Prof. dr hab. Inż. Tomasz Sterzyński

Review of the doctoral dissertation under the title “Dynamic creep and fatigue properties of novel nanostructured biomaterials using network structure”, by Dipl.-Ing. Christian Götz

This work was completed at the Department of Polymer and Biomaterials Science of the Faculty of Chemical Technology and Engineering of the Westpomorian Technical University in Szczecin, under the supervision of Prof. dr. hab. Eng. Mirosława El Fray and of Prof. dr. Judit Eva Puskas.

The text of the dissertation is written in English on 92 pages, contains the summaries in English, Polish and German, a list of abbreviations, a list of 210 cited publications, the author's CV and, additionally a list of publications in which the Candidate is a co-author.

The purpose and scope of work have been defined in an unambiguous and transparent manner. The author, on the basis of extensive literature research, proves that a significant increase in the production of thermoplastic elastomers, used also as medical implants, is observed in the world. However, due to the dynamic type of loads, resulting from their use as elements of the human body, the problem of possible fatigue crack of implants, due to cyclic loading became important now-a-days. Therefore in a certain condition the fracture growth may result in a complete destruction, by a rupture of the implants.

Thus, the main task of the research presented in the dissertation is the modification of polymers used currently for the production of implants, in order to obtain the required strength, especially to dynamic loads, while maintaining their medical properties. This goal fully meets the modern needs in the field of medical implants, and also has a scientific justification in the field of polymer modification, as an activity in the field of materials engineering of polymeric materials. Therefore, it should be stated that the doctoral dissertation presented by Dipl.-Ing. Christian Götz is based on assumptions of scientific research, having unquestionably scientific importance, and exposes also significant application values.

The literature studies of fatigue domain, with particular emphasis on material fatigue and the analysis of fatigue properties in materials, are presented in a separate chapter. The literature review of research on biomaterials used in medical applications is discussed, including elastomeric biomaterials and methods of modifying the mechanical properties of elastomers, being the main object of scientific interest of the doctorate. In addition, this chapter also deliberates literature know-how in the field of fatigue studies of polymer-based biomaterials. Thus the wide literature studies concern not only the characteristic of the elastomers, but also the way and methods of its modification published world-wide. The papers published by the scientific team of prof. Volker Abetz, prof. Judit Puskas and prof. Mirosława El Fray are also taken into consideration.

Two classes of thermoplastic elastomers were selected for the experimental studies of the mechanical properties dependence on its network structure and applied additives. The first group involves the elastomers, multiblock copolymers (poly(aliphatic/aromatic-ester)s, where after polymerization the cross linking was achieved by means of radiation, leading to relatively hard materials. The relatively soft block copolymers poly(isobutylene-b-styrene) were chemically cross-linked during polymerization, as well as modified by using carbon black and nanoclay as nano modifiers. Additionally, two medical-grade silicone rubbers, a thermoplastic polyurethane and two linear SIBS block copolymers were used as reference materials; carbon black, layered silicates and clay were applied as nano fillers.

The experimental procedures of production of samples for structure-properties investigations, are characterized in the following chapter. The test methods such as morphology evaluation, thermal characterization of materials, and evaluation of mechanical properties are systematically described. Following types of experimental procedure were applied to describe the samples: transmission electron microscopy (TEM) and atomic force microscopy (AFM) to characterize the morphology, differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and thermal gravimetry (TGA) for the determination of thermal properties of the samples, as well as mechanical and dynamic fatigue testing to characterize the mechanical properties of primary samples and its modifications.

It should be stated that the above-mentioned research and measurement methods belong to currently modern measurement techniques, used widely in investigations analogous to those presented in the evaluated doctoral dissertation. The author's ability to choice research methods appropriate to the aim of the work, allowing for comprehensive characteristics of block copolymers and their modification was confirmed. Though, as stated above, the selection of methods is correct, but it would also be beneficial to realize studies of gradient of changes in structure and properties, especially for implants of a certain thickness, greater than the thickness of samples used in the presented work.

The purpose of an extensive research of implant materials is to constitute them in such a way, that the using time would be as long as possible, to avoid the need for costly and unfavorable replacement of implants. Hence, ageing studies conducted in appropriate physiological fluid environments would also be a beneficial complement to this project. Such aging studies of the materials, which potentially could be applied in medicine, are missing.

The next part of the doctoral dissertation is an extensive compilation and discussion of experimental results for all samples prepared from basic thermoplastic elastomers and their modifications. This part of the dissertation is divided into three main parts, which discuss successively the influence of e-beam crosslinking process on the fatigue properties of poly(aliphatic/aromatic ester) copolymer, the effect of chemically produced network structure of polyisobutylene- based thermoplastic elastomers on the material properties, as well as the assessment of material properties of dendritic polyisobutylene based thermoplastic elastomers modified with nano modifiers.

The overall assessment of the thesis is very positive, Dipl.-Ing. Christian G**ö**tz presented in an orderly and exhaustive manner all issues related to the basic scope and purpose of the work.

Nevertheless, the following questions and doubts need to be clarified.

At the point 6 it is mentioned that the e-beam irradiation was selected between 0 and 700 kGy, these are the set values, the question is what were the real values, and what is the depth of penetration of this radiation in the polymeric samples?

The TEM micrographs on the page 35 are of poor quality, difficult to assess the effects discussed,

The AFM micrographs on the page 36 represent the surface observation, it is therefore difficult to conclude about a general "well ordered structure".

By the analysis (page 36) of the glass transition, melting enthalpy and crystallinity a typical DSC graph as registered is missing. As in this case a PBT is of a low crystalline, it should be taken into account that the crystallization of this polymer is strongly processing and post-processing conditions dependent.

Figure 6.3 the comment "Tg of irradiated PBT26 shifted to 50 deg. C" is not visible on the run of the graphs of E''.

The results presented in table 6.2 and on Figure 6.4 should determine the effectiveness of e-beam radiation, while the real changes (improvement) of modulus and elongation are within the measurement error thus are relatively small.

The e-beam irradiation induced cross-linking is mentioned several times, but a real proof in a form of cross-linking measured values are missing, instead of indirect values are given, such as changes of particular mechanical properties.

The difference in number of cycles by breaking of PBT irradiated and not irradiated are explained by micro domains destruction (page 44), a conclusion drawn from literature [187]. What is the reason of such effects and how the destruction of micro domains may be experimentally proofed?

On page 45 it is written „During the dynamic loading the number of entanglements decreases and the chemical bonds are responsible for carrying the load"? Is this a conclusion from the research or drawn from literature?

Pls explain how can one directly characterize the cross-linking from the DSC measurements? (page45)

Overall, a number of conclusions in the dissertation concerning the entanglements, cross-linking, fracture of macromolecules etc. are formulated based on the measurements of modulus and elongation. Pls explain these procedures, and confirm how exactly are these conclusions.

What features must a material for biomedical applications have? It would be worth to compile these features for example in a form of the table.

Concerning the glass transition it is probable more reasonable to speak about the range of glass transition, and not about the temperature of glass transition, because this transformation always takes place in a certain temperature range.

Pls explain how the Tg values in table 6.5 have been detected, since they do not coincide with the curves in Figure 6.13 b and c. For the Tg which values were taken into account, the E" or the tangent delta? The same question concerns the table 6.11.

On Fig 6.21 the directly registered runs are represented; for the clarity of analysis the run of the smoothed values would be more adapted.

There are a number of abbreviations included in the text; not all of them are summarized at the tables of abbreviations included in the text.

At the crystallography bibliography a number of maxima for the diffraction spectra of CB may be found. How may just one maxima, ascribed to amorphous domain on figure 6.24, be explained.

What kind of interaction may exist between neat polymer and CB fillers, as it is mentioned on page 64? Also on page 71 it is mentioned that strong polymer-filler (CB) interaction leads to an improvement of dynamical and statical properties; what kind of interaction can it be?

A significant increase (6 to 8 times) of stresses, due to the addition of CB, is shown in the table 6.13. Pls explain the mechanism of CB induced improvement of mechanical properties by modified dendric polyisobutylene-based thermoplastic elastomers with poly(p-methylstyrene) hard blocks.

On Fig. 6.28 the fracture surfaces are not well visible.

Most of the above mentioned remarks and doubts are debatable and do not lower the generally positive assessment of the doctorate thesis.

Despite a certain number of uncertainties mentioned above, the doctoral dissertation is properly written, the individual stages are presented in a logical way. The primary objective of the work, which was to develop an alternative material with required resistance to fatigue loads for medical applications, to replace silicone, was fully met. A number of modified thermoplastic elastomers, with their wide mechanical characteristics, permitted for the selection of innovative medical polymer materials with properties allowing their potential use in place of the silicones, was presented so far.

This work is of significant scientific importance by deepen the knowledge in the field of evaluation of mechanical properties of modified thermoplastic elastomers and their composites. The application importance of research results of novel materials with potential use in the field of medical implants, should also be noted.

The doctoral dissertation of Dipl.-Ing. Christian Götz meets the conditions in accordance with Article 187 of the Act of 20 July 2018, Law on Higher Education and Science, presenting the general knowledge of the Candidate, his ability to independently conduct scientific work and to solve the scientific problems.

Based on the above presented evaluation of the doctoral dissertation of Dipl.-Ing. Christian Götz I apply to the Council of Materials Engineering Discipline of the West Pomeranian University of Technology in Szczecin to admit the Candidate to further stages of the doctoral procedure in the field of engineering and technical sciences, at the discipline of materials engineering.

Taking into account the appropriateness of the conducted research, the wide scope of work, the large number of evaluated materials and their modifications, as well as the manner of editing and presentation the doctoral dissertation of Mr. Dipl.-Ing. Christian Götz I apply to the Council of the Discipline of Materials Science for its distinction.

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