

## Abstract

Epoxy resins represent an important category of thermosets widely as coatings, electronic encapsulants, matrices for composites, etc., due to their beneficial properties, such as strong adhesion, high chemical and electrical resistance, and good processability. However, their curing reactions present some limitations, such as using catalysts (for example, organometallics, complexes and MOFs) which are active at high reaction temperatures. In most cases, these catalysts are toxic and require organic solvents. Consequently, alternative non-toxic catalysts/initiators that can promote well-controlled fast curing under mild conditions have been explored while maintaining sufficient thermomechanical properties of the formed epoxy networks.

In this thesis, three different epoxy ring opening reactions induced by various imidazolium ionic liquids (ILs) were studied.

The first subsection (4.1) discusses the step-growth epoxy-dicarboxylic acid polymerization in an imidazolium IL medium conducted under mild conditions ( $T = 80\text{--}120\text{ }^{\circ}\text{C}$ ). The IL was shown to act as both a solvent and an initiator/catalyst for the reaction. In addition, IL-anions (chloride, bis(trifluoromethylsulfonyl) imide, or methanesulfonate) strongly affect the progress of the reaction. It was found that the  $\text{Cl}^-$  anion is the most effective epoxy ring-opening initiator, suitable for the production of glassy epoxy networks.

In the second subsection (4.2), the epoxy-anhydride copolymerization in the presence of imidazolium metal-containing ILs (MILs), bearing tetra-chlorinated iron, cobalt or zinc, and imidazolium metal-free, 1-butyl-3-methylimidazolium chloride (BMIMCl) is investigated. It was observed that MILs significantly accelerated epoxy-anhydride cross-link reaction more than the metal-free BMIMCl, especially at low temperatures, due to MILs' ability to activate a rapid anhydride ring opening resulting in the formation of carboxyl groups, that initiated further polyesterification. Despite various MILs-initiated pathways (polyesterification, imidazole and counter-anion), the alternating epoxy-anhydride copolymer chain was formed. Finally, MILs-induced crosslinking resulted in homogeneous network build-up producing glassy thermoset materials with increased cross-link density, a high glass transition temperature and excellent thermal stability.

The last subsection (4.3) describes the cycloaddition reaction between carbon dioxide ( $\text{CO}_2$ ) and epoxy monomer in the presence of BMIMCl, and MILs, which showed the anionic

Cl<sup>-</sup> initiation of the oxirane ring. The ILs used promoted fast and high yields of cyclic carbonates (up to 99% within 1 h). The subsequent aminolysis of the cyclic carbonates with a monofunctional amine led to the conversion into  $\beta$ -hydroxyurethanes without using an additional catalyst.

It has been demonstrated that ILs can be considered as novel additives for various epoxy systems enabling, the epoxy ring opening, the epoxy crosslinking with functional compounds, and the CO<sub>2</sub> absorption and cycloaddition to epoxy.