Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Aleksandr Vedernikov

PhD Program: Mathematics and mechanics

Title of Thesis: Effects of technological regimes on structural performance of pultruded profiles

Supervisor: Assistant Professor Alexander Safonov

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

Dear Jury Members,

I would like to express my gratitude to all of you for valuable comments and suggestions aimed at Ph.D. thesis improvement. Your experienced opinion contributed to the enhancement of submitted thesis. Point-to-point responses to the reports of the Jury Members are presented below. All the raised issues were carefully addressed in the updated version of Ph.D. thesis.

Sincerely yours,
Aleksandr Vedernikov

Professor Costanzo Bellini

Comment 1: *The English language is good and the usage of the technical terms is correct, but there are some typos and other minor errors to be emended. In particular, pay attention to the use of verb tenses.*

Reply 1: Thank you for recommendation. Text of Ph.D. thesis went through additional proofreading.

Comment 2: *Subsection 1.3.1 outlines what has not been investigated in the previous research activities, but it is recommended that a summary of the pulling speed/composite quality trends that have been observed be added at the end of this subsection, perhaps even in tabular form, so that the reader can quickly get a picture of the situation.*

Reply 2: Thank you for your comment. Done.

Changes made: Thus, the trends in pulling speed / composite quality studies observed by pultrusion researchers can be summarized as follows:

- Experimental studies of pultrusion at various pulling speeds in the range of 12.5 to 4000 mm/min, conducted with profiles of various cross sections: L-shape and I-shape beams, rods, flat laminates, etc.;
- Experimental studies on the influence of pulling speed on mechanical properties, morphology, and formation of internal defects in pultruded composites;
- Development of numerical models of heat transfer, resin curing, pulling force and pultrusion process, and their successful validation by numerous pultrusion experiments at different pulling speeds; development and experimental validation of models describing occurrence of process-induced defects in relation to selected technological parameters of pultrusion process;
- Experimental demonstration that reduced pulling speeds improve mechanical properties of pultruded composites; in addition, it has been shown that improvement in the mechanical properties can also be achieved by the post-cure treatment;
- Experimental demonstration that the maximum number and quality of profiles are obtained at pulling speeds corresponding to the highest pulling force;
- Demonstration that increase in the pulling speed leads to an increase in the corresponding centerline temperature of the composite, registered at the die exit;
- Demonstration, that degree of polymerization, measured at the die exit for the composites manufactured at low pulling speeds, is higher than that of profiles manufactured at high pulling speeds. However, the polymerization of composites, happening at the post-die region, is significantly higher for profiles manufactured at the high pulling speeds, as compared to those manufactured at lower pulling speeds;
- Experimental demonstration of feasibility of microwave-assisted pultrusion at different pulling speeds, and of the UV-cured out-of-die bent pultrusion process.

Comment 3: *At the end of page 25, it is recommended to better explain the reasons for considering convective heat exchange also within the die, i.e. where there is contact between two solids, instead of thermal contact.*

Reply 3: Thank you for this observation. Additional explanation was inserted.

Changes made: The stage inside the die block was modelled with account for convective heat exchange instead of the thermal contact, in accordance with the state-of-the-art approach to modelling of pultrusion heat transfer problem, described by Batch (55). For this purpose, a sufficiently high value of the coefficient of convective heat transfer between the die block and the profile (h_{die}), constituting 5000 $W/(m^2 \cdot K)$, was assumed.

Doctor Wahid Ferdous

Comment 1: *All the results and relationships are explained based on the observation of bubbles and voids in the laminates. It is important for the author to explain how other researchers will use the results of this study since their laminates might not contain bubbles and voids as this one does.*

Reply 1: Thank you for your comment. This information was added to Section 12.2 “Practical implementation”

Changes made: In this study the influence of pultrusion process conditions on structural performance of pultruded composites was investigated. Various combinations of technological regimes have been investigated, with resulting profiles meeting or failing the requirements of international standards for pultruded composites. In the future, researchers and practitioners aiming to increase the profitability of pultrusion process while preserving the performance of produced profiles may use the pipeline, relationships and findings presented in this Ph.D. thesis to select the optimum technological regimes.

Comment 2: *According to the author, high pulling speeds can increase pultrusion output by at least 1.7 times without compromising the mechanical performance of produced profiles as compared to profiles produced at regular speeds. What is the maximum pulling speed that needs to be mentioned clearly?*

Reply 2: Thank you for your query.

Indeed, high pulling speeds can increase pultrusion output by at least 1.7 times without compromising the mechanical performance of produced profiles as compared to profiles produced at regular speeds. This conclusion was made based on the results of mechanical tests (see Table 3.2), demonstrating that an increase in the pulling speed from the regular pulling speed (600 mm/min) to high pulling speed (1000 mm/min) still allows to produce pultruded composite profiles suitable for structural applications and meeting the requirements of international standards in terms of mechanical performance [1] and geometric deviations [2]. Thus, the value 1.7 was obtained by dividing 1000 mm/min by 600 mm/min. On the other hand, it has been shown that pulling speed of 1400 mm/min leads to a significant decrease in the mechanical properties of the produced profiles and the formation of severe internal defects, violating [1] and [2], respectively. Therefore, in this particular pultrusion experiment the maximum pulling speed is 1000 mm/min.

It is clear that for each individual pultrusion experiment the optimum technological regimes will depend on the multitude of various factors, such as profile geometry, raw materials, their proportions and contents, fiber impregnation and resin infiltration techniques, pulling force and pulling speed, and temperature and heating conditions. Thus, no study can state the single universal value for each parameter of pultrusion process (such as the optimum heating temperature, the maximum pulling speed, etc.). That is, for each experimental set-up these parameters will be individual. However, this study shows the approach to selection of technological regimes, and highlights the points deserving attention, in order to increase the profitability of the process and prevent formation of bubbles, voids, and shape distortions impairing the structural performance of pultruded profiles. In other words, this work assists in solution of technological challenges of pultrusion process, described in Chapter 1, further promoting the application of structural pultruded profiles both in construction sector, demonstrating the largest demand for pultruded profiles, and in other engineering sectors. Practical implementation of the technological regimes selection pipeline studied here will, in the first place, reduce expenses for costly trial-and-error approach used in selection of pultrusion technological regimes; second, it will improve the dimensional precision of produced profiles; and third, it will allow the use of higher pulling speeds and, in turn, to increase the profitability of pultrusion production while maintaining mechanical performance of manufactured composite profiles, required by international standards.

[1] EN 13706-2:2003 Reinforced plastic composites - Specifications for pultruded profiles - Part 3: Specific requirements
[2] EN 13706-2:2003 Reinforced plastic composites - Specifications for pultruded profiles - Part 2: Methods of test and general requirements

Changes made: It is clear that for each individual pultrusion experiment the optimum technological regimes will depend on the multitude of various factors, such as profile geometry, raw materials, their proportions and contents, fiber impregnation and resin infiltration techniques, pulling force and pulling speed, and temperature and heating conditions. Thus, no study can state the single universal value for each parameter of pultrusion process (such as the optimum heating temperature, the maximum pulling speed, etc.). That is, for each experimental set-up these parameters will be individual. However, this study shows the approach to selection of technological regimes, and highlights the points deserving attention, in order to increase the profitability of the process and prevent formation of bubbles, voids, and shape distortions impairing the structural performance of pultruded profiles. In other words, this work assists in solution of technological challenges of pultrusion process, described in Chapter 1, further promoting the application of structural pultruded profiles both in construction sector, demonstrating the largest demand for pultruded profiles, and in other engineering sectors. Practical implementation of the technological regimes selection pipeline studied here will, in the first place, reduce expenses for costly trial-and-error approach used in selection of pultrusion technological regimes; second, it will improve the dimensional precision of produced profiles; and third, it will allow the use of higher pulling speeds and, in turn, to increase the profitability of pultrusion production while maintaining mechanical performance of manufactured composite profiles, required by international standards.

Comment 3: *It is also necessary for the author to explain the negative effects of pulling speed on the samples' quality. How does the higher pulling speed affect the curing of pultruded composites? What is the effect of pulling speed on composite brittleness?*

Reply 3: Thank you for your comment.

Negative effects of pulling speed on pultruded samples' quality (i.e. occurrence of voids, bubbles, delaminations, and spring-in distortions) were studied and discussed in the course of this Ph.D. project both experimentally and numerically in the Chapters 6, 7 and 9.

Numerical results presented in the Chapter 10 demonstrate slower curing at higher pulling speeds (see Fig. 8). Findings of the Chapter 6 experimentally proves that increase in the pulling speed leads to slower curing of composite (see Fig. 3b).
The influence of pulling speed on the compressive, tensile, flexural, interlaminar and in-plane shear properties of pultruded composites was studied in the Chapter 6, while the effects of high pulling speeds on the flexural and interlaminar shear performance of pultruded composites were investigated in the Chapter 7. However, the relationships between pulling speed and other mechanical properties of pultruded composites are yet to be established. In particular, the influence of pulling speed on the brittleness, fatigue, durability, and creep of pultruded profiles requires deeper analysis. It has been additionally outlined in Chapter 12.3

Changes made: The influence of pulling speed on the compressive, tensile, flexural, interlaminar and in-plane shear properties of pultruded composites was studied in the Chapter 6, while the effects of high pulling speeds on the flexural and interlaminar shear performance of pultruded composites were investigated in the Chapter 7. However, the relationships between pulling speed and other mechanical properties of pultruded composites are yet to be established. In particular, the influence of pulling speed on the brittleness, fatigue, durability, and creep of pultruded profiles requires deeper analysis.

Comment 4: *In section 1.3.1, the information should be presented as a story rather than as a number of small paragraphs. There is currently a lack of coherence among the paragraphs.*

Reply 4: Thank you for your valuable suggestion. Presentation style was modified to provide more coherence among the paragraphs. Please, see the manuscript.

Comment 5: *Research gaps and novelty of this study should be clearly identified.*

Reply 5: Thank you for this recommendation.

Section 1.4 "Novelty and scientific contribution" was introduced, where the novelty and scientific contribution of this Ph.D. thesis is highlighted.

Research gaps of previous studies were initially mentioned at the end of the following Sections:
- "1.3.1 Studies investigating the effects of pulling speed"
- "1.3.2 Studies investigating the effects of additives"
- "1.3.3 Studies investigating shape distortions"

Changes made: This Ph.D. project contributes to the pultrusion state-of-the-art and makes another step toward tackling the challenges listed in Section 1.1, by filling the research gaps mentioned in Section 1.3. More specifically, the novelty and scientific contribution of this Ph.D. thesis can be represented as a bulleted list as follows:

- This project is the first attempt to analyze mechanical properties, spring-in, matrix cracking and delaminations as functions of the pulling speed, using a holistic approach. A relationship between these properties and the pulling speed used has been established;
- This work is the first one to demonstrate that high speed pultrusion of large cross-section composite structural profiles is not only feasible, but it also makes it possible to increase production rate by tens of percent at only a slight sacrifice in mechanical performance of pultruded composite structural profiles, as compared to their counterparts produced at regular pulling speeds;
- This study became the first one to develop a numerical model of pultrusion process in the ABAQUS software suite with the use of user subroutine mechanism, making it possible to model the process of spring-in formation in pultruded composite structural profiles produced at different pulling speeds. The model was successfully validated in the course of two experiments conducted at the interval of 6 months, studying pultruded profiles produced at three different pulling speeds. Besides, this work is the first one to study the contributions of chemical and thermal shrinkage leading to spring-in distortions occurred in the pultrusion process. Also, a relationship between these contributions and selected pulling speed was established. Based on contributions of chemical and thermal shrinkage, methods of increasing the process output while preserving the given spring-in value through the use of the post-die cooling tool, or through the use of additives reducing chemical shrinkage of polymer matrix were proposed and analyzed;
- This work is the first one to study time-dependent behavior of process-induced shape distortions, such as spring-in and warpage pultruded L-shaped composite structural

profiles. Besides, it is the first one to study experimentally the influence of pulling speed on the shape distortions increment in time;

- This study is also the first one to study the influence of additives — aluminum hydroxide ($Al(OH)_3$) flame retardant, and zinc stearate ($Zn(C_{18}H_{35}O_2)_2$) internal release agent reducing the pulling force — on polymerization kinetics of vinyl-ester pultrusion resins and, in turn, on the choice of pulling speeds;
- Besides, this study is the first one to demonstrate the possibility of producing pultruded composite laminates exhibiting shape memory properties, showing a considerable promise for future structural applications.

Comment 6: *The scientific contributions should be presented briefly in a separate section in the conclusion. Currently, this is explained in a descriptive manner.*

Reply 6: Thank you for your valuable recommendation. Section 1.4 "Novelty and scientific contribution" was introduced, where the novelty and scientific contribution of this Ph.D. thesis is highlighted. Please, see the response to the Comment 5.

Comment 7: *A separate section should be devoted to describing how this study will benefit society (practical implementation).*

Reply 7: Thank you for this useful suggestion. This information was added to Section 12.2 "Practical implementation".

Changes made: In this study the influence of pultrusion process conditions on structural performance of pultruded composites was investigated. Various combinations of technological regimes have been investigated, with resulting profiles meeting or failing the requirements of international standards for pultruded composites. In the future, researchers and practitioners aiming to increase the profitability of pultrusion process while preserving the performance of produced profiles may use the pipeline, relationships and findings presented in this Ph.D. thesis to select the optimum technological regimes. It is clear that for each individual pultrusion experiment the optimum technological regimes will depend on the multitude of various factors, such as profile geometry, raw materials, their proportions and contents, fiber impregnation and resin infiltration techniques, pulling force and pulling speed, and temperature and heating conditions. Thus, no study can state the single universal value for each parameter of pultrusion process (such as the optimum heating temperature, the maximum pulling speed, etc.). That is, for each experimental set-up these parameters will be individual. However, this study shows the approach to selection of technological regimes, and highlights the points deserving attention, in order to increase the profitability of the process and prevent formation of bubbles, voids, and shape distortions impairing the structural performance of pultruded profiles. In other words, this work assists in solution of technological challenges of pultrusion process, described in Chapter 1, further promoting the application of structural pultruded profiles both in construction sector, demonstrating the largest demand for pultruded profiles, and in other engineering sectors. Practical implementation of the technological regimes selection pipeline studied here will, in the first place, reduce expenses for costly trial-and-error approach used in selection of pultrusion technological regimes; second, it will improve the dimensional precision of produced profiles; and third, it will allow the use of higher pulling speeds and, in turn, to increase the profitability of pultrusion production while maintaining mechanical performance of manufactured composite profiles, required by international standards.

Comment 8: *Journal articles and conference papers should be listed separately on Page 6, as they are not equally weighted. Procedia Manufacturing, IOP Conference Series, are these journals? It is also important to clearly differentiate between the one that has been published and the one that is currently under review. Some of the articles maintain high standards while others are published in journals outside the top quartile. It is important to focus on quality rather than quantity.*

Reply 8: Thank you for pointing out this observation. Done.

Comment 9: *Overall, this is a good piece of work that identifies some key challenges in producing pultruded composites more efficiently.*

Reply 9: Thank you for high evaluation of the thesis and time spent for careful reading.

Professor Clement Fortin

Comment 1: *The thesis submitted by Aleksandr Vedernikov is of very high quality and logically structured in 12 chapters comprising 8 chapter based on research papers that are well integrated into the overall document. The experimental and simulation methods presented in the thesis are also of high quality. The author has published 14 papers related to his work. They are published in high level journals and conferences all relevant to the research work. The subject of the research work is directly related to practical engineering applications which could be of great value to civil engineering practice. The level of English in the thesis is also excellent, it is clear and easy to comprehend.*

I have no specific corrections required before the defense.

Reply 1: Thank you for high evaluation of my Ph.D. thesis and effort spent.

Professor Ugur Koklu

Comment 1: *A high-quality doctoral dissertation has been done. In his thesis, he investigated the possibility of increasing the profitability of the pultrusion process while maintaining the structural performance of the produced composite profiles. The main content of the thesis topic is up-to-date, and the methods used in the thesis are new. In addition, scientific results in accordance with the international level and up-to-date technology have been obtained. It was stated that 11 publications were made within the scope of the thesis study. Published journals are generally good. But some journals are really high quality. Congratulations to the Ph.D. candidate and Supervisor for the high-quality thesis work.*

Reply 1: Thank you for high appreciation of my Ph.D. dissertation as well as your time spent for reading it.

Professor Ivan Sergeichev

Comment 1: *This is a suggestion rather than a strict recommendation. It would be nice to include an "Acknowledgment" section in the Ph.D. thesis, thereby appreciating the contribution of Alexander's scientific peers, colleagues, and professors related to the development of the Ph.D. project.*

Reply 1: Thank you for your suggestion. Acknowledgment was added to the text of the Ph.D. thesis.

Comment 2: *Although the novelty of the thesis is obvious, I would recommend developing a section where these main points might be clearly stated.*

Reply 2: Thank you for this comment. Additional Section 1.4 "Novelty and scientific contribution" was introduced.

Changes made: This Ph.D. project contributes to the pultrusion state-of-the-art and makes another step toward tackling the challenges listed in Section 1.1, by filling the research gaps mentioned in Section 1.3. More specifically, the novelty and scientific contribution of this Ph.D. thesis can be represented as a bulleted list as follows:

- This project is the first attempt to analyze mechanical properties, spring-in, matrix cracking and delaminations as functions of the pulling speed, using a holistic approach. A relationship between these properties and the pulling speed used has been established;
- This work is the first one to demonstrate that high speed pultrusion of large cross-section composite structural profiles is not only feasible, but it also makes it possible to increase production rate by tens of percent at only a slight sacrifice in mechanical performance of pultruded composite structural profiles, as compared to their counterparts produced at regular pulling speeds;
- This study became the first one to develop a numerical model of pultrusion process in the ABAQUS software suite with the use of user subroutine mechanism, making it possible to model the process of spring-in formation in pultruded composite structural profiles produced at different pulling speeds. The model was successfully validated in the course of two experiments conducted at the interval of 6 months, studying pultruded profiles produced at three different pulling speeds. Besides, this work is the first one to study the contributions of chemical and thermal shrinkage leading to spring-in distortions occurred in the pultrusion process. Also, a relationship between these contributions and selected pulling speed was established. Based on contributions of chemical and thermal shrinkage, methods of increasing the process output while preserving the given spring-in value through the use of the post-die cooling tool, or through the use of additives reducing chemical shrinkage of polymer matrix were proposed and analyzed;
- This work is the first one to study time-dependent behavior of process-induced shape distortions, such as spring-in and warpage pultruded L-shaped composite structural profiles. Besides, it is the first one to study experimentally the influence of pulling speed on the shape distortions increment in time;
- This study is also the first one to study the influence of additives — aluminum hydroxide ($Al(OH)_3$) flame retardant, and zinc stearate ($Zn(C_{18}H_{35}O_2)_2$) internal release agent reducing the pulling force — on polymerization kinetics of vinyl-ester pultrusion resins and, in turn, on the choice of pulling speeds;

- Besides, this study is the first one to demonstrate the possibility of producing pultruded composite laminates exhibiting shape memory properties, showing a considerable promise for future structural applications.

Comment 3: *Generally speaking, this thesis is well-written, however additional proofreading would improve the quality of English and eliminate minor typos and grammatical errors.*

Reply 3: Thank you for the advice. Text of Ph.D. thesis went through additional proofreading.

Comment 4: *Overall, I believe, that Alexander made a significant contribution to the composite materials domain. The results of his Ph.D. project are novel, top quality, and scientifically sound, thus, fulfilling all the formal requirements of the Ph.D. project. I wish Alexander all the best in his future scientific endeavors. Having said that, I would like to recommend proceeding to a formal thesis defense.*

Reply 4: Thank you for these kind words and high appreciation of my Ph.D. thesis.

Professor Igor Shishkovsky

Comment 1: *I would like to hear the author's comments on the scalability of the numerical models he built. Is there enough studies to build large structures from pultruded profiles (bridges, buildings, etc.)*

Reply 1: Thank you for your query. Indeed, pultruded profiles are applied in the engineering practice and utilized in various large structures such as bridges and bridge decks, cooling towers, building elements and complete building systems, marine construction, transportation, and energy systems [1]. Application of numerical modelling tool for the simulation of pultrusion manufacturing process, involving production of large structural profiles, is being widely used by scholars and practitioners [2-4]. In this Ph.D. project existing models were extended further to account for effects that haven't been considered and studied previously.

[1] Vedernikov A, Safonov A, Tucci F, Carlone P, Akhatov I. Pultruded materials and structures: A review. J Compos Mater 2020;54:4081–117. https://doi.org/10.1177/0021998320922894.
[2] Safonov AA, Carlone P, Akhatov I. Mathematical simulation of pultrusion processes: A review. Compos Struct 2018;184:153–77. https://doi.org/10.1016/j. compstruct.2017.09.093.
[3] Baran I, Cinar K, Ersoy N, Akkerman R, Hattel JH. A review on the mechanical modeling of composite manufacturing processes. Arch Comput Methods Eng 2017;24:365–95.
[4] Baran I. Modelling the Pultrusion Process of Off Shore Wind Turbine Blades, Department of Mechanical Engineering, Technical University of Denmark, Ph.D. Thesis, 2014.

Comment 2: *The author practically did not study the influence of the environment on the behavior of its materials - humidity, high or low pressure, excess or lack of nitrogen, carbon dioxide, aggressive media (acids, alkalis, arctic conditions), etc.*

Reply 2: Thank you for valuable remark. Indeed, mentioned topics were not investigated in the course of this Ph.D. project. However, the necessity to study these problems was additionally highlighted in Section 12.3.

Changes made: Although the influence of environment on structural behavior of pultruded profiles is actively studied today, the future trends will require investigation of relationships between technological regimes of pultrusion and the ability of produced profiles to resist environmental effects, such as increased humidity, high or low pressure, thermal exposure, excess or lack of nitrogen, carbon dioxide, harsh environments such as acids, alkalis, sea water, arctic conditions, hygrothermal and freeze-thaw environments, etc.

Comment 3: *Therefore, the thesis by Aleksandr Vedernikov is a comprehensive and self-contained study, which should be deserving the PhD degree. No issues to be addressed further.*

Reply 3: Thank you for the positive evaluation of my Ph.D. thesis and effort spent.