Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Oleg Lebedev

PhD Program: Materials Science and Engineering

Title of Thesis: Study of deformational behavior of electrical conductivity of polymer composites with different nanofiller distribution types

Supervisor: Assistant Professor Sergey Abaimov

Name of the Reviewer: Prof. Alexei Buchachenko

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** **Date: 31-08-2020**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The Thesis submitted by Oleg Lebedev to fulfill the requirements of the Skoltech PhD degree in Materials Science and Engineering addresses the correlation between conductance and deformation of the polymer composites with specific non-uniform distribution of the conducting filler. Practical importance of this topic is well rationalized in the Introductory section of the Thesis. Indeed, conducting polymer materials need to be optimized for various applications. Electric measurements provide a very convenient tool for non-destructive materials diagnostic in operation mode and requires specially designed conducting networks for materials monitoring. The simplest case of uniform filler distribution, well known from percolation theory, normally requires high filler contents to reach the threshold. It is not cost-efficient and may have negative effect on the mechanical properties of the composite. Structured (or segregated) filler layouts can significantly reduce the conductivity threshold and special approaches to form such filler distributions have been developed. Supplementing these approaches with suitable models is a deserving task that fully justifies the goals set in the Thesis.

The research exposed in the Thesis exploits consistent methodology that combines experimental part (preparation of the samples using a method justified by literature search, characterization of their mechanical and electric properties and imaging that reveals their structure) and theoretical part (building structure model based on real imaging, setting up the mesh for finite element calculations, modeling the deformations and calculating the conductivity using simplified resistance models for the composite). Each step is described in details, enough for both general understanding and reproduction. This methodology is followed uniformly from the case of strongly segregated anisotropic filler (multi-walled carbon nanotubes, MWCNT) in Chapter 3 to the case of filler (carbon black and MWCNT) agglomeration in Chapter 4 and, finally, to the composites reinforced by glass fibers, which requires incorporation of the proposed model into three-level multiscale model in Chapter 5. Overall, the Thesis structure is quite logical and easy to follow.

* *On this background, Concluding section looks quite poorly written. Being messy, it reflects more the content on the work rather than its essential lessons. I think it should be rewritten to summarize the main findings in a clear and structured way. I would also be pleased to learn author's view on the future development of the topic.*

Going back to the main goal of the Thesis – development of the "models for the correlation of electrical properties and applied deformation, taking into account the structure of materials, and verified by experimental methods", I would say that it was formally achieved. However, I would consider the research presented as a preliminary step of such modeling. Indeed, the approach developed essentially uses structural information on the composite available only by imaging technique. Thus, it lacks the predictive power unless a wide knowledge exists on what determines the filling structure – its own nature and state? Polymer matrix? The way of composite formation? Are there prospects to make the modelling predictive considering typical compositions and formation methods without prior experiment? These questions do not reflect the drawbacks or omissions in the work, but the answers are valuable for the future progress. This is why I advise to tackle them in the comment (*) above.

My real criticism addresses the verification of the model with respect to experimental data as it presented in the Thesis (Chapters 3 and 4, as the most relevant examples). To my understanding, comparisons are far from being quantitative. The main issue is inconsistent treatment of various uncertainties that prevents (at least me) to gain full understanding of the validity of the model and overall requirements to electric material diagnostics. The way the author uses for comparison (the slopes of linearized dependences) implies two sources of uncertainty in both experimental and simulated data: variation from sample to sample and linearization, not to mention inherent accuracy limits of the particular characterization technique and model approximations. In the Thesis, they are neither discerned nor consistently evaluated. See, for instance, Figure 7. Experimental data obtained for the "series of samples" are shown without any error bars. Linearization looks good, but the Figure 17 for another composite shows significant scattering of the measured points. Does it persist in the first case? Is it systematic (each sample gives slightly different quasi-linear dependence) or just reflects accuracy of the measurements? What is the overall uncertainty of the experimentally deduced slope? One cannot attest the accuracy of the modeling not knowing the uncertainty of the reference data. Furthermore, Figure 7 shows the scatter of the model results for three samples investigated. It is also significant and also left unexplained – does each sample give particular curve with the individual slope? How the variation from sample to sample matches those seen in the measurements? Important issue – the sensitivity of the model to the structure of the samples of the same material – was not addressed. Instead, the whole shadow of points was smoothed (unclear how) and the single slope is derived. The corresponding errors discussed in what follows seemingly reflects only the linearization, not sample statistics (?). The question is – how many samples should be studied to get reliable slopes from the measurements and modeling? On the other hand, Figures 26 and 27 in Chapter 4 show quite wide error bars, sometimes making different results indistinguishable. Where they come from? And finally, what about the uncertainties featured in the Figure 28, which I consider as one of the most telling for assessment of the model?

** *I feel the need to present error analysis of the measurements and modeling in more rigorous and clear way. At least, the sources of uncertainties and error bars should be clearly identified and quantified.*

Despite the above problem in data analysis and presentation, I still consider the Thesis as a solid work initiating perspectives for modeling and understanding of the dependence between mechanical and electric properties of polymer composites. Its results were published in appropriate scientific journals and presented at the topical conference. The work done by Oleg Lebedev certifies him as a qualified researcher with experience in both composite formation and multi-scale modeling covering a wide range of theoretical and mathematical methods and algorithms.

I think that the Thesis submitted can be brought to Thesis defense providing that the points (*) and (**) are properly addressed. In addition,

(***) *I do recommend to proofread the Thesis carefully. There are few Russian-like wordings ("card" instead "map", "radiuses", Russian in the caption to Fig.24), misspellings, formatting inaccuracies, etc.*

Provisional Recommendation

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*
☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*
☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*