. In 2016 Prof. Hirth was elected as the Vice President for Innovation and International Affairs at Karlsruhe Institute of Technology KIT.*

Dr. Achim Weber*, studied chemistry at the University of Stuttgart. In 2000 he joined the Fraunhofer Institute of Interfacial Engineering & Biotechnology (IGB) as a scientist and project manager, and the Institute for Interfacial Engineering (IGVT) at the University of Stuttgart. In 2006 he became a Group Manager and since 2011 he is Deputy Head of the Department of Interfacial Engineering and Material Science at the Fraunhofer IGB. His main interest is the forming and understanding of smart, nanoscopic materials and its surfaces for applications in Pharmacy, Medicine, Environment, Material and Biotechnology*