Referee´s report on PhD. thesis of

Bandu Madhukar Kale

„ Multifunctional Cotton Fabric with TiO2 Loaded Cellulose“

Professor Miroslav Černík

The presented thesis consists of 90 pages divided into 7 major chapters plus References and List of publications. The thesis deals with cotton fabrics loaded with cellulose - nano TiO_2.

Abstract summarizes content of the thesis with major results.

Chapter 1 (Introduction) is about background of the topic – cotton fibres, application on ZnO and TiO_2 for self-cleaning of the fibres and antibacterial activity of the fibres. There is also definition of the problem to be solved – coating of cellulose for use as self-cleaning, antibacterial, antifungal and stiffness fabric.

Chapter 2 (Aim and objectives) defines objectives of the thesis – investigation of different properties of cellulose- TiO_2 cotton fabric.

Chapter 3 (Literature review) is a very illustrative introduction into the topic, cotton, self-cleaning materials (e.g. example of well-known lotus effect), antibacterial fabric, antifungal fabric, stiff fabric, functional nanoparticles and fabric materials.

Chapter 4 (Experimental) deals with methods used for preparation of fabrics and characterization. Major part is a description of measurement of different properties of the fabrics, e.g. mechanical, photocatalytic, antibacterial and antifungal properties, dyeing properties.

Chapter 5 (Results and discussion) Besides other characteristics of the fabrics with different loading of titanium oxide, degradation of Orange II and red wine stain under UV light are the most interesting.

Chapter 6 (Conclusions) summarizes the determined results of the thesis. The thesis shows new route to make self-cleaning, antibacterial, antifungal and highly stiff cotton fabric. Cellulose - TiO_2 nanoparticles were coated to the surface of cotton by roller padding. All these properties were evaluated and compared for different content of TiO_2. Surface morphology showed attachment of cellulose to cotton fibres by hydrogen binding. This theory was not fully confirmed and it is based on strong attachment and resistance against washing out. Also titanium oxide nanoparticles are hold in a thin coated film on the surface of the cotton fabric. These theories are not so strong and I am not convinced on these types of binding together.
The samples have strong resistance against washing, author said, but the results are disputable. Why the sample with 10% of TiO_2 lost its blue color intensity strongly than 3 and

5% solution and after 10 time washing it is below value for these two concentrations (Figure 29). Even in blue color intensity at different TiO_2 additions are different on Figure 28 and 29.

There was no effect of TiO_2 on stiffness of the cellulose fabric. Table 1 which shows amount of added cellulose-TiO_2 per gram of cotton fabric shows the same added amount for all TiO_2 concentrations. If this is true, the effect of added TiO_2 on fabric properties cannot be evaluated.

Other presented results are confirmed by experiments and they are likely right.

Chapter 7 (Applications and future works) contains examples of products which can be later developed based on tested technology.

Referee remarks, question and conclusions

The thesis is logically divided into chapters, the content is explained illustratively, and all determined results are simply described.

QUESTIONS

1. I do understand the weight of fabric after coating in cellulose-TiO_2 solution as it is described in Table 1 (p.31). Why the weight after coating in more TiO_2 concentrated solution is lower? And what is the content of TiO_2 on fabric for different TiO_2 solution?
2. Who made the antibacterial and antifungal experiments? Could you describe results on Figures 37, which are not readable in the presented form? Is the reduction of *Staphylococcus Aureus* for 3% TiO_2 really 96.7%? Figure 37a) shows different results, or at least from bad quality of the picture it looks like?
3. Are the SEM photographs on Figure 24 really representatives? Why figure b) and f) are similar and the others different?
4. Why Figures 28 and 29 differed. Figure 29 w/o washing should correspond to Figure 28 or not?

Imperfections and recommendations

Language of the thesis is very good and thesis is nicely written. I did not find many errors and mistypes. Some examples:

1. soltion (p.30), wrong equation (4) (p.18), TiO2 without subscript in whole Abstract.
2. Titanium (Ti^{4+}) atoms (and similarly) are not atoms but ions (cations).
3. Some sources of pictures are missing and I do not expect they are drawn by the author (e.g. Fig. 4, 12)
4. Symbols in eq.10 (p.31) are wrong (what are the indexes?)
5. Figure 27 caption is wrong - e, f are missing.

Referee´s conclusion

The presented thesis is logic, has all necessary parts and show the author understand his work and he is able to put results logically into appropriate parts. The above mentioned recommendations and questions are not so significant, that they decrease the scientific merit of the thesis. There are no significant recommendations for next author´s work. The language is good and fully understandable.

The thesis is good and meets all criteria to be taken to the defence.

In Liberec (Czech R.) on October 30, 2017 **Prof. Dr. Ing. Miroslav Černík, CSc.**

Opponent's review

This opponent's review was elaborated based on Ing. Jana Drašarová, PhD. (dean of Faculty of Textile, Technical University in Liberec) assignment for review Ph.D. dissertation thesis (ref. no. TUL-17/4814/025833, dated 26. 6. 2017) of **Bandu Madhukar Kale "Multifunctional Cotton fabric with Nano TiO_2 Loaded Cellulose"**. Tutor of the Ph.D. student was Prof. Ing. Jiří Militký, CSc.

Thesis presented was studying new route to make cotton fabric self-cleaning, antimicrobial, antifungal and highly stiff.

The main objective was the preparation of cellulose – TiO_2 coated cotton fabric and its characterization for organic stain removal, inhibition efficiency against bacteria's, and disinfection of cotton fabric from fungal colonization.

Major results of this thesis was focused on developed of novel method for quantification of cellulose fractions by simulating X-ray diffraction patterns, degradation of orange II dye under UV light, effect of cellulose coating on dyeing, color fastness, perspiration fastness, rubbing and washing fastness. Antimicrobial and antifungal activity was tested as well. Durability was the major concern with those methods.

The multifunctional cotton fabric was prepared with cellulose - TiO_2 solution on the surface by roller padding machine at time 20 s with same time using of sulfuric acid (60 %) for treat fabric. The coated fabrics were evaluated for their perspiration fastness using the test method ISO 105-E04. Furthermore, there were applied methods of X-ray analysis, SEM morphology and colorimetry analysis for optimization of amount surfactants. The chosen methods fully characterize studied cotton surface for given purposes. Mechanical and photocatalytic properties were tested as well.

Stiffness of treated fabric was affected by cellulose concentration, there was no effect of TiO_2 presence, and thus this procedure can replace traditional starching method. In opposite, antimicrobial and antifungal properties were affected by TiO_2 under 3 %.

Applied methods used by the applicant were modern up to date measuring techniques and give exhaustive information about the studied material and its use.

Proposed application of multifunctional cotton fabric can be commercialized to make self-cleaning suiting, shirting and women wear etc.

From the formal point of view, results of the theses and the thesis itself were well written, results were presented in the form of tables and graphs. Thesis represent typical material science oriented study focused on treatment cotton fabrics as a self-cleaning material for textile industry.

Thesis were written in English language in the form of the monograph. Total number of references cited in the thesis was 152. There were cited fundamental research articles as well

as the latest publications. However the format of the reference list was not fulfilling requirements of the citation standard CSN ISO 690.

Results of the thesis of the applicant **Kale B. M.** were published in 5 scientific papers in impacted international journals where applicant was first author in all cases. He was attending several scientific conferences at home as well as abroad.

Questions to be answered during thesis defense:

1) How many washing cycles will keep modification functional on a fabric?
2) Which mechanism of the attachment of the pigments do you expect to be acting at the particle solid surface interface?

Based on the latter mentioned facts and by the course of law (Higher Education Law No. 111/1998. Sb.) §47 I recommend to accept the PhD. dissertation thesis of Bandu Madhukar Kale, for defense.

In Zlin, August 1, 2017

Doc. Mgr. Barbora Lapčíková, Ph.D.

Associated professor for materials science and engineering
Tomas Bata University in Zlin