

Review of Ph.D. Thesis

M.Sc. Sonia Bujok:

Microwave-assisted preparation of polymer materials

The aim of the work is the preparation of biodegradable polyester whose mechanical properties can be improved by the presence of inorganic layered material. The intention is to "cheapen" the process of synthesis of new materials in terms of energy consumption by performing a polymerization process in the presence of microwave radiation. The work is written clearly in English and has the usual division of chapters with a logical sequence.

The introductory chapter is a literary survey on the topic. First, a microwave assisted ring opening polymerization (ROP) is described with an orientation mainly to ϵ -caprolactone polymerization. Furthermore, the mechanisms of ϵ -caprolactone polymerization are described in a clear form. The following part is devoted to the preparation of polyester nanocomposites. It is stated that the preparation of polyester/LDH nanocomposites by in situ procedure with the participation of conventional heating and microwave irradiation is given less attention in the literature. Layered double hydroxide (LDH) is used as a filler in the preparation of polymer (nano)composites and also a versatile material in catalysis of organic reaction. These benefits were motivation for the preparation of poly(ϵ -caprolactone) nanocomposites. At the end of the introductory chapter, the role of ionic liquids as catalysts, interfacial agents and solvents in microwave polymerization of cyclic compounds is described.

The aims of the work are clearly and concisely defined based on a critical analysis of the findings from the introductory chapter.

In the Experimental work section, it is stated which methods she used to prepare and characterize the prepared materials and which worker performed the analysis. Usually, the type of device is also stated, which is missing in this part of the work. It is inconvenient for readers to refer to page 54. The author prepared two types of LDH containing ionic liquids and further performed polymerizations. Experimental procedures are not listed here. I think that there could have been procedures or a reference to the relevant work given in Appendix No, etc.

The main part of the work Results and Discussion gives an overview of the results achieved with reference to the publications outputs (Appendices 1-4). The author is mostly in the first place and her contribution on publication outputs is high. I am convicted, that the reviewers certainly helped to fine-tune the manuscripts with their recommendations and comments and reduced work of the reviewer of the thesis. The results of the work are well processed and logically sorted.

I appreciate synthesis of layered double hydroxides functionalized with ionic liquid and their detailed characterization. The author and her supervisor are surely pleased to expand the scientific knowledge of ϵ -caprolactone microwave-assisted polymerization in the presence of LDH containing ionic liquids including kinetic evaluation of the process. The mechanism of non-catalyzed and catalyzed polymerization of ϵ -caprolactone is clearly presented graphically including the individual stages of the process. An integral part of the work are application related measurements of gas permeability, including water vapor and antimicrobial effects of prepared materials against pathogenic bacterium *E.coli*.

Conclusions from these studies point to the right direction of research in this area. It is clear from the publication outputs that the work has contributed to the expansion of scientific knowledge.

I have a few questions, comments, and topics to discuss

Abstract – first paragraph belongs to introduction.

Page 15. Linear polyesters (PLA, PHB, PCL, PBS, PBAT, PHB) are biodegradable, At present, their use as packaging materials is economically disadvantageous.

Page 33. “TGA of freshly dried $\text{Ca}^{2+}/\text{Al}^{3+}$ LDH enabled to determine the exact content of water”. Is there another method for determining the exact water content for confirmation? The content of water in polymerization mixture is crucial because affects the course of caprolactone polymerization.

Page 39. What is the accuracy of the determination of ϵ -caprolactone content in the reaction mixture from SEC?

Are you sure that macrocycle formation contributes to increasing dispersity? Did you notice a cyclic dimer of ϵ -caprolactone in the polymerization mixture?

Page 41. Table 3. In headline of the table $M_n \cdot 10^3$, I think it is not correct. The same problem in Table 6.

Page 42. Table 4. Accuracy of enthalpy of fusion and crystalline phase content (1 decimal place)!

Page 47. “During the course of biodegradation, the PCL dispersity (\bar{D}) is decreased due to preferential cleavage of short PCL chains”. Is it the statement Ok? Biodegradation test with mixed microorganisms cultures lasted 4 weeks. This time is too short to evaluate sensitivity to degradation.

In conclusion, I can state that the submitted work is well prepared and the above comments do not in any way reduce its high scientific level. Therefore, I recommend the work for the defense.

Prague, September 17th, 2021



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