Synthesis of biobased building blocks from vegetable oils: toward platform chemicals

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Polyurethanes are traditionally prepared by reacting an oligomeric polyol and a diisocyanate. Whereas the isocyanate component is always derived from petrochemical feedstocks, the polyol component could come from biobased resources. The use of biobased polyols for the manufacture of polyurethanes is a real positive point for the envi-ronmental impact of polymers. It is all the more interesting to use biobased polyols in PU synthesis since polyols represent the major part of PU, generally between 60 to 70% in weight of PU. Vegetable oil-based polyols could be synthesized from varied oils which, except castor oil, have to be chemically fonctionnalized to meet the polyurethane production requirements. Transesterification and epoxydation are already industrially used for the production of polyols from oleochemicals. The thiol-ene reaction represents another interesting toolbox for the functionalization of unsaturated vegetable oils. Indeed, this reaction of “click chemistry” allows photochemical or thermal initiation, undemanding synthesis conditions thanks to the insensitivity to oxygen inhibition, and leads to high yields with basic purification procedures. Firstly, our team used reactive molecules bearing hydroxyl or amine functions to synthesize tailored modified vegetable oils. Secondly, we extended the use of thiol-ene on vegetable oils to the synthesis of new polyamine and polyacids building blocks for polymer synthesis. From polyfunctional building blocks made from vegetable oil, we followed two pathways to synthesize biobased polyurethanes: firstly, we used polyols in standard polyurethane synthesis to produce partially bio-based polyurethanes. Then, we synthesized biobased dicyclocarbonate and biobased oligomeric polyamines, that react together to form isocyanate-free polyurethanes. It is all the more interesting since cyclocarbonates could be synthesized by functionalization of glycerol, produced in large quantities by the transesterification of natural triglycerides as part of bio-diesel production. This method leads to totally biobased polyurethanes. In both cases, polyurethane materials synthesized were characterized by physicochemical analyses and thermal characterizations.