

Design of Biocompatible Non-Isocyanate

Polyurethane Elastomers for the 3D Printing of Biomedical Implants

Anna Pierrard^a, Sofia F. Melo^{b,c}, Quinten Thijssen^d, Sandra Van Vlierberghe^d, Patrizio Lancellotti^{b,e}, Cécile Oury^b, Christophe Detrembleur^a, Christine Jérôme^a

^a *Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, Department of Chemistry, University of Liège, Allée du 6 août 13, Building B6a, 4000 Liège, Belgium.*

^b *GIGA Cardiovascular Sciences - Laboratory of Cardiology, University of Liège, Avenue de l'Hôpital 11, Quartier Hôpital, Building B34, 4000 Liège, Belgium.*

^c *Faculty of Medicine, University of Liège, Avenue Hippocrate 15, Quartier Hôpital, 4000 Liège, Belgium.*

^d *Polymer Chemistry and Biomaterials Group, Centre of Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4, 9000 Ghent, Belgium.*

^e *Department of Cardiology - Centre Hospitalier Universitaire (CHU) of Liège, University of Liège Hospital, Liège, Belgium*

Polyurethanes are polymers produced in very large quantities each year and used in many everyday applications, particularly due to their remarkable and tunable mechanical properties. Their biocompatibility also makes them suitable for the biomedical field, in which they are currently clinically employed. Unfortunately, they are industrially synthesized from highly toxic isocyanates, which are responsible for environmental and health issues. To avoid this synthesis problem, safer and greener alternative synthetic routes have been developed, leading to so-called non-isocyanate polyurethanes (NIPUs), that in some cases bear additional hydroxyl groups next to their urethane linkages.

In this work, we take advantage of these hydroxyl groups by functionalizing those of a new polyether-based NIPU by a CO₂-sourced cyclic carbonate molecule carrying a pendant unsaturation, which subsequently allows its photocrosslinking with various polythiols by thiol-ene reaction. NIPU elastomeric networks with adjustable physico-chemical properties, and especially excellent tunable mechanical properties, are thereby designed. Rheology experiments performed on the formulations demonstrated short gel times, which confirmed their suitability for light-based 3D-printing processes. The digital light processing printing technique was then chosen to 3D print various objects with a resolution down to the micrometer scale. Finally, *in vitro* biocompatibility and hemocompatibility tests proved the non-toxicity of these NIPUs towards human fibroblasts and blood components, respectively.

These biocompatible 3D-printable polyether-NIPU elastomers are therefore suitable for the design of various structures adapted to the needs of personalized medicine and have great potential for future biomedical applications, including the elaboration of elastic scaffolds for the tissue engineering of soft tissues.