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OPPONENT OPINION

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“Biodegradable polyesters and polyanhydrides for advanced application”

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The preparation and possibility of advanced application of biodegradable polyesters and polyanhydrides were investigated, during the Author's work. The field of experimental work is focussed to the actual problem of both waste management and biopolymer synthesis, namely to the production of new kinds of biodegradable polyesters and polyanhydrides.

The length of the thesis is 98 pages without list of figures, abbreviations and reference list. It is divided into two main parts: theoretical background and experimental part. The reference list contains 253 references. The Author also attached a list about her publications: 5 journal articles and 4 papers in conference proceeding. The large number of references well supported the scientific discussion in the theoretical background of the work.

The PhD doctoral thesis is well edited work, containing new experimental results, which was published in impacted scientific journals.

The theoretical part of the doctoral thesis contains 32 pages. That section summarizes the main background of the experimental work, focussing to the different biopolymers and their derivatives. In this part, the Author tries to present the opened an unsolved problems in the field of biodegradable polyesters and polyanhydrides. It was concluded, that there are some areas, where lots of information is needed for complex view of problem and further results are necessary for advanced application of polyesters and polyanhydrides biopolymers; especially to reach advanced biocompatibility, cytotoxicity or biomedical and packaging application. The structure of theoretical part is logical containing lots of relevant information. What does Author think, biopolymers have economical and other benefits or only environmental/chemical? What are the main worldwide trends regarding bioplastic, biodegradable polymer market?

Only limited typewriting was found in the first part.

- General typewriting that the point at the end of the sentence is after the reference, while sometimes that is before the reference. E.g. "... for certain applications. [79]." (at page

18), "... reported by Anderson et al. [82]" and "... the assimilation occurs (F). [85]" (at page 19), "... crystallinity degree etc." (at page 25), "... steric hindrance. [148]" and "... attraction of isocyanates. [149,150]" (at page 31).

- Some paragraphs begins without "Tab" (e.g. "Poly(lactic acid) has been ... " (at page 41)), while others with "Tab" (e.g. "The chain linking ... " (at page 41)).

The experimental part contains three main sections: (a) novel chain linked PLA/PEG synthesis and their application in nano-encapsulation, (b) optimization of melt polycondensation for sebacic acid polyanhydride focussing to application as drug delivery device, (c) high molecular weight polyester urethane synthesis and characterization.

One of the strengths of the Author's work, that different advanced instrumental and other analytical methods (e.g. FTIR, GPC, DSC, Py-GC-MS, NMR, and SEM) and advanced synthesis ways were applied and used during the experimental work. On the other hand Author was participated in scientific projects belongs to her PhD work.

Regarding the experimental work, PLA/PEG copolymers with different NCO/OH content were synthesized belongs to the first section (Chapter 2.1.) using HMDI and MDI. The experimental work is imposing; however it is not clear, why NCO/OH ratios of 2.3, 2.7 and 3.2 were used for polymer synthesis? Based on results it was concluded, that HMDI resulted better properties than using MDI, which was to the difference in amorphous and crystalline structure of products using HMDI and MDI. Authors give an explanation about the possible cause of the mentioned difference, comparing that with results based on others' work on page 55. What does Author think, the real background of the difference was caused by the difference in polarity or rather sterical properties of the chemicals? It is important result, that nanoparticles could be prepared using solvent evaporation, which was demonstrated and supported by SEM result. According to Figures 31 and 32, the number average molecular weight of PLA-PEG copolymers with HMDI was very close using 2.7 and 3.2 HMDI, however there was larger difference in tensile properties using 2.7 and 3.2 HMDI. What was the possible cause for the phenomenon?

Chapter 2.2 summarizes the experimental results focussing to poly(sebacic anhydride) synthesis using lots of different catalysts. I think, one of the most valuable parts of this section is the really wide range catalyst testing. Results showed that high molecular weight polymer could be synthesized using CaO catalyst. Based on TGA and Py-GC-MS it was concluded that the polymers had two steps degradation mechanism, and the second step was belongs to the degradation of primary degraded products. Author write, "This paper focuses on the synthesis of ..." at page 83. I think the correct sentence is "This section focuses on the synthesis of ...".

Biocompatible non-toxic polyester polyurethane based polymers were successfully prepared by metal free catalytic process for biomedical application and then investigated in section 2.3. Samples could be degraded by hydrolytic test and had moderate cytotoxicity. It was a decreasing tendency both in Young modulus and tensile strength of samples using 2% PEG as function of PEG molecular weight; while the Young modulus increased and a maximum value of tensile strength was found in the order of P4, P5 and P6 samples. What was the possible cause for these phenomena? Similar phenomenon was found regarding Tg, because it had increasing tendency following the order of P1, P2 and P3 (using 2% PEG), while P5 has the highest Tg using 1% PEG. Probably, it could be explain by the difference in polymer structure occurred by the different length of PEG.

Only couple of mistyping errors are remained in the theoretical section:

- Pages 41: "... availability [188]]"
- Page 43: "1,,4-BD"
- Page 45: "... Inova 400nspectometer."
- Sometimes the point at the end of the sentence is after the reference, e.g. "... degradation velocity [161]." (at page 41), while in some case that is before the reference e.g. "... PEG bonded to PLA). [191,197] Prepolymer ..." (at page 49).
- Page 61: What means "The similar hydrolysis experiment (°C and 55°C) was performed by Hiltunen and co-workers ..." ? Maybe the number before °C is missing.
- Page 68: There is point after the title of "2.2. Synthesis of poly(sebacic anhydride): effect of various catalysts.", however in general there is no point after the chapter titles.
- Page 88: "... additional crosslinking of polymer. [157,199]."
- Page 90, Figure 45: Young modulus is the correct instead of "Yung modulus"
- Page 91: "... ; its progress is depicted in Figure: ."

Based on the written thesis, my opinion, that it is well edited work containing valuable information in the field of biodegradable polyester and polyanhydride synthesis and advanced application. Author concluded important and relevant results, which could help the further development belongs to biopolymers. Therefore I recommend awarding the PhD degree for Ing. Alena Pavelková.



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