

FROM: Miroslav Raab, Professor of Macromolecular Technology
SUBJECT: Report on Doctoral Dissertation
**“Production of Nonwoven Fabrics by Using Silk Fibers via Electrospinning Technique:
or in Czech:
“Příprava netkaných textilií s obsahem hedvábných vláken získaných metodou
elektrostatického zvlákňování”**
submitted by
Nongnut Sasithorn, M.Sc.
to the
Technical University of Liberec, Faculty of Textile Engineering
DATE: March 2016
OPINION: Recommended

Technical university of Liberec is internationally acknowledged due to discovery and further development of a special device for the continuous production of nanofibers. The device has been successfully produced by the Elmarco company and received the trade name Nanospider. At the Technical university further research is being conducted to improve the Nanospider technology and find new prospective applications for various types of nanofibers. This dissertation is an important contribution to such efforts.

The comprehensive 142-page Dissertation focused on the preparation of nanofibers from regenerated silk fibroin and its blends with polycaprolactone. The subject area is well selected and topical, as also shown by recently published books. The topic of the dissertation is very interesting scientifically and important both from the point of views of economy and ecology. So, it could show new ways for ecological processing of silk waste.

The Dissertation is well structured. After a short “Introduction” it contains “Theoretical part” together with a review of relevant literature (40 pages). The introductory part is accompanied by a list of references (87 items). This part shows that the author understands well the complex relationships between individual levels of hierarchical structure of silk and is aware of the relevant literature on electrospinning of silk fibroin. Next part of the Dissertation is “Experimental” (16 pages). The starting materials, preparation of spinning solutions and electrospinning processes themselves are described in this part. Moreover, in vitro test of the interaction between prepared webs and living cells are reported. Finally, the part “Results and discussion” summarizes all obtained results and also the useful experience gained during the PhD study. The text is written in understandable English, though the English style would benefit from some more proofreading. Formally, the Dissertation has a very good level and the text is accompanied by well selected and carefully prepared illustrations. I have only two remarks to the theoretical and experimental parts: First, the difference in mechanical strength between native silk and various types of regenerated silk would deserve a comparison and structural explanation. Second, the composition and preparation of spinning solutions would need a clearer description and presentation, perhaps in a form of a table. I recommend to present such a diagrammatical table during the defense.

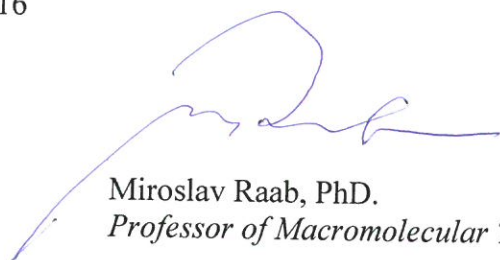
From the list of references it follows that the candidate appears as co-author in two conference contributions, one publication in a special issue of a Research Journal and one publication in Journal of Nanomaterials. Unfortunately, the corresponding reference (Ref. 51) is incomplete. Definitively, some further original publications would be possible and desirable.

I have some questions to the author that can initiate discussion during and after the defense.

- (1) There are two possibilities how to improve mechanical strength of silk fibroin nanofibers, namely: a) controlling supermolecular structure of fibroin and b) blending fibroin with other polymers. Try to compare briefly these two approaches.
- (2) How stable are the silk fibroin solutions ?
- (3) Which applications of silk fibroin mats are perspective ?

These questions do not deny the original work of the candidate and the very good standard of the presented Dissertation. The aim of the doctoral study, as specified on page 18, has been successfully achieved. Clearly, the obtained results will be useful for the future research at the Faculty of Textile Engineering and show a good scientific level of the whole University. The very positive role of the supervisor, Assoc. Prof. Lenka Martinová, is here obvious. The candidate has proven an expertise in needleless spinning on one hand and a promising class of nanomaterials on the other. Her scientific work is original and independent. Besides, the amount of work is quite substantial. I recommend the Dissertation for the award of PhD. degree by the Technical University of Liberec.

March 23, 2016



Miroslav Raab, PhD.
Professor of Macromolecular Technology

Report on PhD thesis
Nongut Sasithorn: „Production of nonwoven fabrics by using silk fibres *via*
electrospinning technique“

The subject of this thesis is related to the utilization of needleless electrospinning technique for fabrication of nonwoven sheets from silk fibroin and silk fibroin/polycaprolactone solutions. The topic is very interesting as the silk electrospun fibre sheets and its blends with polycaprolactone are promising materials for biomedical applications. The thesis deals mainly with the spinning process and it comprises two relatively independent parts. The first one is focused on a new solvent system for silk fibroin dissolution and screening different variables in preparation of electrospun nonwoven sheets. The second one deals with the biocompatibility of prepared materials and with their potential utilization in enzyme immobilization.

The chapter Theoretical and literature review, based on up-to-date references, comprises brief information about silk fibre and its characteristics, about fundamentals of electrospinning and state of the art in electrospinning of silk fibroin. This chapter has been written very comprehensively in a good language. The chapter Experimental describes the used materials, experimental processes and analytical methods. Some queries to this part are as follows:

1. Proper chemical nomenclature is poly(lactic acid), poly(lactic acid-*co*-glycolic acid), abbreviation for gram is g, not gm. – p. 61
2. To specify the used rheometer, the measuring geometry must be specified (coaxial cylinders, cone-plate or plate-plate?) Also specification of measuring spindle should be added. – p.62
3. The description of preparation of the “traditional silk spinning solution” is not fully clear. Why was the composition of $\text{CaCl}_2/\text{EtOH}/\text{H}_2\text{O}$ ternary solvent expressed in molar ratio? Ratio 1/2/8 moles represents 111g CaCl_2 / 92g EtOH / 144g H_2O . Is this the composition that was used? What does mean the ratio silk:solvent 1:10 (w/v)? It must be specified as $\text{g}\cdot\text{cm}^{-3}$, $\text{kg}\cdot\text{m}^{-3}$, $\text{g}\cdot\text{L}^{-1}$, etc. The concentration 12% (w/w) is not clear as well. Does it mean 12 wt.% (i.e. 12 wt. parts of silk and 88 wt. parts of solvent) or 12 wt. parts of silk on 100 wt. parts of solvent (phs)? – p. 65
4. Similarly, in Table 4.1 a correct caption should be possibly “Effect of added CaCl_2 to 8 wt.% silk fibroin/formic acid mixture on some properties of created solutions” instead of “Effect of concentration of CaCl_2 on properties of silk fibroin solution 8 wt.%”, because the concentration of CaCl_2 was not specified. – p.76
5. The spinning experiments were carried out under different air humidity, cf. 35-40% (p.66), 38% (p.67), and 23.5% (p.70). How does the humidity affect the particular electrospinning process? This variable was not studied but it might be important. – see p. 42

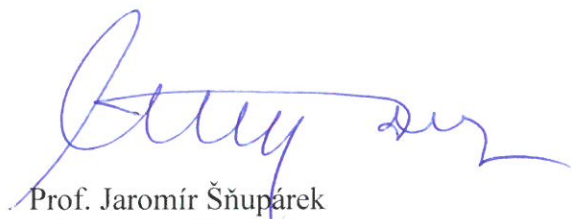
The chapters Results and discussion and Conclusion were well elaborated, unfortunately, the language is not that good as in the previous chapters. The most important achievements of this part were finding the feasible composition of CaCl_2 /formic acid solution for electrospinning silk and silk/polycaprolactone blends and evaluation of processing variables with respect to properties of electrospun fibre sheets. Author did confirm very good biocompatibility of the fabricated materials as well as their potential application as support for

enzyme immobilization. In summary, the thesis represents a good contribution to improving the knowledge in the field of silk fibroin electrospinning and utilization of the prepared fibrous materials in biomedical applications.

Conclusion

In conclusion, it can be stated that the subject of thesis is highly relevant and that the candidate achieved the aim using modern experimental and analytical methods. By choosing the approach and method of elaboration Ms. Nongut Sasithorn manifested her ability of independent a creative scientific work. By a successful solution of a research problem, she brought new findings and showed a good grasp of scientific methods of work. As Ms. Nongut Sasithorn thus fulfilled the appropriate conditions, I recommend her thesis for defending. After the successful defense, I recommend to confer a scientific degree of Ph.D. upon the candidate.

Pardubice, 2016-03-17



Prof. Jaromír Šňupárek
University of Pardubice
FCHT - Institute of Chemistry and Technology of
Macromolecular Materials

Reviewing report

PhD thesis: Production of Nonwoven Fabrics by Using Silk Fibres via Electrospinning Technique

PhD Candidate: Nongnut Sasithorn, Technical University of Liberec

Reviewer: Dr. Xin Wang, School of Fashion and Textiles, RMIT University, Australia

The research work of the thesis focuses on the scaled up fabrication of nanofibres from silk fibroin either as solely or blended with polycaprolactone, with application potentials as biomaterials and waste water purification. As nanofibre has great application potential and silk products are promising in different industrial areas, this research work has great significance in both academia and industry.

Needleless electrospinning method has been utilised in this research, which is properly fulfilled the purpose of large scale production of nanofibre from silk fibroin. A new solvent system containing calcium chloride and formic acid was invented to properly dissolve silk and a blending electrospinning of silk fibroin and polycaprolactone was applied to fabricate silk fibroin nanofibres with proper mechanical properties. These methods and approaches successfully fulfilled the proposed aims of the study.

The results of the thesis are correct according to the reviewer's knowledge, and the candidate has contributed greatly to the knowledge of fabrication nanofibres from silk fibroin and its application in biomaterials and water treatment.

While the candidate properly wrote the thesis according to scientific standard and critical thinking, it is greatly recommended to have a careful proofreading so as to improve the language and correct typos and grammar.

As there is no publication list of the candidate in the thesis, the reviewer cannot comment in this regard.

Considering the academic merits and significance of the research work in this thesis, I recommend the PhD. Thesis for defence.