Functionalization of vegetable oils and their derivatives for new bio-based polyurethane coatings

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Vegetable oils and their derivatives were used to synthesize new precursors suitable for polymer synthesis. Firstly, mercaptoethanol was grafted onto unsaturated triglycerides by thiol-ene coupling to yield polyols. Experimental parameters of mercaptoethanol addition were investigated and optimized, and yet several by-products were identified. Indeed, disulfide formation and intermolecular recombination occurred. Despite these side-reactions, by-products bear hydroxyl functions, suitable for further reaction. Interestingly, thiol-ene coupling reaction can be performed under mild conditions, requiring neither solvent, nor controlled atmosphere, and the crude product could be purified by an easy procedure. This efficient functionalization was also applied to vegetable oil methyl esters, yielding telechelic diols with ester and amide bonds. The second synthetic strategy used ring opening of epoxydized vegetable oils. The reaction between vegetable oil oxiranes and several bio-based carboxylic acids led to a wide range of polyester polyols. Thus, the synthesized intermediates allowed to formulate various polyurethanes, which exhibited glass transition temperatures ranging from -10℃ to 100℃.

Moreover, either esterification or thiol-ene coupling were performed on glycerin carbonate, leading to new dicyclocarbonates. Isocyanate free polyurethanes were then obtained from those dicyclocarbonates, opening the way for fully bio-based polyhydroxyurethanes.

The new precursors, and the polymers therefrom, were deeply characterized and some of them were tested at a pilot scale