

Review Report for the Doctoral Thesis

Title: Investigating the influence of different additives on the mechanical properties and biodegradation of PHB and PBS

Author: Ahmad Fayyaz Bakhsh

Supervisor: prof. Mgr. Marek Koutný, Ph.D.

Institution: Tomas Bata University in Zlín, Faculty of Technology

Degree programme: Technology of Macromolecular Compounds

Degree course: Chemistry and Materials Technology

Date: October 10, 2024

Reviewer: Ing. Jana Navrátilová, Ph.D., Tomas Bata University in Zlín, Faculty of Technology, Department of Polymer Engineering

The doctoral thesis authored by Ahmad Fayyaz Bakhsh focuses on the controlling biodegradation of selected biopolymers, namely PBS and PHB, by natural substances such as lignin and various terpenoids. The topic is of a high interest in terms of acute solutions for plastic waste management. The use of biodegradable polymers is one of the options to address the accumulation of plastic waste in the environment. Controlled biodegradation in soil or compost can help to increase the use of biopolymers in various applications.

The work focuses mainly on two biopolymers, PHB and PBS, partly also on PLA and its blends. The main aim of the research is to increase the biodegradation time and thus the durability of these polymers in the environment. The materials could then be used e.g. in agriculture. In this work, natural substances such as variously modified lignin and essential oils (EO) are used as antioxidants and antimicrobial agents to extend the lifetime. The focus is on two types of lignin (alkali and organosolv) and three types of EO (thymol, eucalyptol and limonene).

In addition to biodegradation, the effect of additives on mechanical and thermal properties is also investigated. The rate of biodegradation is monitored by measuring mineralisation and by burial testing, and the surface of samples during degradation is observed by scanning electron microscopy. It is important to mention that the effect of terpenoids as antimicrobial agents was observed only in the case of PHB material, while the effect of lignin as an antioxidant was observed for both PHB and PBS materials.

Overall, the topic of the thesis is very well chosen and the set objectives are important from a practical point of view and can find practical application.

The results of this work show that the addition of both terpenoids and lignin can significantly affect the biodegradation rate of PHB and PBS, even in very small amounts. The combination

of both components in different ratios could be interesting. It would then be possible to controllably produce a polymer blend with the necessary durability for a specific application.

The thesis of Mr. Ahmad Fayyaz Bakhsh makes significant scientific contributions by expanding the understanding of biodegradation of PHB and PBS modified by natural additives. The research offers practical solutions to improve the sustainability.

Although the paper presents a number of interesting results, it also contains some ambiguities and shortcomings.

From a formal point of view, the work is of a poor standard, containing numerous grammatical, stylistic and typographical errors. Some of the references to figures are incorrect, some of the figures are not clear and the format of the figures is not uniform. The scales of the micrographs are often illegible. The labelling of the samples is inconsistent and makes it difficult to interpret the results.

In the theoretical part, various statistics are presented for the most part, it would be appropriate to address the concretionary problem of biodegradation in more depth and to perform a more thorough research. It would also be useful to discuss the test results more in relation to the chemical or structural nature of the additives, especially in the case of terpenoids. (Why do different types of terpenoids give different results?)

The Collaborative Studies chapter 5.3.1 Biodegradability of PLA/PHB for cups, in my opinion, is not appropriate as part of a doctoral thesis. It is applied research for a company where there is no clear identification of samples and it is basically impossible to draw conclusions from the results and to relate material composition and degradation behaviour.

In conclusion, this doctoral thesis contributes to the field. I recommend the acceptance of Ahmad Fayyaz Bakhsh's thesis for the award of the doctoral degree.

Below are several questions for the thesis. In particular, questions 1, 5, 6 and 7 should be answered.

1. On page 45 it states that essential oils (EO) are usually used to increase the crystallinity of PHB. How do they work? Table 3 shows the crystallinity values of the samples and the addition of EO does not seem to have a significant effect on the crystallinity. What is the explanation?
2. It is interesting to compare Figure 15 and Figure 17. The PHB samples here differ in the amount of EO. If the degradation conditions are the same, why is the mineralization time of pure PHB fundamentally different (the scale on the x-axis is different in the figures)?.
3. SEM images are generally commented on very briefly, could you better describe what is seen in Figure 19 and how the extent of degradation can be estimated?
4. On page 47 it is stated that after 32 days of biodegradation only a sample with eucalyptol can be found. However, Table 3 shows the crystallinity value after 32 days also for the limonene sample. Why?

5. The data shown in Table 4 were obtained from the first heating? It is very interesting that pure PHB shows only one melting temperature before degradation and two after 16 days of degradation. Can you explain this? Could it be recrystallization, as you explain these two melting temperatures in the case of mixtures of PHB and EO (there are, however, two melting temperatures even before degradation)? It would be useful to show full melting thermograms.
6. Since degradation occurs preferentially in the amorphous phase, I would expect a gradual increase in crystallinity over time. However, according to your results, this does not occur (Table 3). Can you explain this?
7. On page 64 you state that mixing PLA and PHB in the melt leads to re-esterification reactions to form a copolyester. Does this change the T_g of the resulting copolymer? Could the change in T_g then play a role in biodegradation? In your case, have you verified that re-esterification has actually occurred? In the case of Figure 27 it looks like yes - complete mineralization of all samples (but without knowing the exact composition of samples) and in the case of Figure 29 and 30 it looks like no - the mixtures show a small percentage of mineralization.

Zlín, October 10, 2024

Jana Navrátilová, Ph.D.