

Review report on the Ph.D. thesis of Marwa Rebei

entitled

Use of ionic liquids for preparation of epoxy materials

The focus of the submitted Ph.D. thesis of M.Sc. Marwa Rebei falls into the current field of polymer research, namely the issue of epoxy resins, being used in many areas, such as electronics, composite materials, or coatings. The Ph.D. thesis deals with the application of several imidazolium-based ionic liquids as catalysts/initiators of important reactions of the epoxy group, specifically its reaction with dicarboxylic acid, anhydride, or carbon dioxide. The research was focused on assessing the catalytic effect of various ionic liquids on the copolymerization or cycloaddition reaction of the epoxy group as well as on the properties of the resulting epoxy materials. An important part of the Ph.D. thesis was also the study of the mechanism of individual epoxy ring-opening reactions. When solving the issue, a sustainable and ecological approach was also taken into account, which consisted not only in the use of ionic liquids throughout the entire research but also manifested itself in sub-parts of the research, for example in the use of bio-based epoxy monomer as the basic epoxy resin or in the subsequent use of epoxy products of the ring-opening cycloaddition reaction for the production of non-isocyanate polyurethane materials.

The Ph.D. thesis of M.Sc. Marwa Rebei is prepared in the form of an annotated set of selected publications. It is written with a minimum of formal, spelling, and stylistic errors. Suitable experimental methods were used for the successful processing of the topic, the outputs of which were adequately evaluated and provided sufficient information about the structure of the synthesized materials and their physico-chemical properties. The discussion of the research results is conceived logically, I also positively evaluate the chronological continuity of the experiment. In terms of content and expertise, the Ph.D. thesis is therefore prepared at a high level.

The success of the submitted Ph.D. thesis is documented by publication outputs. From papers that have already been published in high-quality impacted scientific journals (3 published papers and 1 submitted paper), it is quite clear that the Ph.D. thesis brings original scientific results. In 3 of these publications, M.Sc. Marwa Rebei is the first author, which indicates her significant contribution.

The outputs of the Ph.D. thesis of M.Sc. Marwa Rebei fully fulfill the set goals. In this work, the catalytic and initiation effects of metal and non-metal-based ionic liquids were studied finding that the metal-based ionic liquids appear to be promising and universal functional additives for epoxy systems. The reaction mechanisms of the epoxy group were clarified, and sufficient attention was paid to the evaluation of the properties of the resulting

epoxy materials. The obtained results were adequately discussed and summarized. I consider the chosen topic and the results of the Ph.D. thesis to be very valuable not only in terms of scientific contribution but also in terms of application potential. From the overall solution of the chosen issue, it is quite evident that not only the candidate, M.Sc. Marwa Rebei, as well as the training workplace, must be evaluated very highly in terms of the quality of scientific work.

I have the following questions for the candidate:

- 1) What were the reasons for choosing the specific imidazolium metal-based ionic liquids, especially for the cobalt compound? Have new types of metal-based ionic liquids recently appeared in the field of catalytic/initiating action in epoxy polymerizations? Which other metals, as part of the ionic liquid anion, do you consider potentially suitable for this utilization?
- 2) There is a statement on page 20: "Epoxy-amine and epoxy-acid polymerization are typical reactions of step-growth polymerization, while epoxy-anhydride follows chain-growth polymerization". Could you explain why the epoxy-anhydride copolymerization reaction doesn't belong to step-growth polymerizations?
- 3) Table 2 shows dynamic DSC results for different DGEBA/MHHPA formulations. The decrease in T_{onset} of the curing reaction in the case of DGEBA/MHHPA/BMIMFeCl₄ was explained sufficiently, but a significant reduction in T_g (compared to other formulations) has not been discussed. Could you give a reason for this phenomenon? Related to this question, can you explain the difference in the plasticization ability among the metal-based ionic liquids (results presented in Table 3)?
- 4) The introduction of the Ph.D. thesis states that ionic liquids also show potential recyclability at the end of the reaction. Was this aspect dealt with in any way during the research? If so, was it possible to recycle a significant proportion of the ionic liquid from the hardened epoxy resin, and did the type or plasticizing ability of the metal-based liquid affect its recoverability?
- 5) When trying to find the optimal amount of individual metal-based ionic liquids, molar concentrations were used (Table 3), and on page 47 it is stated: "These optimized MIL amounts were significantly lower (by 7-fold for BMIMFeCl₄ and 3-fold for (BMIM)₂CoCl₄ and (BMIM)₂ZnCl₄) compared with the metal-free IL (BMIMCl) and conventional catalyst (1MIM), which is advantageous from an economic and environmental point of view." I admit that molar concentrations have a noticeable meaning, but from an economic and ecological point of view, mass concentrations may be

more decisive. If we convert the molar concentration to mass concentration (which was done in Table 4), then a significant reduction in the amount of metal-based ionic liquid occurred only for BMIMFeCl₄. Therefore, in my opinion, the statement on page 47 in the case of (BMIM)₂CoCl₄ and (BMIM)₂ZnCl₄ is incorrect.

- 6) Why BMIMFeCl₄, showing the most promising activity in epoxy-anhydride copolymerization, wasn't used for testing the catalytic properties in epoxy-CO₂ cycloaddition reaction?

Conclusion:

In my opinion, the submitted Ph.D. thesis of M.Sc. Marwa Rebei is a successful scientific work that meets the requirements set for works of a similar type. It brings original scientific results that have already been published. Therefore, I fully recommend her for admission to the defense. I also recommend after the successful defense of the submitted Ph.D. thesis, M.Sc. Marwa Rebei to be awarded the scientific title of **Ph.D.**

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