DIRECT 3D PRINTING OF POLYESTER AND POLYCARBONATE NETWORKS

Katharina Ehrmann[1], Danijela Kojic[1], Stephan Schandl[1], Raffael Wolff[1], Thomas Koch[2], Jürgen Stampfl[2], Robert Liska[1]

[1]Institute of Applied Synthetic Chemistry, Technische Universität Wien, Austria, [2]Institute of Materials Science and Technology, Technische Universität Wien, Austria

Polyesters and polycarbonates are versatile (bio)degradable materials, which are particularly interesting for biomedical applications. Therefore, their manufacturing via stereolithographic methods such as laser- or digital light printing stereolithography is highly desirable for the customized fabrication of degradable biomedical devices.

However, traditional stereolithographic processes are highly dependent on the reactivity and viscosity of photosensitive resins, particularly when printing macroscopic constructs. Therefore, typically utilized photopolymerization methods rely on radical photopolymerization. While mixed photopolymerization via radical and cationic mechanisms became available a while ago via photoacid generators, which form radical cation intermediates and subsequently cations upon irradiation, 3D printing via purely cationic photopolymerization remained elusive until recently. Now, pure epoxide resins can be printed via cationic ring-opening polymerization in stereolithography. However, ring-opening polymerizations are dependent on ring strain and prone to side reactions, limiting their reactivity drastically compared to radical photopolymerization.

This is particularly limiting when polymerizing larger rings with more versatile functionality, such as lactones, cyclic carbonates, spiro-orthoesters or spiro-orthocarbonates. With the rise of hot lithography, such monomers become printable for the first time due to increased reactivity at elevated temperatures. We have demonstrated 3D printing of pure polyesters[1-2] and polycarbonates[3] via ionic ring-opening polymerization. In-depth photopolymerization analysis has elucidated the pathways of ionic polymerization reactions at high temperatures. Bulk photopolymeric specimens of different compositions have been analysed with respect to their thermomechanical properties, revealing easy tuneability within a wide range of mechanical properties. Furthermore, volumetric shrinkage of bulk specimens was eliminated entirely through double ring-opening photopolymerization of spiro-monomers. Finally, successful 3D printing via cationic photopolymerization has been demonstrated.

References

1. Mete, Y.; Seidler, K.; Gorsche, C.; Koch, T.; Knaack, P.; Liska, R., Polymer International 2022, 71 (9), 1062-1071.
2. Kojic, D.; Ehrmann, K.; Wolff, R.; Mete, Y.; Koch, T.; Stampfl, J.; Baudis, S.; Liska, R. Polymer Chemistry 2023, 14 (42), 4809-4818.
3. Schandl, S.; Koch, T.; Stampfl, J.; Ehrmann, K.; Liska, R. Reactive and Functional Polymers 2023, 182, 105460.