

Review of Doctoral Thesis

1. PhD candidate
Risha Rufaqua, MSc, MBA / risha.rufaqua@vut.cz
2. Name of PhD programme
Design and Process Engineering (Mechanical Engineering Design)
3. Title of PhD thesis
The Biochemical Process of Lubricant Film Formation Inside Hip Joint Replacement
4. Principal supervisor
doc. Ing. Martin Vrbka, Ph.D. / martin.vrbka@vut.cz
5. Co-supervisor
Dr. Dipankar Choudhury / dc020@uark.edu
6. Reviewer
Prof. ing. Alessandro Ruggiero, Ph.D. / ruggiero@unisa.it
Department of Industrial Engineering, University of Salerno, Italy
7. Overview of the scope of PhD thesis¹
Evaluate: Very Good
Justification for evaluation: Arthroplasty is a surgical procedure consisting in the physical replacement of an unhealthy natural human synovial joint with an artificial one. The artificial joints have to guarantee biocompatibility, fixation, mobility, load capacity, stability and minimal friction and wear of the tribo-system. The wear phenomenon in a joint is affected by several factors, like the coupled materials, the geometry of the tribopair, the roughness of the contact surfaces, the load conditions and the lubrication of the tribosystem, hence the lubricant film formation chemistry on hip implant material surfaces, with synovial fluid components, plays a key role on the tribological behaviour of artificial joints. The proposed PhD Thesis aims to investigate the synovial lubricated film formation and its chemisorption on the THR implant surfaces considering various combination of implants materials. The approach was mainly based on Raman Spectroscopic techniques and on pendulum hip simulator for the friction coefficient assessments.
8. Significance of the topic and clarity of problem statement
Evaluate: Very Good
Justification for evaluation: The objective and the problem statement of the investigation is clearly exposed in the framework of scientific literature. The used method is approached by introducing two different

¹ Overview of the scope of PhD thesis is a short description of objectives of PhD thesis's research and summary of main findings and scientific achievements.

studies focusing on the chemical structure of synovial film the friction coefficients measurement. A chemical analysis, including the tribological and biological properties of the SF after total joint replacement to aid in comprehension of the process, was developed. The experiments conducted in the ball-on-cup configuration considered two types of commercial ceramic hip implant pairs, namely BIOLOX®forte and BIOLOX®delta, to explore the biochemical responses of SF lubricants in the ceramic interface. The conducted researches allowed to clarify the chemistry of lubricant film formation on hip implant material surfaces while concerning on the compositional variability of the SF lubricants.

9. Knowledge of existing literature

Evaluate: **Good**

Justification for evaluation: In this Thesis the investigated topic was introduced in the framework of recent and relevant scientific literature, even if, in my opinion, this part of the Thesis lacks of a more detailed tribological knowledge on this topic. In fact, in the last years more and more hip lubrication models were proposed by several authors aimed to give a detailed modelling of the synovial film during the gait considering mixed hydrodynamic/elasto hydrodynamic lubrication modes. A complete discussion on this issue could contribute to a more complete description of the scientific framework on THR lubrication.

10. Choice of methods and technical soundness

Evaluate: **Very Good**

Justification for evaluation: The choice of the investigation methods, in my opinion, represents the main novelty of this Thesis. Raman spectroscopic technique was used to analyse the chemical structure of lubricant film by SF components, considering also fluid of different concentrations. The performed experiments allowed to obtain results on which components of SF are adsorbing chemically on hip implant material surfaces while lubricant film formation within artificial joint replacement and how the SF changing the chemical structure of its constituents due to artificial hip implant. Moreover, several different combinations of hip implant materials were considered to perform an extensive analysis of film formation, which took in to account measurement of the friction coefficient of several couples of hip implant materials, lubricated by various SF. A comparison of the frictional results in the framework of the Raman data was also performed, allowing to investigate how the frictional coefficients differing with the SF chemical change in the hip joint replacement

11. Quality, originality and significance of the results

Evaluate: **Very Good**

Justification for evaluation: The obtained results appear interesting and promising for a more detailed comprehension of the lubrication phenomena in total hip replacements. In particular in this Thesis, was introduced Raman spectroscopy in this area of research as a novel tool to investigate SF film characteristics. The proposed methodology is characterised by several advantages as non-destructiveness, contactless measurements, without the demand for sample preparation and rapidity. Raman spectroscopy allowed to observe that after the tribological test, SF spectra showed verily different fingerprints compared to before test lubricants spectra. The obtained results were discussed carefully and allowed to obtain very interesting conclusions for the several tribo-systems investigated.

12. Quality of attached papers

Evaluate: **Very Good**

Justification for evaluation: The attached papers are: 1) Rufaqua R, Vrbka M, Choudhury D, Hemzal D, Křupka I, Hartl M. A systematic review on correlation between biochemical and mechanical processes of lubricant film formation in joint replacement of the last 10 years. *Lubrication Science*. 2019- 2) Rufaqua R, Vrbka M, Hemzal D, Choudhury D, Rebenda D, Křupka I, Hartl M. Raman analysis of chemisorbed tribo-film for metal-on-polyethylene hip joint prostheses. (*Journal Biosurface and Biotribology*) 3) Rufaqua R, Vrbka M, Hemzal D, Choudhury D, Rebenda D, Křupka I, Hartl M. Analysis of chemisorbed tribo-film for ceramic-on-ceramic hip joint prostheses by Raman spectroscopy. (Submitted to the *Journal of Functional Biomaterials*). ;31(3):85-101. Paper 1) is a Review paper published on a prestigious Journal which deals on the correlation between biochemical and mechanical processes of lubricant film formation in joint replacement of the last 10 years. Paper 2) is an interesting paper aimed to investigate the biochemical reaction during the formation of lubricant film the in case of a cobalt- chromium ball on an ultrahigh-molecular weight polyethylene, while in paper 3) was investigated the possible lubricant mechanism in ceramic-on-ceramic hip joint prostheses, biochemical reactions of the synovial fluid and the corresponding frictional coefficients.

13. Overall assessment, strengths and weaknesses (based upon the above evaluation categories 8–12)

Evaluate: **Very Good**

Justification for evaluation: The submitted Thesis was aimed to investigate the chemical behaviour, including the tribological and biological properties of the SF, after total joint replacement to aid in comprehension of the process. By using a pendulum hip simulator, the tribological behaviour of THR's were investigated also considering the friction coefficients of the contact pairs. The use of the Raman spectroscopic technique allowed to understand the chemical reactions between the SF and implant material. Cobalt-chromium ball on an UHMWPE cup arrangement was investigated to reveal the reactivity of metal against PE contact pairs. The experiments conducted in the ball-on- cup configuration also considered two types of commercial ceramic hip implant pairs, namely BIOLOX®forte and BIOLOX®delta. In my opinion the strengths of the Thesis is in the novelty of the proposed techniques (Raman Spectroscopy and Pendulum Hip Simulator) to deeply investigate the connection between chemical and tribological behaviour of synovial fluid in the lubrication of several type hip replacements. The weaknesses is the absence of any theoretical lubrication model, necessary to understand the tribological behaviour in terms of frictional behaviour of the investigated tribo-systems.

14. Questions and comments

I have one concern about the figures: The figures are usually recalled and commented on in the text....

15. Conclusion

PhD thesis is an independent scientific work that presents a novel solution to a significant problem in the research area and demonstrates the candidate's ability to conduct independent research.

YES

16. Date and signature

Review of Doctoral Thesis

1. PhD candidate
Risha Rufaqua, MSc, MBA / risha.rufaqua@vut.cz
2. Name of PhD programme
Design and Process Engineering (Mechanical Engineering Design)
3. Title of PhD thesis
The Biochemical Process of Lubricant Film Formation Inside Hip Joint Replacement
4. Principal supervisor
doc. Ing. Martin Vrbka, Ph.D. / martin.vrbka@vut.cz
5. Co-supervisor
Dr. Dipankar Choudhury / dc020@uark.edu
6. Reviewer
Anna Neus Igual Muñoz / anna.igualmunoz@epfl.ch
EPFL SCI STI SM
7. Overview of the scope of PhD thesis¹
Very good The main goal of the thesis is to describe the surface films formed on different material biomedical implants as a function of the chemical composition of the synovial fluid. The research work also aims at understanding which are the main components responsible for the biofilm formation and how operating conditions in the implants may modify the chemistry of the synovial fluid. To do that, an experimental approach was considered combining tribological tests and Raman spectroscopy. A tailored tribometer set-up was build-up allowing for testing a ball-on-cup configuration (mimicking the geometry of a hip joint replacement) and Raman Spectroscopy was carried out on the tested samples and fluids. Justification for evaluation: 100 – 200 words.
8. Significance of the topic and clarity of problem statement
Excellent Nowadays, hip and knee joint replacements are of the most common surgery to replace natural joints when different dysfunctionalities occur (i.e. arthrosis, accident). However, their durability is still a critical clinical issue which is limited to typically 10-15 years and, in some cases, to shorter periods (earlier

¹ Overview of the scope of PhD thesis is a short description of objectives of PhD thesis's research and summary of main findings and scientific achievements.

failure). The artificial joints constitute a tribological system operating in an aqueous fluid (synovia), thus the understanding of the involved phenomena is a pre-requisite to increase the lifetime of those implants. The problem is clearly described in the introduction and the need for considering all system parameters (material, mechanical, chemical and physical conditions) to address such a problem is highlighted.

Justification for evaluation: 100 – 200 words.

9. Knowledge of existing literature

Very good

The state of the art of the present thesis has been divided in five sections including the analysis of: chemistry of synovial fluid, fluid film thickness and lubrication properties, tribological properties of synovia, spectroscopic techniques for synovia analysis and material characterization. Due to the complexity of the topic and its multidisciplinary character, some of aspects were treated in different grade of detail. Maybe a deeper justification of why Raman spectroscopy was selected and a Table comparing the advantages and limitations of the technique with respect to others (FTIR, SEM-EDX, XPS, AES...) would be interesting. Some specific literature on tribocorrosion of CoCrMo alloys (even in-vivo) could be added as relevant references.

Justification for evaluation: 100 – 200 words.

10. Choice of methods and technical soundness

Very good

In order to achieve the goal of understanding the role of synovial fluid components on the formation of film surfaces tribological tests combined with surface chemistry characterization was chosen. The selection of a ball-on-cup tribometer mimicking the geometry of a hip joint implant is appropriate for that. I have just missed the full report of the experimental conditions such as sliding velocity and contact pressure. The material properties of the tested materials should also be included (Young modulus, poisson ratio, hardness). The number of repetitions of each test should also be stated.

The characterization of the tested surfaces and the simulated human fluids were characterized before and after the tests by Raman Spectroscopy. According to the optical images, those surfaces are not homogeneous so, it could be important to know where the Raman spectra were carried out (locally?, as average surface?).

Justification for evaluation: 100 – 200 words.

11. Quality, originality and significance of the results

Very good

The results show that chemistry of the different simulated synovial fluid properties change as a function of testing conditions, which is a new contribution to the field and a very significant outcome for the clinical application. The combination of different experimental techniques allowing for understanding some of the involved phenomena in the degradation mechanisms of biomedical implants is sound. Furthermore, the consideration of all different materials commonly used in joint implants (polymers, metals and ceramics) constitutes a valuable point of the research work. From this point of view, the thesis is very ambitious and does not allow to enter in all details of all considered systems, although it gives a significant overview.

Justification for evaluation: 100 – 200 words.

12. Quality of attached papers	
Very good	
The research work carried out during the thesis has generated three papers published in journals related to the fields of biotribology, lubrication and biomaterials. One of the papers is a review paper which allows to place the thesis work within the frame of the field. It reviews the published literature dealing with the correlation between mechano-chemical interactions leading to the formation of lubricating films in joint implants. Another paper was published in an open access journal. In general, the three published papers demonstrate the significance of the obtained results as far as they were accepted in relevant journals of the field.	
Justification for evaluation: 100 – 200 words.	
13. Overall assessment, strengths and weaknesses (based upon the above evaluation categories 8–12)	
Very good	
In general, the work carried out in the present thesis constitute a new contribution to the field of biotribology in joint implants. It is an ambitious work which aims at describing the influence of synovial fluid components on the formation of surface reaction films on different materials. The complexity of the system and the consideration of all kind of materials impedes to get a deep insight into the involved formation mechanisms but, on the other side, it also gives an overall view of the broad range of applications. The designed experimental approach seems appropriate although a more detailed justification of the selected techniques could be helpful.	
Justification for evaluation: 100 – 200 words.	
14. Questions and comments	
15. Conclusion	
PhD thesis is an independent scientific work that presents a novel solution to a significant problem in the research area and demonstrates the candidate's ability to conduct independent research.	
YES	
16. Date and signature	
14/06/2021	

Please note

- A. Evaluate categories 7 to 13 using the following scale: unacceptable, acceptable, satisfactory, good, very good, excellent. The qualification of 'excellent' should only be given for a PhD Thesis in the top 3% of the research in your field of expertise.
- B. E-mail the completed form to: Klara.Javorceková@vut.cz

Principal supervisor's final report on the PhD study

1. PhD candidate
Risha Rufaqua, MSc, MBA / risha.rufaqua@vut.cz
2. Name of PhD programme
Design and Process Engineering (Mechanical Engineering Design)
3. Title of PhD thesis
The Biochemical Process of Lubricant Film Formation inside Hip Joint Replacement
4. Principal supervisor
Doc. Ing. Martin Vrbka, Ph.D. / martin.vrbka@vut.cz
5. Co-supervisor
Dr. Dipankar Choudhury / dc020@uark.edu
6. Stays at other institutions (min. 7 days)
No internships were realized.
7. Teaching activities
No teaching activities were realized.
8. List of main publications
R. Rufaqua, M. Vrbka, D. Choudhury, D. Hemzal, I. Krupka, and M. Hartl, "A systematic review on correlation between biochemical and mechanical processes of lubricant film formation in joint replacement of the last 10years," <i>Lubrication Science</i> , vol. 31, no. 3, pp. 85-101, Apr, 2019. (IF 2019: 1.812 ; ENGINEERING, MECHANICAL: Q3)
R. Rufaqua, M. Vrbka, D. Hemzal, D. Choudhury, D. Rebenda, I. Krupka, and M. Hartl, "Raman analysis of chemisorbed tribo-film for metal-on-polyethylene hip joint prostheses," <i>Biosurface and Biotribology</i> , vol. 7, no. 1, pp. 11, May, 2021. (Scopus CiteScore 2020: 1.0)
R. Rufaqua, M. Vrbka, D. Hemzal, D. Choudhury, D. Rebenda, I. Krupka, and M. Hartl, "Analysis of chemisorbed tribo-film for ceramic-on-ceramic hip joint prostheses by Raman spectroscopy," <i>Journal of Functional Biomaterials</i> , vol. 12, no. 2, pp. 18, May, 2021. (Scopus CiteScore 2020: 7.3)
9. Assessment of the supervision process
Good

The supervision process was on a friendly basis. The process was based on one-month main meetings and on-demand discussions with supervisor, co-supervisor and colleagues from Biotribology Research Group. The candidate was always well prepared to discuss the issue of the dissertation including reflection of critical comments. The final thesis and research papers were prepared in time and in sufficient quality. The candidate was not involved in teaching activities provided by our institute, because her specialization is chemistry and not mechanical engineering. Also, no internships in the field of biotribology were realized due to the birth of her child followed by a period of maternity and parental leave. Risha attended one international conference (Engineering Mechanics in Svatka in Czech Republic), where she presented partial results of her research. She also contributed with her results to the presentation at the international conference (STLE Annual Meeting and Exhibition in the USA), without her personal participation. The outputs of her PhD thesis have been three research papers.

10. Assessment of the candidate's ability to work independently

Very good

The candidate worked independently, based on the discussion with me and my colleagues from the lab and other experts from the field of biotribology and chemistry. I would like to highlight the cooperation with Dr. Dušan Hemzal from Masaryk University in the field of Raman spectroscopy and also with co-supervisor Dr. Dipankar Choudhury from University of Arkansas. The candidate independently designed a methodology of experiments based on the state of the art, performed experiments, and, according to the results analyses, she formulated conclusions. All of the publications, where she is listed as the main author, were prepared by herself. The candidate did not supervise any bachelor's or diploma's theses and did not significantly participate in the other research projects of our biotribological team. The candidate did not complete any internships.

11. Assessment of the contribution that the research makes to knowledge in the field

Good

The PhD thesis is composed from three papers. One of them was published in the journal "Lubrication Science" with impact factor, and two papers were published in the Scopus journals "Biosurface and Biotribology" and "Journal of Functional Biomaterials". The main scientific output of this thesis is a new experimental approach to determination of tribo-chemical lubrication mechanisms inside hip implants by combining the Raman spectroscopy method and frictional tests carried out on the pendulum hip joint simulator. The research work is focused on understanding which are the main components responsible for the lubricant film formation and how operating conditions in the implants may modify the chemical composition of the synovial fluid. A weakness of the PhD thesis is that the contact surface of the polyethylene socket was not analysed by Raman spectroscopy. The metal-on-polyethylene contact pair is one of the most widely used pairs in clinical practice. This is quite a pity because, otherwise, the thesis contains interesting results. I also find the thesis lacking a better correlation of the results with the research works dealing with tribology of implants, e.g., in terms of lubrication regimes, film thickness and wear.

12. Other comments

none

13. Conclusion



**INSTITUTE OF MACHINE
AND INDUSTRIAL DESIGN**



**Faculty of Mechanical Engineering
Brno University of Technology**

PhD thesis is an independent scientific work that presents a novel solution to a significant problem in the research area and demonstrates the candidate's ability to conduct independent research.

YES

16. Date and signature

22/06/2021

Please note

- A. Evaluate categories 9 to 11 using the following scale: unacceptable, acceptable, satisfactory, good, very good, excellent.
- B. In each category 9 to 11 explain reasons for evaluation using between 100–200 words.
- C. E-mail the completed form to: Klara.Javorceкова@vut.cz