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Controlling ring opening in poly(furfuryl alcohol) for tuning properties

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PURPOSE OF THE ABSTRACT

Among the wide variety of bio-based polymers, few can withstand high temperatures and chemical aggressivity. Poly(furfuryl alcohol) (PFA), a bio-based thermoset is capable of showing such performance. It is nowadays mostly used as a sand binder for metal casting mold [1]. Indeed, this bio-based thermoset can resist high temperatures for longs periods of time (T5% ~300°C for pure PFA). Nonetheless, this thermostability comes with high brittleness as a downside. Thus, limiting the applications of PFA. The properties of PFA take their origin from the complex chemical structure of this thermoset. Indeed, PFA is a dense network of furfuryl units linked together by methylene bridges and Diels-Alder crosslinks. The crosslink density and thus chain mobility can be somehow tuned using a side-reaction occurring during the polymerization. As a matter of fact, all along the polymerization the furan unit can open into ?-diketones. Falco et al. demonstrated that introducing open structures in the PFA lead to a decrease of Tg, T5%, crosslink density as well as its' Young modulus. [2] Therefore, controlling the Degree of Open Structures (DOS) could be an asset to tune the properties of PFA. To do so, we adapted existing carbonyl quantification methods to PFA systems. [3]. The first one is titrimetric method based on derivatization with a small hydroxylamine. The second one is using a derivatization with a fluorinated phenyl hydrazine followed by 19F NMR spectroscopy. The results obtained with both methods are consistent and have been check with 13C quantitative solid-state NMR. Depending on the method used, the chemical accessibility of the carbonyls can be assessed. Indeed, the nature of the derivatizing agent plays a role in the DOS value. The NMR gives lower DOS than the titrimetric one. The gap has been attributed to steric hindrance within the PFA and/or presence of acetals in the systems. Finally, the control of the DOS was studied during the polymerization. A wide range of catalyst was studied as well as the proportion of water. Overall, the maximum DOS reach was of 0.15, i.e. 15% of open structures.

FIGURES

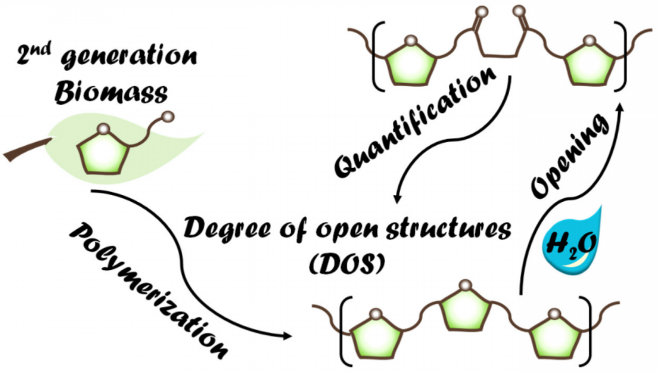

FIGURE 1

Graphical abstract

Graphical abstract of the talk

FIGURE 2

KEYWORDS

Bio-based poly(furfuryl alcohol) | Degree of Open Structures | Carbonyl quantification | Furan ring-opening

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BIBLIOGRAPHY