Vegetable oil-based 5-membered cyclic carbonates as bio-based building blocks for NIPU foams: catalysis, synthesis and kinetic aspects

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Significance and Relevance

In this work, the catalyzed CO_2 cycloaddition of epoxidized soybean oil (ESBO) to produce 5-membered cyclic carbonates has been studied from the catalytic and kinetic point of view. The reaction product, i.e. carbonated soybean oil epoxy (CSBO) has been successfully utilized in the aminolysis reaction with a bio-based diamine for the synthesis of fully renewable isocyanate-free polyurethane foams (NIPU) through a self-blowing approach.

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Introduction and Motivations

Globally, agricultural waste deriving from e.g., agro-industries, crop residues and livestock accounts for approximately 2 billion tons per year. The valorization of this huge amount of biomass is indeed extremely urgent in the circular economy viewpoint. For instance, vegetable oils can be readily extracted by decomposition and further treatment of biomass and utilized as feedstock for the production of value-added products, such as biopolymers and biopolymers building blocks[1]. In particular, epoxidized vegetable oils i.e., soybean oil epoxy (ESBO), are promising precursors for the synthesis of non-isocyanate polyurethanes (NIPU). The catalysed cycloaddition of CO_2 to ESBO produces a multifunctional five-membered cyclic carbonate i.e., soybean oil cyclic carbonate (CSBO) which is particularly interesting as the precursor of NIPU[2].

In this work, the carbonation of ESBO was performed in a stainless-steel reactor autoclave (Parr) under solvent-free conditions, at relatively high temperatures and CO_2 pressures and in the presence of quaternary ammonium salt halides as catalysts. The kinetics of the reaction has been studied by varying the operating parameters i.e., temperature, pressure and catalyst load, and the final product has been further utilized to synthesize non-isocyanate polyurethane (NIPU) foams with the self-blowing approach.

Materials and Methods

The soybean oil epoxy (ESBO) has been fully characterized by IR and GC-MS to determine the fatty acids content. The carbonation of ESBO was performed in a stainless-steel reactor autoclave (Parr) in solvent-free mode, at relatively high temperature and pressure of CO_2 and in the presence of quaternary ammonium salt halides. In particular, tetrabutylammonium bromide, chloride and iodide (TBAB, TBAC, TBAI) were tested and compared. Very precise kinetic studies were conducted with the best catalyst by varying the reaction temperature (80-130 °C), CO_2 pressure (10-30 bar), catalyst loading (2.5-10 wt%) and stirring rate (200-500 rpm). The reaction products were analyzed both qualitatively and quantitatively with ^{1}H-NMR 500 MHz employing $CDCl_3$ as solvent, after careful validation of the analytical method by comparison with the well-established Jay's oxirane titration[3].

At the end of the reaction, the catalyst was separated from the product by solvent extraction with ethyl acetate and water. Finally, ethyl acetate was separated in the rotavapor at approximately 65 °C, 100 mbar and 50 rpm. The final product CSBO was then reacted with 1,4-diaminobutane together with suitable catalysts/fillers to successfully obtain NIPU foams.

Results and Discussion

The kinetic experiments were conducted with tetrabutylammonium chloride (TBAB) as the catalyst, being the most active among the ones screened. The conversion of the soybean oil epoxy (ESBO) and the yield of the cyclic carbonate (CSBO) were measured by quantitative ^{1}H-NMR. The conversion results were then compared with titration of the epoxy group in order to validate the analytical method. Both techniques confirmed the full conversion of ESBO after 24 h of reaction at 130°C and 40 bar from the disappearance of epoxy peaks in the area 2.8-3.2 ppm (Figure 1). In the same conditions, IR measurements confirmed once again the full conversion of the ESBO since the peak in the region 815-950 cm^{-1} (C-O-C stretching of oxiranes) disappeared after the carbonation experiment. At the same time, the production of the CSBO was confirmed by the appearance of a band at 1800 cm^{-1}. Regarding the yield of CSBO, it was overall higher than 80-90%; however, the formation of keto-byproducts was observed in the NMR spectra at 2.4 ppm and it occurred through a parallel reaction network respect to the main reaction. As revealed by the kinetic experiments, the reaction temperature and the catalyst amount had a strong influence on both the reactant conversion and the product yield, while CO_2 pressure had overall a milder effect on the system. After separation of the catalyst by liquid-liquid extraction, pure CSBO was obtained and then mixed with 1,4-diaminobutane (putrescine) to obtain NIPU foams. Different formulations were tested varying the starting material/fillers kind and amounts. It was observed that blending CSBO with another bio-based cyclocarbonate i.e., butanediol bis(cyclocarbonate) (BCC) resulted in the best performance of the final material thanks to the presence of unsubstituted methylene groups. The resulting NIPU foams were thermally, chemically, and morphologically characterized.

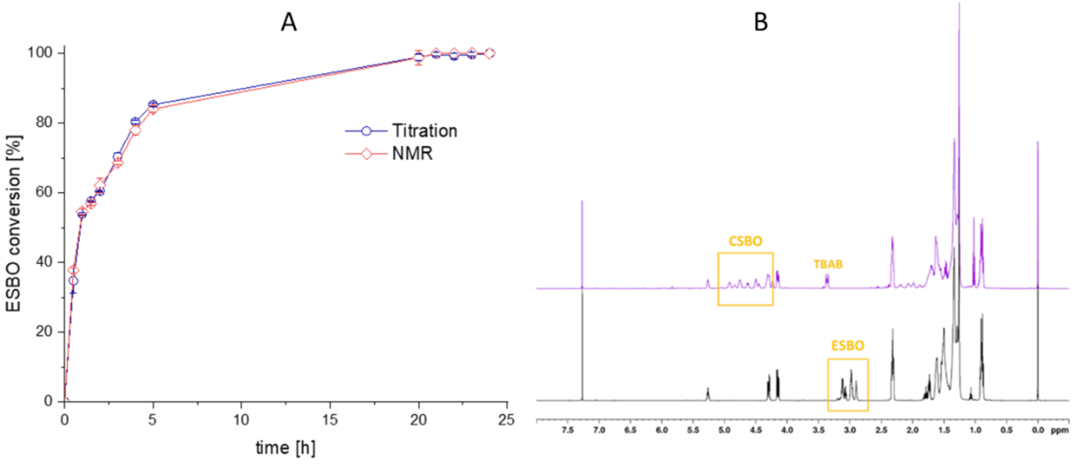

Figure 1. Reaction scheme of limonene dioxide carbonation (A). Temperature effect on the kinetics of CO_2 cycloaddition of limonene diepoxide (B).

References

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