Lodz University of Technology
Institute of Polymer and Dye Technology

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Prof. Dr. Dariusz M. Bieliński, DSc, Eng.

REVIEW OF THE DOCTORAL DISSERTATION

by Mr. Christian Götz, MSc

titled: *"Dynamic creep and fatigue properties of novel nano-structured biomaterials using network structures"*, prepared under the supervision of Prof. Dr. Mirosława El Fray, DSc, and a co-supervision of Prof. Dr. Judit Puskas.

1. Formal issues

The basis for writing this review is the Resolution of the of the Discipline of Material Engineering Council of the West Pomeranian University of Technology from 4th of June 2024, and a letter from a Head of the Discipline Council of the University, in connection with the activities carried out in the procedure for awarding the academic degree of PhD for Mr. Christian Götz, MSc (ZUT/RDIMat/16/2024).

The purpose of the review is to determine whether the doctoral dissertation submitted for evaluation by Mr. Christian Götz, MSc, meets the customary and statutory requirements specified in Art. 187 of the Act from July 20, 2018 *"Prawo o szkolnictwie wyższym i nauce"* (*in Polish,* Dz. U. 2018 poz. 1668 z późn. zm.).

2. The choice and importance of the topic. Objectives of the research work

Mr. Christian Götz, MSc undertook an important research problem that is worth studying both in the area of new biomaterials and the approach to their fatigue analysis. The medical devices market, apart specificity and increasing demand, also characterizes itself by continuous development. It especially concerns implants, with their requirements and material challenges. These include, among others, the still unsatisfactory mechanical characteristic and fatigue resistance of biomaterials. The ideas to modify the novel class of thermoplastic elastomers (TPEs) by incorporation of selected nano-fillers or their additional crosslinking seems reasonable, because only limited in-depth studies in this area are available. Establishing structure-property relationships could provide a pathway for developing a new class of safer, high performance TPEs for soft tissue applications. Additionally, the literature review demonstrated that there are also no standardized testing methods available to evaluate the fatigue behavior of specific biomaterials. Especially, when talking about silicone breast implants, there exists a lack of knowledge how dynamic loading can affect the material. Testing ready-to-use devices seems to be more a trial and error method than a scientific approach. Therefore, the proposed hysteresis approach to evaluate the stiffness, deformation, loss- and store-work as well as the damping behavior can be seen as a more effective method.

The choice of research topic should therefore be considered accurate, interesting and important not only for cognitive reasons, but also due to the current medical context. Based on a growing demand for alternative biomaterials with outstanding long-term fatigue properties to prevent dynamic rupture of the implant, the candidate selected a promising polymer bases and a family of nano-fillers or e-beam crosslinking, creating network structures, finally modifying properties of the materials. It is important from the point of view of their required functional characteristics. Despite the involvement of many research centers around the world, the problem of reducing dynamic creep of implant polymers, usually made of TPUs or silicones, still remains unsolved.

After conducting a thorough, critical review of the scientific literature in this area (210 references cited) Mr. Götz, MSc formulated objectives and strategy of the dissertation. The hypothesis of the research is that chemical crosslinking and/or nano-scaled additives can alter the dynamic creep and fatigue properties of selected TPEs for soft tissue applications. The scope of the work includes examining the relationships between morphology of the TPEs (macromolecular structure, crosslinking and nano additives) and thermal, mechanical as well as dynamical (dynamic creep and fatigue) properties of the materials.

3. Work structure and research methodology

The work has 88 pages (plus additional 4 pages devoted to the author's CV and scientific achievements). It has a classic layout and is divided into 8 chapters and a bibliography and summaries in Polish, English and German. It contains 59 figures and 27 tables. Bibliography, referring to 210 items, is relevant to the subject of dissertation. Most of them come from the last decade.

The content of the dissertation has been divided into the following chapters:

- Introduction,
- State of the art,
- Objective and strategy,
- Materials,
- Experimental procedure,
- Results and discussion,
- Conclusions,
- Outlook, and
- Bibliography.

After a brief introduction to the world of the medical devices market, the author focuses on the phenomenon of material fatigue, the analysis of its mechanisms through crack propagation research and the application of various kinds of hysteresis tests. In the next chapter, he discusses biomaterials, dividing them into classes, pointing to limitations in use and synthesis/ modification methods aimed at adapting them to work in conditions of exposure to dynamic creep and fatigue. It is a pity that the influence of fillers/nanofillers and the spatial network on the dynamic properties of elastomers was provided without delving deeper into issues related to agglomeration, the spatial network of the filler or the structure of crosslinks.

Two classes of TPEs were studied:

1. materials crosslinked after the polymerization using e-beam irradiation, representing rather hard TPEs, from the group of poly(aliphatic/aromatic-ester)s multiblock copolymers (PEDs), and in contrast
2. rather soft poly(isobutylene-b-styrene) block copolymers (PIBs), chemically crosslinked during polymerization using e-beam radiation, or modified with nan-scaled fillers like carbon black (CB) or organic nano-clay (NC) after the polymerization.

The macromolecular (M_n of PS and PIB arms) and supramolecular structure of the materials studied were very well characterized as well as their morphology (TEM imaging of stained thin

16 Stefanowskiego Street, 90-537 Lodz, Poland
phone (+48 42) 631 32 10, e-mail: polbarw@info.p.lodz.pl, www.polimbarw.p.lodz.pl
Correspondence address:
Żeromskiego Street 116, 90-924 Lodz

sectioned samples). They were compared to several commercial benchmarking materials: two medical-grade silicone rubbers, thermoplastic polyurethane (TPU), and linear SIBS block copolymer. Similarly to the polymers also the fillers used have been extensively characterized. The methods of sample preparation: e-beam crosslinking of PEDs and IBS composites, as well as the preparation of the filled SIBS composites were described in detail. The only exemption remains the commercial grade linear SIBS/nano-clay composite (in Chapter 5.1.3.2 missing the molding and cutting sample steps).

The methods applied to study the samples, which can be divided into groups related to: morphology, thermal and mechanical characterization, have been well selected, but unfortunately not thoroughly described. The information on sample preparation procedure for AFM examination, mass of the samples used for DSC and TGA, as well as the shape of samples for dynamic testing are missing. It is not clear why the author applied a non-standard (100 mm/min) speed of elongation for PED samples subjected to mechanical testing. Additionally, for the description of size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) spectroscopy methodology one is referred to other publications. Any description on WAXS experiments hasn't been provided either. Changes to the polymers studied in terms of crosslink density could be evaluated more precisely and the values derived from DSC spectra compared e.g. to the values calculated from equilibrium swelling measurements. The degree of polymer crystallinity could be also calculated based on DSC data.

Experimental results are presented in the same logical order like in experimental section. First the morphology and thermal properties of the investigated materials have been clarified, followed by the mechanical characterization, in order to get the materials structure-property relationship. The only exemption concerns not carrying dynamic fatigue testing for at least the dendritic SIBS/nano-clay composites (necessity for further research on the material and filler ratio). The reason provided by the author is not convincing at all, leaving an impression that the work has not been completed.

4. Editing, nomenclature and language

The dissertation well introduces the reader to the current state of knowledge, clearly formulates the theses, the objectives and scope of research. It tells step-by-step the story of solving the scientific problem, pointing to the cause-and-effect sequence between experiments and their results.

When assessing the dissertation from the editorial point of view, I confirm that it doesn't contain any glaring errors or omissions. The text suffers from some stylistic and linguistic shortcomings ("typos") that however don't deserve detailed attention. Their number is typical for this type of work. Although the editorial side doesn't raise any major objections, the Author didn't avoid certain errors and nomenclature inaccuracies, the most important of which are listed below.

1. The term silicone rubber is used everywhere, whereas in the matter of fact it is a crosslinked rubber composite filled with silica. Does the Author have any idea to what extent?

2. List of abbreviations

- General remark is associated with the lack of any systematic approach to the list (neither alphabetical arrangement nor sorting abbreviations by type, e.g. materials, techniques, physical quantities).
- Specific remarks:
- Prefix *kilo* should be written with a small not a capital letter.
- Ultimate tensile strength is once abbreviates as σ_{ult} and once as *UTS*. Why the Author doesn't

16 Stefanowskiego Street, 90-537 Lodz, Poland
phone (+48 42) 631 32 10, e-mail: polbarw@info.p.lodz.pl, www.polimbarw.p.lodz.pl
Correspondence address:
Żeromskiego Street 116, 90-924 Lodz

applied a commonly used abbreviation of *TS*?
- Not all abbreviations used have been explained.
2. p. 39, l. 8 top - The term of Young's modulus for elastomers doesn't exists as they do not obey the Hook's law (see Figure 6.4 on the next page).
3. Chapter 8 - The term biocompatibility seems to be used incorrectly. In the thesis only mechanical and dynamical tests have been performed, without any biological studies.

Other remarks:

Figure 1.1, p. 1 - The information presented is out of date. Why the author didn't merge the information from [1, 2] with [3] to be presented in one graph? The same remark concerns Figure 1.2.

Chapter 2.1.1, p. 4, l. 1-2 bottom - Not only physical and material aspects decide fatigue behavior. The author seems to forget about chemical aspects, and what is more not only related to polymer matrix of a composite material.

Chapter 2.1.2.1, p. 6, l. 24-25 bottom - It is hardly to agree with the author that *"if no microcracks are initiated, there should be no fatigue failures which occur"*. The appearance of cracks is sufficient but not necessary condition for deterioration of the mechanical properties of material. It looks like the author doesn't take into account an effect produced by the increase of temperature (able to be locally present even for *"static"* fatigue tests), especially important in the case of generally poor heat conductive polymers. However, he further refers to the amount of heating.

p. 13, l. 2 top - What does the author mean by *"buckling of the sample subjected to strain"*? Classic Euler's theory on buckling is related to samples subjected to compression, not extension.

Table 2.1, p. 16 - If the data on mechanical properties of breast tissue is not available, what was the reason to put this kind of human tissue into the table?

Figure 2.11, p. 19 - The chemical structure presented suggests the same length of hard segments. Is it really the case?

Figure 2.15, p. 24 - Could the author explain the nature of faster degradation and earlier failure of materials characterizing themselves by lower initial dynamic modules in comparison to the materials exhibiting its high values?

p. 44, l. 1 bottom - PBT is less sensitive to dynamic creep than TPU but not silicone. See Figure 6.11 on the next page.

p. 49, l. 11-12 top - It is no wonder that the higher the heating rate the more difficult is to define phase transitions by DSC.

Figure 6.24, p. 62 - Addition of the WAXS spectrum of CB could make the interpretation of X-rays diffraction results easier and more convincing.

p. 66, p. 74, p. 75 and p. 78 - Why [196] and [206] as well as subsequently [192], [209] and [210] references have been marked in red color?

Figure 8.2, p. 81 - It isn't clear if the results presented in Figure 8.2 belong to the author or have been cited from the literature. No reference is provided in the figure caption.

5. Substantive assessment of work. Comments and questions

The dissertation presents the investigation of the influence of network structures on the dynamic fatigue behavior of innovative TPEs. In addition, the author successfully demonstrated how the approach of dynamic hysteresis measurements can be adjusted to study the dynamic creep behavior of materials exhibiting different strength and compliance.

Scientific novelty of the dissertation is, in my opinion, associated with two aspects and namely:

16 Stefanowskiego Street, 90-537 Lodz, Poland
phone (+48 42) 631 32 10, e-mail: polbarw@info.p.lodz.pl, www.polimbarw.p.lodz.pl
Correspondence address:
Żeromskiego Street 116, 90-924 Lodz

1. Experimental techniques applied - Application of SILT method to identify the critical stress of materials and based on this evaluation of their dynamic creep behavior using SLT methodology, and

2. Structural findings of materials:

- M_n of PS and PIB arms are two important parameters, responsible for TS and ε_{max}, as well as exerting a direct influence on the magnitude of E_{dyn} and ε_d of the tested PIB-based copolymers. Merging the above with the beneficial effect of additional branches in the PIB core makes it justified to conclude that static and dynamic mechanical properties of SIBS-type polymers can be fine-tuned by the composition, architecture and molecular weight of the materials.
- Additional chemical crosslinking of PED multiblock copolymers, using various dosages of e-beam irradiation, results in the formation of an additional crosslink network responsible for improving mechanical properties (quasi static and fatigue) of the materials. This shows the high potential for this kind of biomaterials.
- Similarly, the mechanical performance of more elastic SIBS-type polymers can be improved due to their crosslinking. But nevertheless their mechanical properties still remain far away from medical grade silicones.
- Incorporation of considerable amount of CB to dendric SIBS-type polymers results in an enhancement of the short-term and long-term mechanical properties of the materials, providing an alternative solution for the used so far medical grade silicone.
- Nano-clay can be well dispersed only in the dendritic IBS part of SIBS matrix, resulting in significantly improved mechanical performance of the composites.

However, although I rate the dissertation highly, my attention was drawn to the following issues, which I hope will be clarified or supplemented by the candidate during the public defense, and namely:

1. The effect of crosslinks studied is only related to short covalent ones. What is the Author's opinion on the possible influence of longer crosslinks, susceptible for energy accumulation?
2. Figure 6.13, p. 50 - Why the author didn't assign the second relaxation peak at ca. 120°C for L_SIBS31 to a part of PS with restricted motion, similarly to other D_IBS samples? This seems to be justified by lower elongation at break determined for the former in comparison to the latter (Table 6.6 on the next page). Are you sure that L_SIBS31 with a linear triblock architecture e.g. can't contain some longer PS blocks or clusters?
3. What was the idea of comparing crosslinked and additionally reinforced silicone rubber with non-crosslinked and unfilled thermoplastic elastomers in terms of mechanical properties and dynamic characteristic?
4. Chapter 6.3.1 - Why the author choose the reinforcement of D_IBS copolymers with CB instead of silica, what seems to be inappropriate when further the composite is to be compared with the reference filled with silica? Morphology of silica filler in rubber matrix is different as compared to carbon black.
5. Figure 6.23, p. 61, and p. 71, l. 15-16 bottom - Could the author explain why CB is preferentially attracted to the semicrystalline PMS-rich phases? On p. 62, l. 2-3 top is correct - CB preferentially goes into the PIB and interfaces. I would rather expected an easier location of the filler in the amorphous PIB phase. Don't you think it could be related to nucleation of PMS by carbon nanoparticles and is associated with the preparation of the mixtures above the melting temperature of the polymer?
6. p. 61, l. 6 bottom - N 234 CB chosen by the author is not structural CB. The effect would be much more possible when e.g. N 772 was used. It could be a suggestion for further studies to try less active but more structural CB.

16 Stefanowskiego Street, 90-537 Lodz, Poland
phone (+48 42) 631 32 10, e-mail: polbarw@info.p.lodz.pl, www.polimbarw.p.lodz.pl
Correspondence address:
Żeromskiego Street 116, 90-924 Lodz

7. p. 64 - The discussion on polymer-filler interaction could possibly be clarified by performing the bound rubber (BdR) determination. It is likely to put also some light on the postulated "lubrication" mechanism of the PMS chains and the PMS-CB clusters.
8. p. 66, l. 4-6 bottom - I would be careful in formulating such conclusions before checking biocompatibility of the filler, e.g. PAH content in the CB applied.
9. Chapter 6.3.2.1 - What is the possible explanation for the different morphology of the nano-clay composites studied? Again, the polymer-filler interactions can be evaluated by determination of BdR or characterized by Payne effect.
10. Chapter 6.3.2.3 - Why DMTA or WAXS experiments were not performed, similarly to the CB filled composites? The spectra could put more light on the morphology of the composites studied.
11. The scheme 8.1 is only valid for polymer/nano-clay systems, providing the technology of their preparation assures at least exfoliation of the filler nanoplatelets, but it is completely irrelevant to polymer composites filled with CB.

In most cases, the above questions are of a debatable nature and in no way lower my very good opinion about the dissertation submitted by Mr. Götz, MSc.

6. Final conclusion

I hereby declare that the doctoral dissertation submitted to me for evaluation by Mr. Christian Götz, MSc titled: *"Dynamic creep and fatigue properties of novel nano-structured biomaterials using network structures"* - prepared under the supervision of Prof. Dr. Mirosława El Fray, DSc, and a co-supervision of Prof. Dr. Judit Puskas, meets the customary and statutory requirements specified in Art. 187 of the Act from July 20, 2018 *"Prawo o szkolnictwie wyższym i nauce"* (*in Polish*, Dz. U. 2018 poz. 1668 z późn. zm.). In connection with the above, I appeal to the Discipline Council of Material Engineering of the West Pomeranian University of Technology to allow it to be publicly defended.

D. Bieliński

16 Stefanowskiego Street, 90-537 Lodz, Poland
phone (+48 42) 631 32 10, e-mail: polbarw@info.p.lodz.pl, www.polimbarw.p.lodz.pl
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