<u>Review Report for the Doctoral Thesis</u>

Title: **Use of Ionic Liquids for Preparation of Epoxy Materials**
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The doctoral thesis authored by M.Sc. Marwa Rebei focuses on the innovative use of ionic liquids (ILs) in the preparation of epoxy materials. This research is particularly significant in the field of macromolecular chemistry due to the widespread industrial and technological applications of epoxy resins. The thesis is structured to explore the catalytic roles of different types of ionic liquids in various epoxy polymerization reactions, aiming to address current environmental and sustainability challenges associated with conventional epoxy curing processes.

The primary objective of this research is to investigate the efficacy of imidazolium-based ionic liquids as catalysts and initiators in epoxy ring-opening reactions. The thesis is divided into three main experimental studies: i.) Epoxy-dicarboxylic acid copolymerization using imidazolium ILs. ii.) Epoxy-anhydride copolymerization in the presence of metal-based ILs. iii.) Epoxy-CO_2 cycloaddition reactions facilitated by ILs. Each study aims to understand the mechanistic pathways, optimize reaction conditions, and evaluate the thermomechanical properties of the resulting epoxy networks.

The methodologies employed in this thesis are comprehensive and robust, involving both experimental and theoretical approaches. Various advanced characterization techniques such as FTIR, NMR, DSC, TGA, and DMTA are utilized to analyse the chemical structure, thermal properties, and mechanical performance of the synthesized epoxy networks. Density Functional Theory (DFT) calculations are used to support experimental findings and provide insights into the reaction mechanisms at a molecular level.

The research successfully demonstrates that imidazolium ILs can act as both solvents and catalysts in the epoxy-dicarboxylic acid copolymerization. The study highlights the significant impact of IL anions on the reaction efficiency, with chloride anion identified as the most effective in initiating the epoxy ring-opening.

The use of metal-containing ILs in the epoxy-anhydride copolymerization is another innovative aspect of this research. The study reveals that these ILs significantly accelerate the copolymerization process, especially at lower temperatures.

The investigation into the epoxy-CO_2 cycloaddition reaction offers a sustainable approach to synthesizing non-isocyanate polyurethanes.

M.Sc. Marwa Rebei's thesis makes significant scientific contributions by expanding the understanding of ionic liquids in epoxy chemistry. The research offers practical solutions to improve the sustainability and efficiency of epoxy curing processes, which can be directly translated into industrial applications.

While the thesis is exemplary in many respects, a few areas could benefit from further exploration:

Future research could investigate the long-term stability and aging properties of the epoxy networks formed using ILs.

The scalability of the synthesis processes for industrial applications could be more thoroughly examined.

Additional comparative studies with other types of catalysts could further validate the advantages of using ILs.

In conclusion, M.Sc. Marwa Rebei's doctoral thesis significantly contribute to the field. The innovative use of ionic liquids as dual-function catalysts and solvents in epoxy polymerization reactions offers practical and scalable solutions for industrial applications. The comprehensive experimental and theoretical analysis, coupled with the promising results, underscores the high quality and impact of this research.

I strongly **recommend** the acceptance of M. Sc. Marwa Rebei's thesis **for the award of the doctoral degree**.

Questions about the work:

1. What are the main advantages of using ionic liquids compared to traditional catalysts in epoxy reactions? How did you recycle the ionic liquids from the reaction and with what efficiency?

2. How does the structure of anions in ionic liquids affect their catalytic activity in epoxy reactions?

3. How did you optimize the reaction conditions (temperature, humidity, etc.) for epoxy-anhydride copolymerizations using metal-containing ionic liquids? What factors were most important?

4. Can you describe how you used DFT calculations to support your experimental results? What specific information did these calculations provide?

5. What potential do you see for the use of ionic liquids in the industrial production of epoxy materials? What are the main obstacles to their wider adoption?

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