Abstract MRS Spring Meeting & Exhibit

3D-Printability of PPG-poly(hydroxyurethane) Elastomers Using Thermal or UV Curing Processes

The use of additive manufacturing for biomedical applications has recently paved the way for new innovations thanks to its high accuracy and precision, fast fabrication and ability to create custom parts. Since non-toxic polymers available for 3D printing are limited, polyurethanes (PUs) play a key role, especially in the medical field due to their biocompatibility. However, their synthesis requires the use of very hazardous isocyanates which are produced with the even more toxic phosgene. In order to avoid their use, more environmental-friendly synthetic routes for PUs have therefore been developed. Among them, the synthesis of poly(hydroxyurethane)s (PHUs) by the polyaddition of bis(cyclocarbonate)s to diamines emerged as one of the most promising routes due to its simplicity and versatility, and the low toxicity of the cyclic carbonate building blocks. Nowadays, five-membered rings bis(cyclocarbonate)s can even be obtained by coupling CO_2 to epoxides (that can be partially or totally biosourced), therefore valorizing CO_2 as a sustainable chemical feedstock. Since it is challenging to achieve reproducible 3D printed PHU materials, only a few research groups reported strategies to 3D print PHUs.

In this work, two curing approaches of PHUs have been developed and compared to find the best candidate PHU materials for 3D printing in terms of curing rate, thermal, mechanical and rheological properties. For that purpose, poly(propylene glycol)-poly(hydroxyurethane) (PPG-PHU) networks were prepared under thermal or photochemical curing conditions. In the thermal crosslinking approach, a poly(propylene glycol) bis(cyclocarbonate), a diamine and a triamine crosslinker were copolymerized in bulk at a moderate temperature. In the UV crosslinking approach, we developed a simple strategy to introduce allyl functions on PPG-PHUs that were then exploited to crosslink the polymer by a thiol-ene reaction with a tri-thiol compound. The influence of the PPG molar mass and the reaction conditions on the polymerization processes and the final network properties were deeply investigated in the two cases, and the type of amine used (aliphatic or aromatic) was also studied in the thermal curing approach. Rheological measurements show that both systems are highly crosslinked network structures but with different curing rates depending on the curing process used, and that PHU networks are formed faster by the second approach, i.e. UV curing. Based on these findings, a UV curable allyl-hydroxyurethane 3D printable resin was prepared in order to create custom objects by photopolymerization.

In this talk, we will thus present the two ways of production of crosslinked PHUs, as well as the impact of the processes and the reaction conditions on the curing of the resins and the final properties of the materials. Finally, we will show how the best system can be exploited for the facile production of 3D printed objects based on PHUs.