Photo-chemically induced polycondensation of a pure phenolic resin for additive manufacturing[1]

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Bakelite© or phenoplasts are considered the first synthetic polymers in the world. These resins, produced by polycondensation, have always been known for their chemical resistance, excellent flame resistance and thermal stability. Therefore, they are still used today in space and aviation as well as in the automotive industry. Originally, pressure and temperature are required for processing and limited the production of phenoplasts to compression and injection molding. However, with the invention of lithography and 3D printing, new processing possibilities emerged. Previous work in this area has focused on thin-layer photoresists or parts that can only be printed using other polymers as matrix. Here we report a direct 3D printing method, without binders or matrix polymers, using hot lithography, a stereolithography-based 3D printing technology at elevated temperatures. Formulations could be presented that are stable under the selected conditions and yet reactive enough for the printing process. In addition to the onium-salt based photoacidgenerators (PAG), novolaks and curing agents (CA) are required to obtain a solid thermoset. Novolaks are temperature-stable, non-self-condensing phenolic resins that can only form a network with the help of a CA, usually based on formaldehyde. The most satisfactory results were achieved with a self-prepared CA. In simultaneous thermal analysis and photo-DSC experiments we investigated suitable conditions for the UV-induced polycondensation of the phenolic resins.

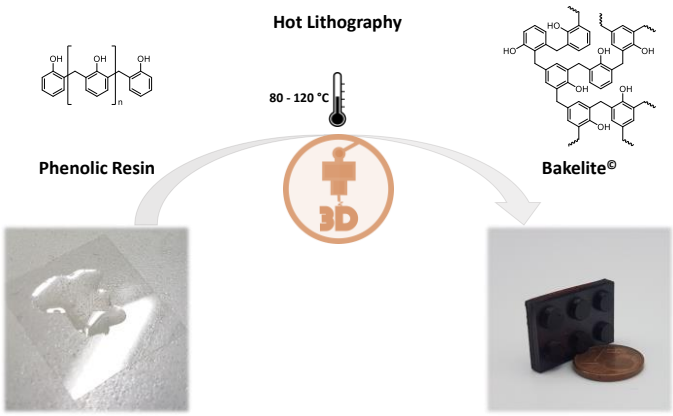

Figure 1: Schematic procedure of this work.

Direct 3D printing with Hot Lithography and post-curing gave bubble-free specimens for mechanical characterization, thus a simple production of complicated structures could be achieved without the conventional complex injection molding. Furthermore it is the first bulk polycondensation process using this technique and moreover the first time that 3D printing of pure Bakelite could be reported.

References

[1] R. Wolff, K. Ehrmann, P. Knaack, K. Seidler, C. Gorsche, T. Koch, J. Stampfl, R. Liska, *Polym. Chem.* **2022**, DOI: 10.1039/d1py01665b.