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A new approach to inkjet printing of high viscosity inks for 3D applications

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Short abstract

By combining recent advancements in high viscosity piezo inkjet and measurement technique for high frequency rheology, we investigate a route to multi-material printing of highly viscous UV polymers that were developed for vat photo polymerization. The application is additive manufacturing of dental prosthesis where a single-material process (vat photo polymerization) should be replaced by a multi-material process (inkjet printing) without compromising the material properties of the prosthesis. We study the printability of UV-polymers from two manufacturers with the recently introduced printhead from Quantica. At temperatures of 60 °C to 80 °C the viscosity and Ohnesorge number lie in a printable range. The integrity of the UV-polymers at elevated temperatures is tested. The (linear) viscoelasticity is studied by oscillatory and vibrational rheology in a frequency range up to 10 kHz and the connection of high frequency rheology to the printability and drop formation in a Quantica printhead is made.

Keywords: high viscosity inkjet, additive manufacturing (3D printing), high frequency rheology

1. Introduction and background: limitations of additive manufacturing and the role of piezo inkjet

Many additive manufacturing (AM) techniques have found their way into manufacturing of customized products in an industrial scale overcoming their former limitation to prototyping. An overview over additive manufacturing can be found in ISO/ASTM 52900 (International Organization for Standardization, 2021). Additive manufacturing processes can be categorized according to their functional principles. In powder-based processes layers of spread powder (metal or thermoplastic polymer) are either selectively sintered or molten (powder bed fusion – PBF) or fixed by a binder that is printed into the powder bed (binder jetting – BJ). The glued powder is subsequently sintered or infiltrated with a resin. A widespread process is melting of a thermoplastic filament that solidifies layer by layer into a 3D shape (material extrusion – MEX). Other AM techniques depend on curing of UV-polymers. A UV polymer in a vat is selectively cured by a laser, digital light projector, or LC screen, layer by layer (vat photo polymerization) or UV inks are layer by layer printed by piezo inkjet and cured. (material jetting – MJ). The properties of the various additive manufacturing techniques widely differ depending on the material and manufacturing method.

What all additive manufacturing technologies have in common is the limitation of the materials that can be processed. All methods but material jetting and material extrusion are limited to a single building material. MEX can only extrude materials strand by strand whereas material jetting with piezo inkjet allows to deposit materials drop by drop (voxel by voxel). This enables tailoring the optical or mechanical properties of a 3D structure by combining a set of process materials (like a color synthesis from the process colors CMY).

An important application of AM is manufacturing of medical prosthesis. Building of customized structures of any desired shape is a clear strength of AM as far as the strict requirements on the material properties can be met. On today dental prosthesis as crowns, dentures, splints, and surgical templates are manufactured by vat photo polymerization. Progress in the development of UV polymers allowed to extend the usage of additive manufactured dental prosthesis from provisory use over temporal to permanent use. Main disadvantage of vat photo polymerization is the restriction to a single building material. For manufacturing of (permanent) dentures or crowns shades of color and transparencies need be precisely reproduced what requires expensive manual retouching. Inkjet printing of UV polymers allows printing of several materials, e.g., colors. But a major limitation of piezo inkjet is the viscosity of printable inks. Polymers designed for vat photo polymerization have a viscosity higher than 1 000 mPa·s at room temperature whereas the viscosity of inks for standard piezo printheads is limited to at most 25 mPa·s at operating temperature. The operating temperature depends on the printhead and can go up to 125–130 °C for hot-melt printheads, according to specifications of hot melt printheads (Canon CrystalPoint, 2018; Dimatix Galaxy 256 HM, 2015; Xerox MDF, 2017). The viscosity of polymers strongly decreases with rising temperature but many functional materials do not withstand such elevated temperatures. Moreover, the diameter of particles (e.g., pigments, ceramics) in inkjet inks need be small ($d_{90} < 1$–3 μm, depending on nozzle size), and the volume fraction of solids in inks cannot be too high. Inkjet inks must be chemically stable (free of sedimentation). In printheads with ink circulation a slow sedimentation of solids is tolerable if particles can be redispersed.

After piezo inkjet found its way into industrial applications as of around 2 000, many attempts were made to extend the viscosity range of inks. When the physics of piezo inkjet was understood it became clear that the functional principle of piezo inkjet limits the viscosity of printable inks. For medium viscous inks (~15–20 mPa·s) the pressure drop caused by viscous dissipation in the nozzle makes up most of the pressure that is generated at the nozzle in a piezo printhead. The maximal pressure at the nozzle is limited because the positive pressure wave that accelerates the ink in the nozzle is accompanied by negative pressure waves due to reflections of the sound waves in the printhead cavity. A too strong positive pressure wave cannot avoid strong negative pressure waves that draw air through the nozzle into the pumping chamber what defeats the pumping mechanism. A comprehensive treatment of the functional principle of piezo printheads is found e.g., in the pioneering works (Wijshoff, 2008; 2010).

Beside the technical limits of piezo printheads also a physical border for the detachment of drops from a fluid surface (capillary, nozzle) exist which cannot be overcome by any dispensing technique. This is because detachment of drops occurs through a Plateau-Rayleigh instability. Two-time scales control the breakup of a cylinder of a Newtonian fluid:

$$t_R = \sqrt{\frac{\rho d^3}{\sigma}} \quad \text{and} \quad t_\eta = \frac{\eta d}{\sigma} \qquad\qquad [1]$$

where η, ρ, σ are the viscosity, density and surface tension of the fluid and d is the diameter of the fluid cylinder or nozzle. See e.g., Pekker (2018) for a discussion of the breakup of a cylinder of viscous liquid. With increasing viscosity, the detachment of drops through a Plateau-Rayleigh instability becomes slower what eventually prevents any inkjet process (we do not consider the extrusion of a filament that is cut by a device (valve) as an inkjet process). For Newtonian fluids, the detachment of drops from a fluid surface and the printability of fluids by piezo inkjet is characterized by the Ohnesorge number:

$$Oh = \frac{t_\eta}{t_R} = \frac{\eta}{\sqrt{\rho \cdot d \cdot \sigma}} \qquad\qquad [2]$$

According to Derby (2010) (Newtonian) fluids are printable by piezo inkjet in the range $0.1 < Oh < 1$. The lower border corresponds to formation of satellite droplets and the upper border to a fluid viscosity $> \sim 25$ mPa·s. Many highly viscous fluids are non-Newtonian and their printability cannot be

fully characterized by the Ohnesorge number. More recently Xaar (GB) and Quantica (Germany) developed piezo printheads with an enlarged viscosity range that allow printing of fluids with viscosity up to 60–100 mPa·s, possibly more (Jackson, 2019; Borrell, 2022).

Attempts have also been made to develop digital printing techniques that overcome the technical limitations of piezo inkjet. A successful development is Laser Transfer Printing (LTP), a process based on the Laser Induced Forward Transfer process (LIFT) introduced in 1986 (Serra and Piqué, 2019). LTP is able to print inks with much higher viscosity, larger particle diameter and higher volume fraction of solids than inkjet can. A disadvantage of LTP is the drop generation mechanism that depends on the formation of a vapor bubble. This requires inks that can form vapor bubbles or a sacrificial layer for bubble formation placed beneath the ink film. LFT print engines are large and much more expensive than piezo inkjet engines. This limits the benefit of LTP for multi-material applications.

2. Materials and methods: linking high frequency rheology to printability in a Quantica printhead

The approach followed in this (ongoing) research work is to adapt UV polymers and sols (solid in liquid dispersions) that were developed for vat photo polymerization to the recently introduced printhead from Quantica and possibly to other piezo printheads. The Quantica printhead is not an acoustic printhead, its functional design differs from other piezo printheads (Borrell, 2022; Färber and Hartkopp, 2021). The expected viscosity range is at least up to 100 mPa·s, maybe more. The formation of proper drops from highly viscous fluids is not yet clear. The operating temperature is up to 80 °C. A tradeoff of the design is a large nozzle-to-nozzle distance (1.27 mm) and a rather small maximal printing frequency. The Quantica printheads are in a β-testing stage to date.

In this study, we regard UV-polymers for vat polymerization of dental prosthesis from two manufacturers. The goal is to improve the rheological properties of the dental materials that are important for drop formation without compromising the material properties. This requires to evaluate the relevant rheological properties and to connect them to the chemical composition. This route is not new but advancements in high viscosity printheads and measurement technology cuts out a path for further progress.

Polymers and sols are shear-thinning and viscoelastic fluids. During drop-formation high pressure (up to 1.5 hPa) and high shear rates ($\dot{\gamma} = 10^5–10^6\ 1/s$) act on the ink for a few 10 µs. These conditions cannot be reproduced in standard rheometers. During drop formation an equilibrium state of a non-Newtonian fluid is probably not reached (as it is in a rheometer). It is known that some sols can be printed whose viscosity at low shear rates is much too high. Elasticity plays an important role in the behavior of polymers and sols under short acting stresses and therefore has a strong influence on drop formation (Mackley, Vadillo and Tuladhar, 2016). In oscillatory and vibrational rheology, (linear) viscoelasticity is characterized by a storage module G' and a loss module G'' which describe the spring-like behavior (G'), resp. the viscous dissipation (G'') of a complex fluid. The relation between shear stress $\sigma(t)$ and shear strain $\gamma(t)$ of a complex fluid can be written as:

$$\sigma(t) = (G' + iG'')\gamma(t); \quad \sigma(t) = \sigma_0 e^{i\omega t}; \quad \gamma(t) = \gamma_0 e^{i\omega t} \qquad [3]$$

G' and G'' are functions of the oscillatory or vibrational frequency, a shear modulus G (or several shear moduli) and a relaxation time $\tau = \eta/G$ (or several relaxation times) of the polymer or sol. The functions G' and G'' depend on the physical model of the viscoelastic fluid (Barnes, Hutton and Walters, 1989; Larson, 1999; Mackley, Vadillo and Tuladhar 2016). In order to measure the rheological properties that are relevant for drop formation the oscillation period should be in the order of the time scale for drop formation (10 µs to 100 µs).

3. Results and discussion

We measure (Figure 1) the shear-dependent viscosities of two UV-polymers for vat polymerization of dental prosthesis from two manufacturers (material 1 & 2) and a UV-polymer without fillers or pigments for comparison at temperatures of 25 °C to 80 °C (Anton Paar MCR302 rheometer with cone-plate geometry). At 60 °C to 80 °C the viscosities decrease below 100 mPa·s (from above 1 000 mPa·s at 25 °C) and the approximate Ohnesorge numbers lie close to a printable range. Viscosities in Table 1 are measured at a shear rate of 55 000 s^{-1}. The nozzle diameter of the Quantica printhead that enters into the Ohnesorge number is 60 μm.
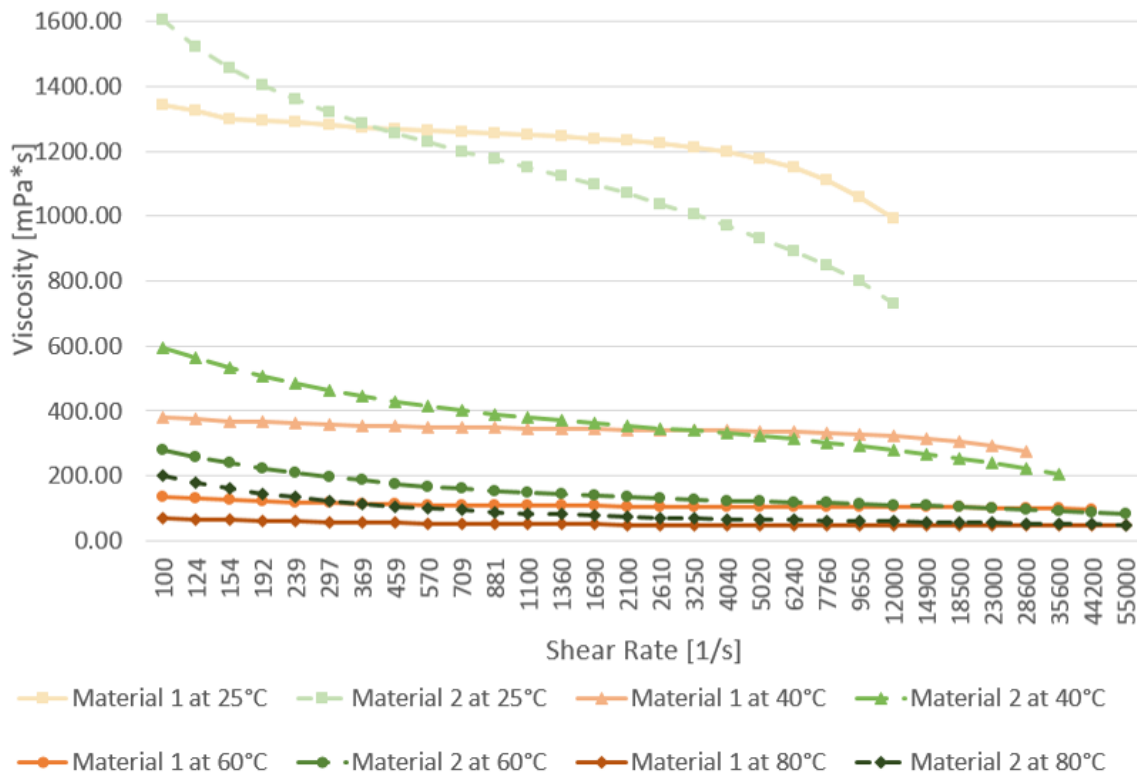

Figure 1: Shear dependent viscosities of the dental materials

Table 1: Basic rheological properties of the dental materials

	Material 1		**Material 2**	
Temperature	60 °C	80 °C	60 °C	80 °C
Viscosity	95 mPa·s	47 mPa·s	83 mPa·s	49 mPa·s
Surface tension	30 mN/m	24 mN/m	38 mN/m	32 mN/m
Density	1.4 g/cm^3	1.4 g/cm^3	1.7 g/cm^3	1.7 g/cm^3
Ohnesorge number	~1.9	~1.0	~1.3	~0.9

Because the dental materials are not designed for processing at elevated temperatures the integrity of the materials was tested. The UV-polymers were stored at 70 °C for 96 h. A UV-LED with 405 nm peak wavelength (M405L3, Thorlabs GmbH) was integrated into the UV module (P-PTD-UV) of the rheometer (Anton Paar MCR302). G' and G'' were measured in oscillatory mode at a frequency of 1 Hz with plate-plate geometry. When the UV-LED was switched on G' quickly increased, indicating the onset of the crosslinking reaction (Figure 2). An effect of degradation due to heating was not observed for any material.
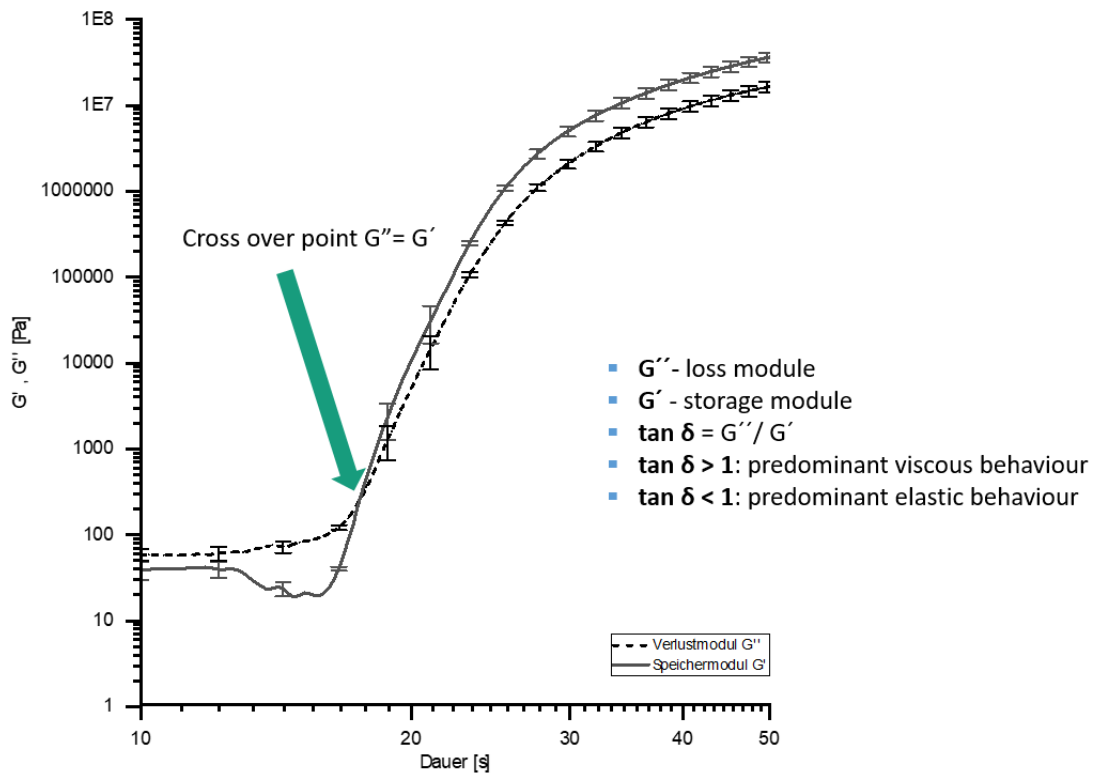
Figure 2: Change of storage module G' and loss module G'' during exposure of the dental materials; the UV-LED is switched on at t = 15 s

We next studied the viscoelastic properties of the UV polymers with a high frequency rheometer (Trijet TriPAV). The functional principle is the vibration of a thin ink film at up to 10 kHz. This allows to evaluate the behavior of polymers and sols under short acting stresses. G' of materials 1 & 2 differ at high vibrational frequencies. A preliminary (not yet reliable) result is shown in Figure 3. We found it difficult to calibrate the TriPAV such that measurements are reproducible.
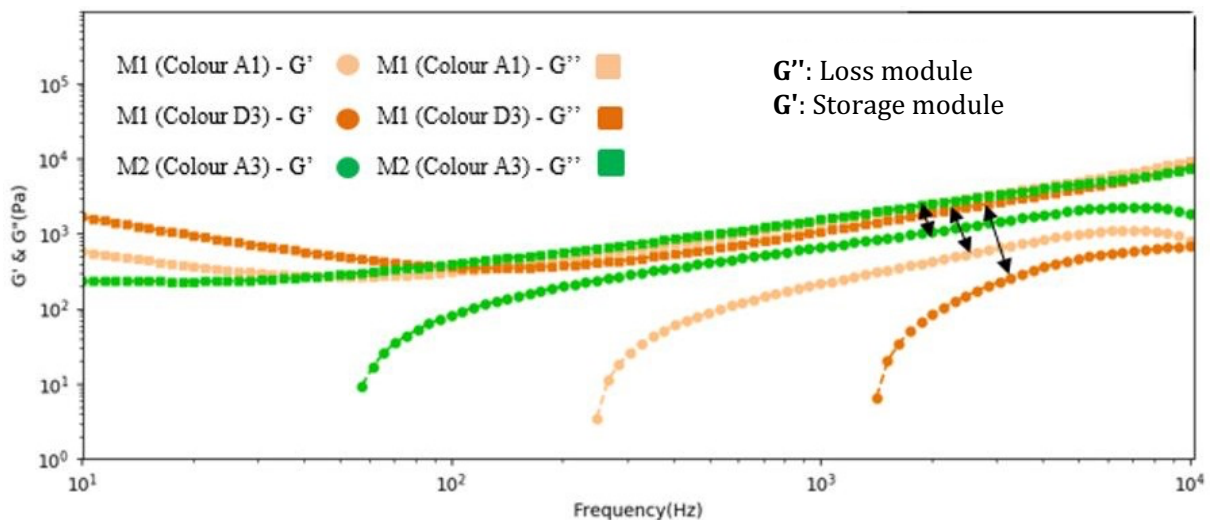

Figure 3: Storage module G' and loss module G'' of materials 1 & 2 measured in the TriPAV (preliminary)

The elasticity of fluids is not only caused by stretching of polymers but also by interaction of suspended particles. These could be insufficiently stabilized pigments. The chemical stability of pigments suffers at elevated temperatures. Therefore, G' and G'' of a UV-polymer without fillers or pigments is studied for comparison.

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A first print test with dental material 1 was conducted by Quantica company. It was shown that the UV-polymer can be printed with the Quantica printhead at 60 °C at a printing frequency of 3.8 kHz. The result was not perfect, strong satellite droplets formed. Reliable measurements of the dental materials with the TriPAV and the connection to drop formation in the Quantica printhead are currently under progress.

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