

Thesis Changes Log

Name of Candidate: Oleg V. 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: Prof. Sergey Abaimov

The thesis document includes the following changes in answer to the external review process.

Name of the Reviewer: Prof. Alexei Buchachenko

1. 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.
2. 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.
3. 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.

1. Conclusions section was rewritten so it now comprises summarization of the main findings, as well as opinion of the author on the future development of the topic. It is now more clearly indicated, that the results at this point of progress should be considered as qualitative. It is also mentioned, what can be done to make them also quantitative.
2. In the experimental section it is now discussed, what sources of uncertainties are. Error bars are added to selected number of points on the presented curves to indicate scatter of the data before averaging.
3. The text of dissertation was revised in terms of English quality.

Name of the Reviewer: Dr. Dmitrii Godovsky

1. Multi-scale modeling procedure for the second system investigated was separated in two chapter for easier comprehension of the material. In the first chapter, PP matrix filled with nanoparticles was studied, while in the second influence of the glass fibers presence was investigated. I think the same separation should be done for the first system as well

(Chapter 3 in the dissertation): first chapter should describe the thin layer, while second will be dedicated to study of 3D segregated structure of modified UHMWPE.

2. Specifications of the nanoparticles and polymers are better to be presented in tables in a designated Materials subsection for easier navigation.
3. It is a good idea to add prediction accuracy (in relative terms) for each set of assumptions in the section 4.4. It can be done for each type of the filler, showing a relative deviation value averaged for all investigated concentration, and separately for each concentration as a plot of prediction accuracy vs. concentration.
4. Errors are missing in table 2 (section 5.3., which is mistakenly named 4.3 in the text).

1. Chapter 3 was divided in 2 chapters for easier comprehension of the material.
2. Specifications of nanoparticles and polymers were put into corresponding tables in a Material.
3. Graphs indicating relative predicting accuracy were added in the corresponding section.
4. Errors were added in Table 2, section numbering was corrected.

Name of the Reviewer: Prof. Alexey Lyulin

1. In the literature review part, some discussion on how the filler aspect ratio and its agglomeration affect the percolation threshold would be desirable;
2. In Chapter 3 please add a brief explanation on the reasons behind the decrease of the electrical conductance with deformation;
3. In Chapter 4 please add figures depicting the dependencies of the slopes of conductance vs. elongation as a function of the distance from the corresponding percolation threshold;
4. The characteristic value (the slope of the conductance-elongation dependency) and the statistical length of a CNT definitions should be added to the relevant pages.

1. Discussion on how filler aspect ratio and its agglomeration affect the percolation threshold was added to the literature review.
2. A brief explanation on the reasons behind the decrease of the electrical conductance with deformation was added in Chapter 3.
3. Figures depicting the dependencies of the slopes of conductance vs. elongation as a function of the distance from the corresponding percolation threshold were added.
4. The characteristic value (the slope of the conductance-elongation dependency) and the statistical length of a CNT definitions were added to the relevant pages.

Name of the Reviewer: Prof. Dmitry Gorin

1. It is well known that there is at least two types of CNTs, namely SWCNTs and MWCNTs. I didn't find explanation for choice of MWCNTs as a model filler in the PhD thesis.
2. page 34, line 2 from top: what does the symbol “%” after “polymer matrix” means?
3. page 37, Figure 1, Figure 1 (a) and (c) – absence of scale bar value
4. page 59, Figure 11, Figure 11 (c) – absence of scale bar value

5. page 72, Figure 8, Figure 18 (b) – absence of scale bar
6. page 72, 4.2.2. Experimental methods – I don't find current voltage characteristic of measured structure. These data are required for confirmation that there are Ohmic contacts. The photos of experimental setup as well as measured samples would be also useful.

1. Explanation on the choice of the MWCNTs was added to the Materials section.
2. Misprint (symbol “%”) was corrected.
3. Missing scale bars values were added to Fig. 1
4. Missing scale bar value was added to Fig. 11
5. Missing scale bars were added Fig. 18. no need for scale bars in Fig. 8.
6. Mention of linearity of current-voltage characteristic of one of measured samples was added. Since all of the samples look identical (black rectangles), pictures of them were considered to be not very informative to be added in the text of dissertation. Experimental setup also is just an Instron paired with a multimeter, which is too was considered to be not too novel to be demonstrated in the dissertation.

Name of the Reviewer: Prof. Albert G. Nasibulin

1. Chapters 3, 4 and 5 start with Introduction, followed by Materials and Methods, Results and discussion and Conclusion sections. This is the structure of a paper, but thesis should summarize these three papers. Introduction is given already in Chapter 1. Materials and Methods usually are gathered as separate chapter, where everything can be described at once. Conclusions are given at the end of dissertation. I would rename these section/change the structure of the thesis and start the chapter without Introduction section.
2. Personal contribution is missing and can be added right after the list of thesis publications.
3. Science is first of all people! My recommendations would be to properly acknowledge people who contributed to this work and papers published and made a basis for the thesis. Money and foundations are of course also important, and should be mentioned after the collaborators.
4. The list of figures and tables (p.11-16) is not necessary, and can be easily cut off without harming the quality of the thesis. This is old style writing of theses, I would call this atavism.
5. Formulas and equations are a part of sentences and should follow the punctuation rules: commas and full periods are missing.
6. Some additional and more specific comments to improve the thesis:
 - p.66, 67: the problem with precision of numbers: “ $(-7\pm 0.2)\cdot 10^{-3}$ versus $(-7.2\pm 0.2)\cdot 10^{-3}$ ” and “ $5.21\cdot 10^{-3}$ versus $(-7.2\pm 0.2)\cdot 10^{-3}$ ”. Table 1: please check the precision of all numbers: how many digits after dots are defined?
 - P.73: number and dimension should be separated: “20atm following by instant cooling in cold water to obtain strips of 1.2mm thickness, width of 12mm and length of 100mm.”

These are just examples, and these should be checked everywhere in the thesis.

1. Structure of the dissertation was reworked so Materials and Methods are presented as a separate chapter. Introductions in each chapter were renamed to reflect that they describe the goal of the corresponding part. Conclusions were renamed so it is now clear that they are summarization of the corresponding chapter.
2. Personal contribution was added after the list of publications.
3. Acknowledgment of all the colleagues who provided support during my work on the thesis was added.
4. The list of figures and tables were removed.
5. Punctuation rules were considered in sentences comprising formulas and equations.
6. Additional changes to the dissertation quality were introduced according to the comments, while also general quality of the English was improved through the text.

Name of the Reviewer: Prof. Stanislav Moshkalev

1. The electrical resistance of the MWCNT network depends mostly on resistances of contacts between individual nanotubes. The contact conditions may change strongly for the networks fabricated with and without polymer matrix, how this is considered in the simulations?
2. For electrical measurements, 4 probes method was employed and only brief description of the method was done, more details on the method are needed.
3. Equation 1 seems to be wrong; the weight must be proportional to the material density.
4. Based on comparison of large amount of experimental and simulation results, the final conclusions were done in very general terms: “it was concluded, that contrast of mechanical properties between insulating regions and electroconductive phase in composite materials with segregated structure plays a significant role”. The differences in mechanical and electrical properties of the fillers and matrix used in the study are very large. So, it would be useful to provide more specific conclusions regarding the effects of fillers and matrix on the properties of the composite and the response to deformations.
5. Throughout the text, many sentences are too long (5-7 lines or even more) and difficult to understand (example: in the page 30 - only 4 sentences, one of them has 9 lines), they should be broken in shorter phrases for easier reading;
6. Chapters 1 and 2 have no Figures/Tables, I recommend to include some figures and tables for better presentation of the material.
7. The English is good, however, several grammar or style corrections need to be done, for example:
 - P. 18: “electrostatic discharge” – should be substituted by “electrostatic protection”,
 - P. 27: “more thousands of articles” – should be “several thousands of articles” or “more than one thousand of articles”,
 - P. 34: “dielectric polymer matrix %” – should be “dielectric polymer matrix percentage” ,
 - P. 47: “The results of these test demonstrated...” – should be “The results of these tests demonstrated...”
 - P. 52: “(COD ~ 0.993)”- what is COD? The abbreviation should be explained first time it appears in the text,
 - P. 83: “...have high value of properties contrast between ...,” - should be “...have high contrast in values of parameters between ...”,

1. It is now more clearly explained that since only relative conductance and the relative conductance changes were considered, it was considered irrelevant if the polymer is present or not between the particles, since all contact conductance values were set to 1. Media influence was only emulated by the conductance decrease law, supposedly reflecting effect of the electron tunneling.
2. 4 probes method was described in more details in the Materials and Methods section.
3. Equation 1 was corrected.
4. In this work, the contributions of the compliance of the insulating regions were qualitatively assessed. In the first case, insulating regions are large polymer granules. In the second case - glass fibers that form the fabric. In the first considered case, the conducting medium (which is a layer of nanotubes located at the boundaries of polymer granules) deforms in the same way as polymer granules, since nanoparticles actually follow polymer. In the second case, the conductive medium, which is a mixture of PP and nanoparticles, on the contrary, deforms much more noticeably than glass fibers due to the contrast of their properties (high rigidity of glass fibers). A quantitative study of the contrast between the properties of the polymer, matrix and fibers was not carried out, since I thought that the big difference in properties allows to set any values for the matrix and polymer, as long as they are quite different. The study of these effects, including the effect on the simulation result of the fidelity of the real structure of a multiphase composite, is a labor intensive work, and I plan to apply for a grant on this topic this/next year.
5. Many sentences were broken into short ones to improve quality of the text.
6. Some figures were added in Chapter 2 to better present result described in the reviewed literature.
7. Additional corrections to the dissertation text were introduced according to the comments, while also general quality of the English was improved through the text.