Opponent's review

Title: Functional properties of superhydrophobic textiles

Author: Muhammad Zaman Khan

The presented thesis deals with the study of final treatments of textile materials, which contain a synthesis of a highly hydrophobic textile fabric surface and its subsequent use in the field of self-cleaning and separation of non-polar solvents from water.

Thesis contains 121 pages divided into 6 main chapters and contains 10 tables and 59 pictures.

Research in this thesis is divided into 2 separate branches and 6 goals are set. The first branch is the use of fly ash on a cotton substrate, the second direction of research is use of the hydrothermal method to positively influence the growth of inorganic oxide nanoparticles on a textile substrate in order to create a superhydrophobic surface. Two inorganic oxides are chosen, TiO_2 and ZnO. Silane-based compound (OTMS) are also used to create a surface with the required properties.

The first and second chapters contains concise description of superhydrophobic effect and individual goals is defined.

The following chapter contains a literature search of current knowledge in the field of superhydrophobic textile materials with a focus on self-cleaning textiles and use of fly ah, TiO_2 and ZnO. Author do not forget to describe the individual models, which evaluate this treatment. Next part of this chapter is devoted to description of selected published articles focused on the use of the above-mentioned chemical compounds based on silane in combination with inorganic oxides TiO_2 and ZnO.

> I have no significant comments on the above chapters, the chapters are written clearly and with a logical sequence.

The fourth chapter contains the procedures used for surface preparation, whether the use of fly ash on cotton fabric, including the subsequent preparation of a superhydrophobic surface by OTMS, or the use of hydrothermal process in the formation of nanorods of TiO_2, respectively. ZnO for polyester, resp. cotton fabric and subsequent reactions with OTMS. The study of the superhydrophobic surface is performed using standard instrumental analytical methods, AFM or SEM. Quantitative analysis is subsequently performed by EDS, study of Raman spectra and X-Ray diffraction. Finally, the useful properties of the textiles prepared in this way are evaluated by measuring UV protection, as well as determining the contact and roll off angles and the self-cleaning and separation effect. The author does not forget to test the stability of these treatments in different environments, either at different pH or after mechanical dry and wet effect.

> The individual procedures are described in sufficient detail and the methods of evaluation of the prepared superhydrophobic surfaces are chosen appropriately. When author used the standard deviation for individual measurements, I miss the mention of how many measured values it is calculated. I would also recommend writing to the following chemical formula of zinc nitrate: $Zn(NO_3)_2 . 6H_2O$.

In the first part of the results, the doctoral student deals with the preparation of the superhydrophobic surface of a cotton substrate by fly ash. The UV protection of the cotton surface with fly ash and then the above-mentioned characteristics of the hydrophobic surface formed in combination with OTMS

were monitored. The limit of superhydrophobic and mainly self-cleaning properties is reached with 3 wt. fly ash.

The second part of the results deals with the characterization of TiO2 nanorods on a polyester substrate. The presence and distribution of inorganic oxide on the surface of the fibers has been sufficiently demonstrated. The superhydrophobic properties of the fabric prepared in this way have been proven since 1.5 mL of Titanium isopropoxide. The generally known photocatalytic behavior of TiO_2 is studied on to photocatalytically degradation selected azo dye.

The results of the use of ZnO are described in more detail in this thesis, especially concerning the characterization of the resulting nanorods. In contrast to the previous results, the optimization of the hydrothermal process for the preparation of nanorods, on which these results are based, is described here. The superhydrophobic properties achieve best results compared with TiO_2 or fly ash. The possibility of oil / water system separation was subsequently investigated.

Formally, the work is written at a very good language level with a minimum of typing errors. Graphic objects are readable and follow the previous text. I have two comments on the formal page of this thesis:

p. 43 Fig. 26, it would be better to use the same scale in all cases to compare individual SEM images

It ill be better to divide pictures to more captions. The content of this caption should not be divided at the end of the page

My comments on formal part of this thesis do not reduce the quality of the submitted work.

The thesis presents interesting results of experimental work in the field of super hydrophobic systems. The doctoral student demonstrated systematic scientific work. According to the attached list of publications, he also published his results sufficiently (co-author of 12 already published articles, 5 times of them as the main author, co- author of 8 papers at international conferences and 2 chapters in a book). I also appreciate the proposal for the future direction of further research.

My questions:

1. In the graph 25a, p. 41 it is evident that the ground ash has a Max distribution curve in the value of milled fly ash is about 2000 nm in the graph 25a, p. 41, but in the text it is written the size of the part less than 1000 nm (in the graph these sizes are almost zero). Explain this discrepancy.
2. Which %wt of fly ash is used for AFM analysis?
3. How do you explain the ratio of individual elements in a 50 ml sample of ZnO relative to the other concentrations (Table 9, p. 84)?

In conclusion, **I recommend** this thesis for the defense.

In Pardubice on December 2, 2020

Ing. Michal Černý, Ph.D.

Referee´s report on PhD. thesis of

Muhammad Zaman Khan

„ Functional properties of Superhydrophobic Textiles“

Professor Miroslav Černík

The presented thesis consists of 120 pages divided into 6 chapters. The thesis is based on 3 separate topics connected by a principle in a surface modification to get a hydrophobic and self-cleaning surface. The thesis has standard parts - Aims and objectives, Literature review, Research methodology, Results and discussions, and Conclusions and future work. In the end, there are References and a List of author´s publications. The author´s list of publications is extensive.

Abstract

The author made here an introduction to his work and explained the objectives of the study. It is the development of superhydrophobic surfaces by inexpensive, eco-friendly and straightforward techniques with added functionality. He selected fly ash and titanium and zinc oxides, but there is no explanation why these were particularly selected. He then describes three studies for each of the surface modifiers, but what I am missing here (and at the Conclusions as well) is comparing these three methods to each other. The presented thesis looks like three individual works (papers) on the same topic but without connection to make it one solid piece of work.

Chapter 1

introduces the work, where superhydrophobic natural structures and a short history of man-made developments are shown.

Chapter 2

deals with the aims and objectives of the thesis. The prepared modified fabrics have the common aim of increasing their hydrophobicity; moreover, the other properties were aimed, mainly, e.g., UV-blocking, antibacterial properties, flame-retardant, anti-fogging, oil/water separation. In the present thesis, UV protection, self-cleaning, and oil/water separations.

Chapter 3

deals with literature review. There is a sufficient number of literature sources, but the structure of the chapter is slightly chaotic. Some of the parts should be discussed in more detail, and some, which have no significant influence on the results, should be shortened. Some literature sources are also missing (e.g., the first equation- de Broglie, author? Source?). Some errors are here as well (e.g., "…negative electrons and oxygen combined into O_2^{-}"; it is superoxide radical (anion)).

Chapter 4

is about the methodology. It describes materials, fabrics coating with three different methods, and various methods of surface characterization. In general, the chapter consists of all methods applied, but some of the descriptions are relatively short without sufficient details (e.g., for roughness determined by AFM it is mentioned "software calculates the surface roughness").

Chapter 5
is about the results. There is a lot of excellent results for all three methods of surface modifications. In all cases, the results show improvement of desired properties of the fabrics. As I wrote already in the Abstract part, a comparison of these three results would significantly improve the work's unification.

Chapter 6
The chapter summarizes the major conclusions of the work. There are the following. The addition of fly ash caused significant improvement of hydrophobicity and UV protection of the surface. Due to the metal content in the ash, the UPF increased by two orders of magnitude. Also, organic/water separation efficiency for toluene, n-hexane, chloroform and ether were higher than 95%.

The addition of titanium dioxide creates nanoflowers. These structures appeared significantly at the dose of 2 ml. The contact angle was increased, and hysteresis decreased. The modified surface also showed promising results to maintain durability against mechanical abrasion, laundering, and chemical and UV action. The surface also exhibited self-cleaning by the degradation of methyl orange.

In the last part, the microwave hydrothermal method was used to grow ZnO nanorods. Additionally, OTMS was applied to incorporate superhydrophobic properties. The determined values of water contact angle and roll-off angle were extreme (170.2° and 1°). The modified fabrics also showed promising results to maintain their durability against mechanical abrasion, laundering, chemical and UV action, and outstanding oil/water separation performance.

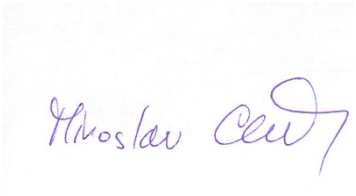
Referee remarks, question and conclusions

QUESTIONS
1. You speak about TiO_2, but photoactivity is connected with only one crystalline structure (anatase). Chemical self-cleaning does not work for the other forms. Are you sure your structures are photoactive? Why in Fig.44, the surfaces of coated polyester fabrics prepared at increasing concentration of TiO_2 has more orange color?
2. Table 9 shows the elemental composition of ZnO nanorods. Why is there a drop in oxygen percentage for 50 mM? It does not correspond with Zn content.
3. Could you make a simple (in table) comparison of all three methods of surface functionalization? Just + and – for selected properties and 3 materials.

Imperfections and recommendations
The thesis is written in perfect English with a minimum of typing errors.

Referee´s conclusion
The presented thesis of M.Z. Khan is logical, has all the necessary parts, and shows the author understands his work. He can make appropriate preparation of the coated fabrics and their characteristics, and put his results into logical and appropriate conclusions. The thesis shows one subject with three various views (surface modifications). The work significantly contributes to knowledge in the subject. There are only a few recommendations for the next author´s work. The language is perfect and entirely understandable.

<u>The thesis is good and meets all criteria to be taken to the defense.</u>



In Liberec (Czech R.) on February 6, 2021 **Professor Miroslav Černík**