Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Hassaan Ahmad Butt

PhD Program: Materials Science and Engineering

Title of Thesis: Carbon nanotube fibers as embedded electrodes for the dual-stage monitoring of multi-functional carbon nanotube nanocomposites

Supervisor: Professor Albert Nasibulin

Co-supervisor: Assistant Professor Dmitry Krasnikov

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 23-11-2023**

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

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The doctoral thesis "CARBON NANOTUBE FIBERS AS EMBEDDED ELECTRODES FOR THE DUALSTAGE MONITORING OF MULTI-FUNCTIONAL CARBON NANOTUBE NANOCOMPOSITES" by HASSAAN AHMAD BUTT is devoted to a relevant and significant issue in modern Materials Science of structural composites applicable in top performance technical systems (aerospace, wind generators, pressure vessels for liquefied natural gas etc.). It is a good dedicated and comprehensive research report having all necessary components to consider it as a firm scientific work. I am generally positively impressed with the scientific soundness, novelty and practical applicability of the results. Methods are adequate and relevant. The quality of publications is acceptable.

Comments are attached.

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*

The doctoral thesis "CARBON NANOTUBE FIBERS AS EMBEDDED ELECTRODES FOR THE DUALSTAGE MONITORING OF MULTI-FUNCTIONAL CARBON NANOTUBE NANOCOMPOSITES" by HASSAAN AHMAD BUTT is devoted to a relevant and significant issue in modern Materials Science of structural composites applicable in top performance technical systems (aerospace, wind generators, pressure vessels for liquefied natural gas etc.). It is a good dedicated and comprehensive research report having all necessary components to consider it as a firm scientific work. Having been generally positively impressed with the scientific soundness, novelty and practical applicability of the main thesis' outcomes I noticed few aspects which are recommended to be addressed before final submission and formal defense. They are given below as the following:

Polymer nanocomposite – better to explain in the beginning what does it actually mean. Nanometer scaled fillers? Nanometer scaled supramolecular structure elements?

Page 3

This thesis showcases the novel application … – too "commercial" beginning, while the theses are about science and research. May I ask to rephrase? E.g. This *thesis is devoted to the scientific foundations of CNTFs synthesis, integration and usage in …*

Page 5

3. Submitted – please, give details about the journal of submission.

Page 6. 4. The same - please, give details about the journal of submission.

Page 7 – To our great regret Professor Alexei Buchachenko died. I would ask you to revise (or include an addition) the paragraph acknowledging him taking into account this sad fact to express our mutual feelings – he was a kind person to be addressed with serious respect.

Page 12. Line 3 - I guess "CNT-polymer nanocomposites".

Page 13 Line 14 – I guess "if they are sensitive to different types of CNTs"

Page 15 – Young's modulus. Y must be capital.

Page 17 Line 3. ~~characterization~~ classification

Page23 . "Although precedence for composite monitoring using CNTFs is present for both

the manufacturing and lifecycle stages of polymer matrix composites, no scientific work,

to the best of the author's knowledge, has addressed their feasibility for monitoring

multifunctional nanocomposites and their properties such as electrical conductivity and

piezoresistive response, especially those incorporating CNTs in the polymer matrix." Please, rephrase. I see a contradiction in your argument as it is written.

Page 27. Please, specify the polymers used as a base of purchased masterbatches.

Page 31. Discussion on avenues which then have not been used or studied is excessive. The same about twisting (pages 33-34). Please, exclude this, or send it to an Appendix.

Generally ! 3.5.2 must be written more accurate and in details.

Page 34-35. Table 2 – The title seems to be incorrect - "series of SWCNT/epoxy nanocomposites". The density as it given corresponds to powders (and it is following from the text) or very porous foam. Are your nanocomposites porous/foamed?

Figure 8 – scale bar!!!

SWCNTs by OCSiAl? In the Table 1 OCSiAl was responsible for MWCNTs. Please, clear out.

Why do you use wt.%. If wt.% are easily re-scaled to v. % - please, discuss this and give conversion scale. In the science of composites volume fraction only has physical meaning.

Pages 40 and 41 – Figures 12 and 13. Captions: why a, b, c , d are given as CAPITAL? Why subscripts were changed for other characters like e instead of a_1. Please, unify legend in captions in Figures 11-14.

Figure 15. At the page 38 the following compositions were described: 0.005, 0.05, 0.25 and 1.0 wt. In Figure 15 the compositions seem to be different. Please, explain.

Page 45. "SWCNT/epoxy nanocomposites fabricated by the presented route possess electrical conductivities of 0.1 – 1 S/cm at 1.0 – 2.0 wt.% " From Figure 15 I see 0.05 – 5 S/cm. Please, clear out.

Page 46. Keithley, not keithley.

Page 47. 1mm/min on an intron 5969 -> Instron. Can you estimate strain rate in absolute units (s^{-1})? This is more scientific that engineering.

Page 51. "In comparison to metallic electrodes which have a smooth surface and surface oxide layer, this type of electrode is better suited for low contact resistance readings which allows the actual electrical conductivity and piezoresistive response of the materials they are embedded in to the measured" – seems that phrase is incomplete.

Page 53 – Wrong Figure number – must 19. Figures 19 and 20 – the conductivity was discussed in the text above, and resistance is given in Figures – not very polite, imho.

Page 54. "the measured electrical resistance values are almost identical for the same type of nanocomposite mixture as can be seen in Figures 19 and 20." Actually, the size of Figures and scale along Y do not allow to verify this argument with naked eye. Must be improved somehow.

Page 55. "it can be seen that the CNTF diameters provide a negligible difference for both SWCNT and MWCNT mixtures, regardless of the concentration." Also questionable.

"The CNTFs are seen to be more sensitive to the percolation network of the nanocomposite matrix, regardless of whether SWCNT or MWCNTs have been used." Needs to be explained more accurate and details. How do you quantify sensitivity in these experiments?

Page 57. "Variance in detected values can be seen, but it is relatively insignificant and is attributed to batch to batch processing variance". Variance of batches? Which batches? Batches of MW(SW)CNT? Please, explain accurately.

"They provide a more accurate value of resistance since contact resistance is not present, are more sensitive to percolation networks consisting of both SWCNTs and MWCNTs, can detect variances of CNT concentration in nanocomposites and thus can be used for CNT filtration detection." You do not show a piece of facts proving "are more sensitive to percolation networks" !!! Please, make you arguments more accurate or show the proofs! Otherwise it is wishful arguments!

Page 58. "The CNTF-based electrodes show a consistent reading of electrical values whether the 2 or 4-point measurement scheme is utilized. This is extremely important as it reduces the amount of electrical connections and electrodes needed to monitor a material by exactly half, giving the benefits of ease of installation, reliability and reduced areas of inhomogeneity where embedded electrodes may cause mechanical property loss. The consistency of electrical readings allows the CNTF-based electrodes to be used in either 2-point or 4-point measurement schemes without the loss of sensitivity or performance." – this is a good piece of work and writing!!! I like it. That is proven.

Page 60. Again "a batch to batch variance"! What is the batch here?

Page 61. "CNTF electrodes show no significant difference for any of the batches." May I ask where these "any of the batches" are presented and described in the text of thesis?

Page 66. SWCNTs do actually reduce elastic mechanical performance, not MWCNTs! Please, correct your argument "For all nanocomposite samples, it was seen that the addition of CNTs results in a loss in mechanical properties."

Page 73. "Further to note is that the samples which contained embedded metallic electrodes would

fail at the site of the electrode placement, which was not the case for samples containing CNTFs or samples with standard silver contacts and that they failed at a lower number of cycles as compared to their counterparts." Not clear from this which electrodes cause sooner failure. Please, clear out. "by only 1 magnitude" -> 1 order of magnitude

Page 75 "can provide information regarding material health" – no proofs. None of electrode has reliably shown early signs of fatigue.

Page 79. "e. As seen in Figure 30, the embedded metallic electrodes display poor adhesion to both the MWCNT and SWCNT" -> Figure 31.

And now few more generals issues to be addressed:

1) Please, consider to discuss more practical applications – which products and how will be tested or monitored? How to develop a protocol for CNTFs' embedding? Do you expect any local peculiarities in readings if hole, or notch, or macrocrack will occur close to a CNTF electrode?
2) Do you expect some special effects if tension (quasistatic) will be compared with compression, shear, torsion, or complex loading? Please, discuss this in appropriate place.
3) Do you expect any additional benefits if DC current measurements will be replaced with AC current measurements at a range of frequencies? Which effects may appear in AC tests?