Appendix 12a

REVIEW

of dissertation for the acquisition of:

educational and scientific degree " **doctor** "	X
scientific degree **"Doctor of Science"**	
	the true is indicated by the sign "X"

Author of the dissertation:

Assistant prof.		Dimitar	Krasimirov	Dimitrov	UCTM
academic position	scientific degree	name	middle name	last name	workplace

Topic of the dissertation:

Functional thin film coatings with added graphene materials

Scientific area:

5	Technical sciences
code	name

Professional area:

5.10	Chemical technologies
code	name

Scientific specialty:

Technology of silicates, binders and refractory non-metallic materials

The review was written by:

Assoc. prof.	Dr.	Irena	Kirilova	Mihailova	UCTM
academic position	scientific degree	name	middle name	last name	workplace

1. Completion of the provided documents:

A) The dissertation and the competition documents are in full compliance with the Regulations.	4 points	X
B) The documents are complete but do not fully comply with the requirements of the Regulations.	2 points	
C) The documents are not completed in accordance with the requirements of the Regulations.	0 points	

		one of the answers given is marked with the sign "X"

Missing documents and violated standards must be described if response C is marked.

2. Meeting the minimum requirements under the Regulations:

A) The candidate meets the minimum requirements	20 points	X
B) The candidate doesn't meet the minimum requirements	0 points	
		one of the answers given is marked with the sign "X"

It must be filled in if answer B is marked. The publication activity of the candidate is analyzed. The response of the results achieved (quoted) is analyzed.
Dimitar Dimitrov has co-authored in 4 published articles on the topic of the dissertation, referenced and indexed in international databases. According to the requirements in the UCTM statute for attaining academic titles and positions, for scientific and educational degree "doctor", a sum of 30 pts is required for criteria 5-11. The candidate is awarded 43.71pts. 1. Staneva A.D., **Dimitrov D.K**., Gospodinova D.N., Vladkova T.G. Antibiofouling Activity of Graphene Materials and Graphene-Based Antimicrobial Coatings, Microorganisms. 2021;9. https://www.mdpi.com/2076-2607/9/9/1839 - Impact Factor: 4.1; SJR:0.944 **Q2** 2. B. L. Martinov, T.E. Vlakhov, A.D. Staneva, S. Slavov, **Dimitar Dimitrov**, Y. G. Marinov, G. B. Hadjichristov, Synthesis and characterization of nanosized $ZnTiO_3$ doped with of reduced graphene oxide (RGO), Journal of Physics: Conference Series 1762 (2021) 012031 doi:10.1088/1742-596/1762/1/012031 - SJR 0.21; **Q4** 3. Boris Martinov, Stanislav Slavov, Anna Staneva, **Dimitar Dimitrov**, Janna Mateeva, Electric properties of new composites materials based on RGO, nanosized ZnO and Cu nanoparticles, Journal of Physics: Conference Series, 1762 (2021) 012029-SJR 0.21; **Q4** 4. **D. Dimitrov**, A. Staneva, Effects of matrix viscocity on the dispersion of graphene layer separation in epoxy coatings, Journal of Chemical Technology and Metallurgy, in Press SJR:0.196; **Q3** Citings: 36 (Scopus): The article, published in Microorganisms, has been cited 32 times. The article, published in Journal of Physics, has been cited 4 times. It is worth noting that all published work is in Scopus-referenced issues, and that one article is in a Q2 publication with impact factor 4.1. The number of citations is indicative of the wide reach of the published work within the scientific community.

3. The relevance of the topic of the dissertation:

A) The topic is relevant and new (there are no known results on the topic by other authors)	8 points	
B) The topic is relevant and results from other authors are known	6 points	X
C) The topic is not relevant, but results from other authors are known	2 points	
D) The topic is not relevant and no results from other authors are known	1 point	

E) The topic does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The evaluation of the relevance of the dissertation must be substantiated
The topic of the dissertation concerns composite materials – thin film coatings incorporating graphene materials. The relevance can be assessed based on the following: ✓ Graphene materials and nanosized oxide particles are widely investigated due to their promise to address current challenges in the fields of electronics, energy transfer and storage, healthcare and biomedicine; ✓ Thin film materials have a rich history and wide applications due to their indispensable role in optics as well as functional or protective coatings; ✓ Nanocomposite formulation is a contemporary approach to combine the properties of materials and address challenges which the separate constituents would not be able to overcome. The main obstacles concern the production of appropriate nanosized materials and their incorporation in bulk materials or coatings, the latter of which is the case investigated in the presented work. The noted 36 citations are a testament to the wide reach of the conducted research among the academic circles and thus serves as a guarantee to the relevance of the topic of the dissertation.

4. Knowledge of the problems, subject of research in the dissertation:

A) The doctoral student knows in detail the achievements of other authors on the topic of the dissertation	8 points	X
B) The doctoral student is partially familiar with the achieved results on the topic of the dissertation	4 points	
C) The doctoral student has no prior knowledge of the status of the problems in the dissertation	0 points	
		one of the answers given is marked with the sign "X"

The evaluation must be substantiated if answer C is marked.
The dissertation presented demonstrates the candidate's ability to purposefully utilize current scientific literature, to analyze it critically, and to summarize and present other authors' results in a logically consistent manner.

5. Type of research:

A) Theoretical	4 points	
B) Applied	4 points	
C) Theoretical with application elements	4 points	X
D) It does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The level of research must be substantiated if answer D is marked.

The aim of the PhD candidate to combine theoretical research with practical applications is evident by the choice of subject matter , the formulated aims of the work, and the interpretation and discussion of the results produced.

6. Objectives of the research:

A) Realistic and of scientific and / or applied interest	8 points	X
B) Realistic, but not of scientific and / or applied interest	3 points	
C) Unattainable (unrealistic)	0 points	
		one of the answers given is marked with the sign "X"

Objectives must be specified. The type of the set objectives must be justified.
The objective of the conducted studies is the production and characterization of thin film coatings incorporating graphene materials with potential applications in optics and as antibacterial coatings. To this aim, experimental work has been conducted and presented in 4 subchapters based on the composition of the successfully obtained coatings: **1. Thin film optical coatings on polymer substrates** This part of the work discusses material and method selection and presents the synthesis of thin film optical coatings via physical vapor deposition technique (EBPVD). An optical performance assignment is chosen. The coatings consist of stacks of SiO_2, ZrO_2, and Ti_3O_5 thin films with a thickness of 10-15 nm. The optical performance compliance is confirmed by spectrophotometry – anti-reflective and mirror coatings have been successfully produced. **2. Silicone rubber coatings containing GO, RGO, and nanosized ZnO.** The subject of this experiment is to produce novel composites containing ZnO, GO and RGO, and their incorporation is silicone coatings. GO and RGO are synthesized by a modified Hummer's method, and ZnO nanoparticles are obtained via sol-gel synthesis. The obtained composite materials are dispersed in a silicone rubber matrix and applied to glass substrates as coatings. The resulting samples are examined with XRD, TEM and SEM, which confirm the composition and give insight into the morphology and homogeneity of the composites. Antimicrobial tests are carried out by the agar diffusion method. The results show some promising results but also highlight the shortcomings of this method. **3. Epoxy coatings with GPL. Effect of matrix viscosity on the dispersion and delamination of GPL layers.** The following series of compositions studies the dispersion of graphene nanoplatelets GPL in a bisphenol-a based epoxy polymer matrix. After sonication GPL particles are introduced to epoxies of varying viscosity . The working hypothesis is that the increased viscosity will stabilize the suspension and aid to retain the delamination of GPL layers. The samples are examined with TEM and Raman spectroscopy. TEM confirms that the most viscous sample shows the best delamination. The increase of the graphene signal in Raman spectroscopy as viscosity rises points to the larger concentration of stabile suspended fraction in liquid phase, which in turn leads to higher quantities of GPL incorporated in the coating. Additionally, the cross-hatch method was used to determine changes in adhesion. The test determines that the addition of GPL does not worsen the mechanical performance of the coating when compared to unmodified epoxy. **4. Epoxy coatings with GO, GPL, and $ZnTiO_3$.** The final experiment builds on the previous ones by comparing an unfunctionalized graphene material – GPL, with graphene oxide GO. The aim of the study is to compare these materials as stabilizing agents in composites containing nanosized $ZnTiO_3$ particles. The composites are obtained and applied as coatings on glass substrates. TEM and agar diffusion analysis are performed. The conclusion drawn is that GPL helps retain the $ZnTiO_3$ particle size in the 10 nm range, and prevent particle aggregation.

7.Methods of research:

A) Adequate to research and set objectives	8 points	X

B) Partially appropriate, enabling part of the scientific objectives and / or applications to be achieved	4 points	
C) Inappropriate methods	0 points	
		one of the answers given is marked with the sign "X"

Methods must be specified. The type of methods used is justified.
A wide array of methods for synthesis and examination have been utilized in the dissertation – adequately selected and appropriate for the aims. For the production of optical thin films Electron Beam Physical Vapor Deposition (EBPVD) has been used; GO and RGO are synthesized by a modified Hummers method; Nanosized ZnO particles have been obtained by a sol-gel approach. All procedures for production and examination of the materials are described meticulously, which provides reproducibility of the obtained results. For phase and structural characterization, powder x-ray diffraction (XRD), Raman spectroscopy, scanning and transmission electron microscopy (SEM and TEM) including selected area electron diffraction (SAED) and high-resolution transmission microscopy (HRTEM) have been utilized. Concerning specific properties, cross-hatch delamination test has been applied according to ASTM D3359-23 standard to assess mechanical durability of the coatings, and agar diffusion method has been used to determine particle mobility and antimicrobial properties.

8. Contributions of the dissertation:

A) With lasting scientific and / or applied response, they form the basis for new research and applications	20 points	
B) They are of significant scientific and / or applied interest, complete and / or summarize previous research	16 points	X
C) They are of scientific and / or applied interest	12 points	
D) Lack of significant contributions	8 points	
E) Lack of contributions	0 points	
		one of the answers given is marked with the sign "X"

Contributions must be specified. The type of results achieved must be justified.
The main contribution of the dissertations can be formulated as such: 1. A method for the production of optical coatings with specific optical performance (placement, size and shape of the reflection curve) had been proposed by means of EBPVD. The substrate preparation approach has been modified and improved. 2. A procedure for substitution of Ti_3O_5 with ZrO_2 in thin film optical stacks while maintaining optical performance has been proposed. Approaches to compensate resulting deviations have been examined. 3. Novel composite silicone coatings containing RGO and ZnO in different rations have been obtained. The antimicrobial properties of these new materials has been assessed, and the best performing compositions have been found. 4. A comparison between the ability of GO and GPL to associate with nanosized $ZnTiO_3$ has been conducted, and it has been proven that GPL aids to stabilize and retain unaggregated particle size. 5. The influence of the polymer matrix viscosity on the stability of GPL suspensions and graphene-layer delamination has been examined.

It is the view of the reviewer that the highlighted contributions of the dissertation are original and signify scientific and/or applied interest and also conclude previous studies on the topic.

9. Evaluation of the compliance of the dissertation summary with the dissertation:

A) Full compliance	4 points	X
B) Compliance of the main parts	2 points	
C) Lack of compliance of the main parts	0 points	
		one of the answers given is marked with the sign "X"

The evaluation must be substantiated if answer C is marked.

10. Participation of the doctoral student in the achievement of the results of the dissertation:

A) The doctoral student has at least an equal participation	8 points	X
B) The doctoral student has secondary participation	5 points	
C) The participation of the doctoral student is unnoticeable	0 points	
		one of the answers given is marked with the sign "X"

Critical notes must be provided if one of the items B or C is marked.
The dissertation presented, as well as my personal impressions of eng. Dimitar Dimitrov's participation in scientific forums and conferences presenting results from the topic of his dissertation, leave no room for doubt as to his equal participation in achieving the aforementioned results.

11. Critical notes:

A) Lack of critical notes	8 points	
B) Critical notes of a technical nature	7 points	X
C) Critical notes that would partially improve the results achieved	4 points	
D) Significant critical notes	0 points	
		one of the answers given is marked with the sign "X"

Critical notes must be provided if one of the answers C or D is marked.

12. Conclusion

A) The evaluation of the dissertation is **POSITIVE**	This evaluation is assigned to a total number of at least 65 points	X **93 points**
B) The evaluation of the dissertation is **NEGATIVE**	This evaluation is assigned to a total number below 65 points	
		one of the answers given is marked with the sign "X"

To be filled in at the request of the reviewer
The dissertation contains scientific and applied results, which constitute novel contributions to science. The dissertation shows that PhD candidate Dimitar Dimitrov has demonstrated extensive theoretical knowledge of the topic of “Technology of Silicates, binders, and refractory non-metallic materials” and is capable of independent research. The presented dissertation not only covers, but exceeds the requirements in the Law for the development of academic faculty, as well as the UCTM statute for attaining academic titles and positions, for scientific and educational degree "doctor".

05.08.2025	The review was written by:	**Irena Mihailova**
date		signature