Jaymin Vrajlal Sanchaniya is a research assistant at Riga Technical University. He has obtained his Bachelor’s degree in Mechanical Engineering from Gujarat Technical University, India (2015), and a Master’s degree in Mechanics and Mechanical Engineering from Riga Technical University, Latvia (2020). Since 2020, he has been working as a research assistant at Riga Technical University. His research interests revolve around the fabrication, characterization, finite element modeling, and mechanics of nanofibers and nanofiber mats. His dedication to the field is reflected in his impressive publication record, with more than 20 journal and conference articles indexed in the SCOPUS database, spanning areas such as fabricating and characterizing nanofiber mats for the fields of environment and smart materials.
RIGA TECHNICAL UNIVERSITY
Faculty of Civil and Mechanical Engineering

Jaymin Vrajlal Sanchaniya
Doctoral Student of the Study Programme
“Mechanical Engineering and Mechanics (Applied Mechanics)”

A STUDY ON FABRICATION TECHNIQUE, PROPERTIES, AND APPLICATIONS OF PAN NANOFIBERS
Summary of the Thesis

Scientific supervisors:
Associate Professor
Dr. sc. ing. Inga Ļašenko

Professor Dr. sc. ing.
Andrejs Krasņikovs

RTU Press
Riga 2024

Published in accordance with the decision of the Promotion Council “RTU P-04” of 5 June 2024, Minutes No. 04030-9.4.1/3.

The Doctoral Thesis was developed with the financial support of the DAD grant, Riga Technical University's Doctoral Grant programme and the European Social Fund within project No. 8.2.2.0/20/I/008.

Cover picture by Jaymin Vrajlal Sanchaniya.

https://doi.org/10.7250/9789934370854
DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF SCIENCE

To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for defence at the open meeting of the RTU Promotion Council on 18 July 2024, at 14:30 at the Faculty of Civil and Mechanical Engineering of Riga Technical University, Ķīpsalas 6B, Room 420.

OFFICIAL REVIEWERS

Senior Researcher Ph. D. Mārtiņš Irbe
Riga Technical University

Professor Dr. Virginija Daukantiene
Kaunas University of Technology, Lithuania

Professor Ph. D. Yuris Dzenis
University of Nebraska-Lincoln, United States

DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for review to Riga Technical University for promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Doctoral Thesis has not been submitted to any other university for promotion to a scientific degree.

Jaymin Vrajlal Sanchaniya
Date: 02.03.2024

The Doctoral Thesis has been written in English. It consists of an Introduction, 7 chapters, Conclusions, 60 figures, and 8 tables; the total number of pages is 150, including appendices. The Bibliography contains 159 titles.
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**Topicality**

The Thesis embodies a crucial advancement in the domain of nanotechnology, particularly focusing on the exploration and utilization of polyacrylonitrile (PAN) nanofibers. It meticulously investigates the fabrication processes and the mechanical and thermal properties of PAN nanofibers, unveiling their extensive potential across a myriad of applications. This scholarly work not only fills pivotal knowledge voids within the realm of nanofiber technology but also sets a new precedent for future research, emphasizing the innovative capabilities of PAN nanofibers in revolutionizing both materials science and engineering sectors.

At its core, the Thesis presents a comprehensive analysis that bridges significant gaps in current knowledge, propelled by an exhaustive review of literature coupled with a series of rigorous experimental investigations. By delving deep into the fabrication techniques, notably electrospinning, and elucidating the impact of various methodologies on the properties and applications of PAN nanofibers, this study illuminates pathways for optimizing their performance and utility. The exploration of PAN nanofibers in the Thesis not only heralds a breakthrough in enhancing their applicability in filtration, biomedicine, and structural materials but also highlights the Thesis's role as a beacon for future explorations in nanofiber technology, offering a rich foundation for the development of advanced materials and applications.

**Objective of the Thesis**

The objective of the Thesis is to comprehensively analyse and advance the understanding of polyacrylonitrile (PAN) nanofibers by examining their fabrication methods and the effect of both conventional and non-conventional, alongside exploring their mechanical and thermal properties and the wide array of potential applications. The Thesis aims to bridge critical knowledge gaps by employing a detailed literature review, rigorous experimental investigations, and the development of a finite element (FE) model to simulate the mechanical behaviour of PAN nanofibers accurately. By focusing on optimizing the electrospinning process and experimenting with novel fabrication techniques, the research seeks to enhance the performance and applicability of PAN nanofibers in diverse sectors, including filtration, biomedicine, and structural components. The inclusion of non-conventional methods and the formulation of an FE model underscore the Thesis’s commitment to pioneering nanofiber technology, setting a foundation for future innovations and applications in the field.
Research Tasks

The Thesis delineates a series of research tasks designed to explore the multifaceted aspects of polyacrylonitrile (PAN) nanofibers. These tasks are structured to methodically address the fabrication techniques, properties, and potential applications of PAN nanofibers. The outlined research tasks include:

1. **Literature review**: Perform a comprehensive review of existing literature to identify the current state of knowledge, research gaps, and recent advancements in the field of PAN nanofibers.

2. **Fabrication techniques**: Investigate various fabrication methods for PAN nanofibers, with a focus on electrospinning. This includes experimenting with both conventional and novel, non-conventional fabrication techniques to enhance the quality and functionality of the nanofibers.

3. **Develop and validate a finite element (FE) model**: Formulate an FE model to accurately predict the mechanical behaviour of PAN nanofibers. This task involves calibrating and validating the model against experimental data to ensure its reliability and applicability in simulating real-world scenarios.

4. **Experimentally analyse mechanical and thermal properties**: Conduct experimental studies to assess the mechanical and thermal properties of PAN nanofibers. This includes evaluating the effects of fabrication parameters on these properties to identify optimal manufacturing conditions.

5. **Assess the impact of annealing and non-conventional methods**: Examine the effects of annealing and apply non-conventional methods to modify the structural and functional characteristics of PAN nanofibers. This task aims to explore avenues for enhancing the fibers’ performance through post-processing treatments.

6. **Explore the integration of PAN nanofibers into non-crimping laminated textiles**: Delve into the innovative application of incorporating PAN nanofibers into non-crimping laminated textiles, aiming to enhance the structural integrity and functional properties of textile materials. This task focuses on the fabrication process, evaluating the mechanical enhancements, and identifying potential industrial and commercial applications. Through this exploration, the research seeks to open new avenues for advanced composite materials, leveraging the unique properties of PAN nanofibers to offer improved performance and functionality in textile engineering and beyond.
These research tasks collectively aim to advance the field of PAN nanofiber technology by deepening the understanding of their fabrication techniques, properties, and applications, paving the way for innovative uses and the development of next-generation nanofiber-based materials.

**The Subject Matter and the Scope of the Study**

The subject matter of the Doctoral Thesis centres on the exhaustive exploration of polyacrylonitrile (PAN) nanofibers, focusing on their fabrication processes, mechanical and thermal properties, and the wide array of applications these materials can serve. PAN nanofibers, known for their remarkable mechanical strength and thermal stability, stand at the forefront of materials science, offering promising innovations across various fields such as filtration, biomedical devices, structural materials, and more. This study aims to deepen the understanding of PAN nanofibers, from their production to potential industrial uses, bridging significant gaps in current research and contributing to the advancement of nanotechnology and materials science.

The scope of the study is extensive, covering several critical dimensions of PAN nanofibers. Initially, the research delves into state-of-the-art fabrication techniques with an emphasis on electrospinning, a popular method for producing nanofibers due to its simplicity and efficiency. By investigating both conventional and innovative non-conventional electrospinning methods, the study seeks to optimize the fabrication process to enhance the quality and functionality of the nanofibers. Furthermore, the Thesis proposes the development and validation of a finite element (FE) model to predict the mechanical behaviour of PAN nanofibers accurately, providing a robust tool for researchers and engineers.

In addition to fabrication and modelling, the study extensively analyses the mechanical and thermal properties of PAN nanofibers, assessing how different fabrication parameters and post-processing treatments like annealing affect these characteristics. This comprehensive evaluation not only contributes to a deeper understanding of PAN nanofibers but also identifies pathways to tailor these materials for specific applications.

One of the pioneering areas of application explored in this research is the integration of PAN nanofibers into non-crimping laminated textiles. This novel approach aims to revolutionize the textile industry by enhancing the structural integrity and functional properties
of textiles, opening up new possibilities for using nanofiber technology to create advanced composite materials.

**Scientific Novelty of the Thesis**

The scientific novelty of the Thesis is encapsulated in its critical advancements and pioneering methodologies in the study and application of polyacrylonitrile (PAN) nanofibers. The Thesis brings forth unique contributions that extend the frontiers of nanofiber technology, particularly through the exploration of both conventional and non-conventional post-processing techniques to modify and enhance the properties of PAN nanofibers.

A significant novelty of this research is the systematic study of the annealing process as a conventional method to improve the mechanical and thermal properties of PAN nanofibers. By meticulously analysing the effects of annealing PAN nanofibers at various temperatures, the Thesis elucidates the correlation between annealing conditions and the resultant changes in nanofiber properties. This deep dive into thermal treatment provides invaluable insights into optimizing PAN nanofiber characteristics for enhanced performance in applications requiring specific mechanical strength and thermal stability.

Furthermore, the Thesis introduces a novel, non-conventional method involving the dip-coating of PAN nanofibers with a polyvinyl alcohol (PVA) solution. This innovative approach not only differentiates the study but also showcases a creative method to significantly augment the structural integrity and functional properties of PAN nanofibers. By investigating the outcomes of PVA dip-coating on nanofibers, the research reveals enhanced mechanical properties and introduces new functionalities to the PAN nanofibers, opening up avenues for multifaceted applications.

The development and validation of a finite element (FE) model further underscore the Thesis's scientific novelty. This model offers a predictive framework for the mechanical behaviour of PAN nanofibers with random and oriented structure, post-treatment integrating empirical data from PVA dip-coating experiments. This predictive capability is groundbreaking, providing a tool for tailoring nanofiber properties to specific application needs without extensive empirical testing.

Collectively, these novel contributions – ranging from the detailed exploration of annealing effects and the introduction of PVA dip-coating as a non-conventional method to the development of a predictive FE model – signify the Thesis's impact on advancing PAN
nanofiber technology. These innovations not only provide a deeper understanding of nanofiber property manipulation but also pave the way for new applications and improvements in materials science and nanotechnology.

**Practical Value of the Thesis**

The practical value of the Thesis is multifaceted, extending its impact beyond academic research into tangible applications that address contemporary challenges in materials science and engineering. By exploring the intricacies of PAN nanofibers, including their fabrication, modification, and application, the Thesis contributes significantly to advancing technologies and solutions across various sectors.

Firstly, the optimized fabrication processes for PAN nanofibers, including the refined annealing technique and the innovative non-conventional method of dip-coating with PVA, offer industry practitioners new methodologies to produce nanofibers with enhanced properties. These processes allow for the tailoring of mechanical and thermal properties of PAN nanofibers, making them suitable for a wider range of applications, from filtration and protective textiles to components in biomedical devices, thus meeting the increasing demand for high-performance materials.

The practical application of the finite element (FE) model developed in the Thesis provides a powerful tool for predicting the behaviour of PAN nanofibers under various conditions. This model aids in the design and development of nanofiber-based products, significantly reducing the time and resources spent on empirical testing. Manufacturers can leverage this model to simulate different production scenarios and post-processing treatments, optimizing product designs for specific applications with improved efficiency and cost-effectiveness.

Moreover, the application of PAN nanofibers in non-crimping laminated textiles represents an advancement with significant practical implications. By enhancing the mechanical strength and introducing new functionalities to textiles, this application opens up new possibilities in the creation of advanced composite materials. These materials could revolutionize aerospace, automotive, and construction sectors, where the demand for lightweight yet strong materials is continuously growing.

**Research Methods**
The Thesis employs a multidisciplinary approach to research, incorporating a variety of methods tailored to explore the fabrication, properties, and applications of PAN nanofibers in depth. The methods used in the Thesis are categorized as follows:

1. **Experimental methods.** Fundamental to the Thesis, experimental techniques form the backbone of the research. This category includes:

   - *Electrospinning Fabrication.* The process of producing PAN nanofibers through electrospinning, examining the effects of different parameters on fibre quality.
   - *Annealing.* A conventional thermal treatment method is used to modify the mechanical and thermal properties of PAN nanofibers by heating them at predetermined temperatures.
   - *Dip-Coating with PVA Solution.* A non-conventional approach to enhance the nanofibers' properties by coating them with a polyvinyl alcohol solution and analysing the resultant changes in structural and functional characteristics.
   - *Scanning electron microscopy (SEM).* SEM is utilized for the microstructural analysis of PAN nanofibers and provides detailed imagery to assess fibre morphology.
   - *Tensile testing.* This is conducted to measure the mechanical strength and elasticity of the nanofibers, providing data on their performance under stress.
   - *Thermal analysis.* These techniques, including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), are used to determine the thermal properties and degradation temperatures of the nanofibers.
   - *Porosity testing.* An important addition to the experimental regime, porosity testing evaluates the nanofiber mats' pore structure and distribution, a crucial factor for applications requiring specific filtration capabilities or tissue engineering scaffolds.

2. **Finite element modelling (FEM):** This method involves the development of a computational model to predict the mechanical behaviour of PAN nanofibers. FEM is crucial for:

   - Simulating physical behaviour: Offering insights into how nanofibers react under various loading conditions without the need for extensive physical testing.
   - Parameter sensitivity analysis: Understanding how different fabrication and treatment parameters affect the nanofibers' properties, aiding in optimization.
3. **Data analysis techniques.** This category is critical for interpreting the vast amounts of data generated from experimental and simulation methods. It encompasses:

- statistical analysis – employed to analyse the results from tensile tests, thermal analysis, and other experiments to identify significant patterns, trends, and correlations;
- model validation – using experimental data to validate the accuracy of the finite element model and ensuring its reliability for predictive purposes.

**Results Nominated for Defence**

1. *Fabrication of PAN nanofibers with random and oriented structures.* A pivotal outcome of the study is the successful fabrication of polyacrylonitrile (PAN) nanofibers featuring both random and oriented structures. This achievement is foundational to understanding the impact of fibre orientation on the mechanical and physical properties of the resultant nanofiber mats. By manipulating electrospinning parameters, the research delineates a clear methodology for controlling the structural orientation of nanofibers, enabling the production of mats tailored for specific applications.

2. *Impact of annealing on PAN nanofibers.* A comprehensive analysis reveals that annealing significantly improves the mechanical properties of PAN nanofibers, including tensile strength and elasticity. Additionally, the process affects thermal properties, such as thermal stability and degradation temperatures, optimizing the nanofibers for high-performance applications.

3. *Enhancement through dip-coating with PVA solution.* The introduction of a non-conventional dip-coating method with a PVA solution emerges as a novel approach to modifying PAN nanofibers. This treatment not only improves the nanofibers' mechanical properties but also introduces new functionalities, expanding their utility in various fields.

4. *Finite element model validation.* The development and validation of a finite element (FE) model for predicting the mechanical behaviour of PAN nanofibers represent a significant advancement. This model, validated against experimental data, serves as a powerful tool for simulating and optimizing nanofiber performance, reducing the need for extensive physical testing.
Thesis Approbation and Publications

The research conducted for this Doctoral Thesis has contributed significantly to the field of nanofiber technology, resulting in notable publications in both high-impact journals and prestigious conference proceedings. The dissemination of the findings has been structured as follows:

Q1 Journal Articles


Q3 Journal Article


Other Journal Articles and Conference Proceedings

The peripheral research findings have been presented in 14 additional scientific publications, encompassing a wide range of topics relevant to the development and application of nanofiber technologies. These contributions have been documented in peer-reviewed journals and conference proceedings, further showcasing the breadth and depth of the research undertaken.


**Note:** All listed publications have been indexed in reputable databases such as SCOPUS or Web of Science, ensuring their accessibility and visibility within the scientific community.
Chapter 1: Literature Review

Chapter 1 of the Thesis, embarks on a thorough exploration of the existing body of work related to polyacrylonitrile (PAN) nanofibers, positioning this research within the vast landscape of nanotechnology and materials science. The chapter initiates with a historical overview, tracing the evolution of PAN nanofibers from their inception to their prominence in current scientific inquiries. This historical context underscores the significance of PAN nanofibers as a pivotal subject within the materials science domain, showcasing their potential to revolutionize various industrial applications through their unique properties.

The review delves deeply into the myriad of fabrication techniques that have been developed and refined over the years, with a special focus on electrospinning. This segment critically assesses the merits and challenges associated with different fabrication methods, examining how they influence the morphology, alignment, and quality of the nanofibers. Furthermore, the chapter provides an exhaustive analysis of the mechanical, thermal, and chemical properties of PAN nanofibers, highlighting how these characteristics can be tailored through specific fabrication parameters, post-processing treatments, and the integration of various additives or dopants.

An exploration of the applications of PAN nanofibers reveals their remarkable versatility and broad potential, spanning areas such as filtration (Zhou et al., 2022), biomedical devices (Xue et al., 2019), structural materials (Bidhar et al., 2021; Papkov et al., 2013, 2019a, 2019b), energy storage (Al-abduljabbar & Farooq, 2023; Chhetri et al., 2022), and more. This section not only showcases the wide array of applications but also brings attention to key research contributions and case studies that demonstrate the impact of PAN nanofibers in solving real-world problems.

The literature review identifies critical research gaps and future directions, advocating for more focused studies on optimizing fabrication techniques, enhancing functional properties, and uncovering new application areas for PAN nanofibers. The discussion on theoretical frameworks and models, including the role of finite element modelling (FEM) in predicting nanofiber behaviour, sheds light on the theoretical underpinnings that support empirical findings and guide future research endeavours.

Chapter 1 sets a solid foundation for the Thesis by weaving together historical insights, critical analyses of fabrication methods and properties, and a forward-looking perspective on
research trends. It highlights the necessity of bridging identified knowledge gaps and lays down the theoretical and empirical groundwork for the novel research contributions that follow in subsequent chapters.

Chapter 2: Fabrication of PAN Nanofiber Mats

Chapter 2 delves into the detailed methodologies employed in producing polyacrylonitrile (PAN) nanofiber mats, with a special emphasis on electrospinning processes tailored to achieve both random and oriented structures. This chapter serves as a crucial link between the foundational understanding provided in the literature review and the experimental exploration that underpins the Thesis's novel contributions. The content of this chapter is also available for reference in a published format (Sanchaniya, 2024; Sanchaniya, Lasenko, Gobins, et al., 2024).

The chapter begins by establishing the significance of PAN as a preferred material for nanofiber fabrication due to its excellent mechanical properties, thermal stability, and chemical resistance. The discussion then transitions into a comprehensive examination of the electrospinning technique, highlighting its versatility as a fabrication method that allows for precise control over nanofiber morphology. The factors affecting the electrospinning process, including polymer concentration, solvent type, flow rate, voltage, and collector design, are analysed for their roles in determining the quality and properties of the resulting nanofiber mats. Figure 1 shows the SEM images of the produced oriented and random structure of the nanofiber mats using a rotating drum and flat plate collector.

![SEM images](image)

Fig. 1. SEM images of the nanofiber mats: (a) oriented nanofibers and (b) random nanofibers.
Tensile test results are shown in Fig. 2 to elucidate the response of oriented nanofiber structures to tensile forces. The oriented nanofiber specimens exhibited a longitudinal ultimate tensile strength (LUTS) of $(8.9 \pm 0.5)$ MPa along the fibre orientation, markedly superior to the transverse ultimate tensile strength (TUTS) observed in the perpendicular direction at $(1.1 \pm 0.1)$ MPa. This stark contrast in tensile strengths underlines the anisotropic mechanical nature of the oriented nanofiber mats, where fibre alignment significantly influences their tensile properties. In contrast, the UTS values of the randomly structured mats remained consistent across both axes, recording values of $(3.9 \pm 0.4)$ MPa and $(4.0 \pm 0.5)$ MPa, showcasing their isotropic mechanical behaviour.

Investigating stiffness through Young's modulus measurements, oriented nanofiber mats demonstrated significantly enhanced stiffness in the longitudinal direction, with a modulus of $(410 \pm 23)$ MPa, vastly outstripping the transverse measurement of $(53 \pm 5)$ MPa. This again highlights the anisotropic characteristics of these mats. Conversely, Young's modulus of randomly structured mats presented a uniform profile, with measurements of $(103 \pm 4)$ MPa and $(99 \pm 5)$ MPa, illustrating a more evenly distributed stiffness within the material.

Ductility, as evidenced by elongation at break, showed variance across the two structural orientations and directions. Oriented nanofibers attained elongation at break values of $0.19 \pm 0.02$ longitudinally and $0.2 \pm 0.03$ transversely. Meanwhile, randomly structured
fibres displayed enhanced ductility, with elongation at break reaching 0.35 ± 0.03 and 0.36 ± 0.04, respectively.

The TGA curve for virgin PAN, illustrated in Fig. 3, features a green line representing the percentage of mass loss across a temperature range, while the red line, the DTG curve, offers detailed insight into the rate of mass loss, facilitating precise determination of critical temperatures. The analysis of virgin PAN reveals remarkable thermal stability up to 289.5 °C, beyond which degradation begins, as indicated by the onset temperature of 291.6 °C. Between 25 °C and 299.8 °C, a mass loss of 14.15 % was observed, demonstrating the initiation of thermal degradation.

For the PAN nanofibers, depicted in Fig. 4, the TGA and DTG curves show an early mass reduction at 110.6 °C, attributed to the evaporation of N,N-dimethylformamide (DMF) used as the solvent in the electrospinning process, amounting to approximately 3.08 %. The mass loss from 25.0 °C to 158.7 °C registered at 3.08 %, and a subsequent reduction of 1.66 % was recorded from 158.7 °C to 297.6 °C. A notable mass loss of 14.26 % occurred between 264.2 °C and 297.6 °C, indicating a critical phase of degradation.

![Fig. 3. TGA and DTG of virgin PAN.](image)
This comprehensive TGA and DTG analysis sheds light on the thermal stability and degradation patterns of virgin PAN and its nanofibers. The results highlight the thermal transitions and degradation kinetics, which are crucial for understanding the material's performance under high-temperature conditions.

Differential scanning calorimetry (DSC) offers insightful data regarding the thermal transitions of materials by measuring the heat flow associated with material phase changes. In this study, the DSC analysis of virgin polyacrylonitrile (PAN) and PAN nanofibers during the thermal cycle provides a detailed examination of their thermal behaviour.

The initial heating phase, illustrated in Fig. 5, shows that virgin PAN exhibited a heat absorption of 30.06 J/g, while the PAN nanofibers demonstrated a slightly lower heat uptake of 26.88 J/g. This phase revealed two significant peaks in the heat absorption profile, likely corresponding to the solvent evaporation process.
Fig. 5. The first heating cycle of virgin PAN vs PAN nanofibers in DSC.

The subsequent heating cycle, captured in Fig. 6, further refined these observations. The Tg for virgin PAN was recorded at 101.8 °C, with the PAN nanofibers displaying a Tg around 96.0 °C, marking a reduction of approximately 5%. Moreover, the change in heat capacity (Delta $C_p^*$) between the two materials indicated a significant disparity; virgin PAN showed a Delta $C_p^*$ of 0.202 J/(g·K), whereas the PAN nanofibers registered a lower value of 0.116 J/(g·K), representing a 42% decrease.

Fig. 6. The second heating cycle of virgin PAN vs PAN nanofibers in DSC.

This chapter concludes with an in-depth understanding of the fabrication techniques for PAN nanofiber mats with different structures, including the strategic modifications applied to
optimize their mechanical performance, thermal resistance, and porosity. This detailed exploration of methodologies not only underpins the Thesis's contributions to the field of nanofiber technology but also highlights the broader implications for materials science and engineering, particularly in applications requiring precise control over nanofiber mat properties.

**Chapter 3: An FE Model for Determining the Mechanical Properties of Electrospun Nanofiber Mat**

Chapter 3 delves into the development and validation of a finite element (FE) model designed to predict and analyse the mechanical behaviour of electrospun PAN nanofiber mats. This chapter stands as a crucial component of the Thesis, bridging the gap between empirical experimentation and theoretical simulation, thereby offering a powerful tool for understanding the nuanced mechanical properties of PAN nanofiber mats without the need for exhaustive physical testing. The content of this chapter is also available for reference in a published format (Sanchaniya, Lasenko, Gobins, et al., 2024).

The chapter begins by underscoring the importance of accurately modelling the mechanical properties of PAN nanofiber mats, given their potential applications in various fields that demand materials with precise mechanical characteristics. The FE model's development is grounded in the comprehensive data gathered from the experimental phases detailed in previous chapters, incorporating variables such as fibre orientation, diameter, distribution, and the effects of post-processing treatments like annealing and dip-coating with PVA.

In constructing the finite element (FE) model, a sophisticated geometric modelling strategy was utilised, centred on devising a parametric representation to meticulously mimic the structure of nanofibers. As depicted in Fig. 7, certain controlled parameters were instrumental in the geometrical formulation of nanofibers, serving as the cornerstone for the FE model's establishment. The inception of this parametric model involved delineating straight fibres with a consistent diameter, arranged uniformly over a specified plane, characterised by the domain's known length ($D_L$) and height ($D_H$).
These boundary conditions, pivotal in simulating the response to both longitudinal and transverse strains, as depicted in Figs. 8 (a) and 8 (b), are meticulously crafted to monitor the reaction forces elicited by the displacement applied in the longitudinal direction. Specifically, the displacement applied to the fibre ends spans up to 20% of the domain's length, imposing restrictions to negate movement in the Y and Z axes for longitudinal loading and in the X and Z axes for transverse stress, thereby ensuring a controlled examination of tensile behaviour.

The material model considered for the FE model is as follows: the elastic behaviour of the material is described in Equation (1), which relates stress ($\sigma$) in the material to strain ($\varepsilon$) through Young's modulus ($E$), where $\varepsilon_y$ is the yield strain:

$$\sigma = E \cdot \varepsilon \ for \ \varepsilon \leq \varepsilon_y.$$  

(1)
The non-linear behaviour of the elastic-plastic transition is described in Equation (2):

\[ \varepsilon = \frac{\sigma}{E} + \left( \frac{\sigma}{K} \right)^n, \]  

where \( K \) is the strength coefficient, and \( n \) is the hardening exponent.

For the damage model, which predicts the energy that must be absorbed by the individual nanofiber to fail under stress, Equation (3) is used, which is based on the concept of fracture energy and linear plastic displacement:

\[ G_f = \frac{1}{2} \sigma_f \cdot \Delta_f, \]

where \( G_f \) is the fracture energy (\( \mu \text{N}/\mu \text{m} \)) representing the energy absorbed by the individual nanofiber until failure, \( \sigma_f \) is the stress at failure, and \( \Delta_f \) is the linear plastic displacement at failure.

Together, these equations form the basis for the material model used in the study, enabling comprehensive analysis of the mechanical behaviour of nanofiber mats from elastic response through plastic deformation to ultimate failure.

Figure 9 delineates the normal stress along the X-axis in an oriented nanofiber mat subjected to displacement.

Fig. 9. Normal stress along the X-axis for oriented nanofiber mat under displacement.

Figs. 10 and 11 exhibit the normal stress and von Mises stress, respectively, in the randomly structured nanofiber mats under displacement.
Fig. 10. Normal stress along the X-axis in the random structure of nanofibers under X-axis displacement.

Fig. 11. von Mises stress in random fibres under the Y-axis displacement.

Figure 12 synthesizes the FE model's prognostications concerning the mechanical behaviours of nanofiber mats with both oriented and randomly structured fibres, where the grey region represents experimental results, and the red line represents the results obtained from the FE model. Regarding the random structure, empirical data suggested analogous mechanical responses across both transverse and longitudinal orientations. The FE model successfully mirrored this finding, indicating almost indistinguishable stress reactions for both axes in the random configuration.
Fig. 12. Comparison of FE model predictions for (a) oriented and (b) randomly structured nanofiber mats, highlighting its accuracy in simulating mechanical behaviours.

Fig. 13 shows the impact of the fibre diameter on the mechanical properties of the nanofiber mat.

Fig. 13. Effect of the nanofiber diameter on elastic modulus and UTS.

The study delved into the impact of fibre orientation on the mechanical properties of nanofiber mats, with orientations scrutinised at 10 degrees, 30 degrees, and 45 degrees. Fig. 14 shows the impact of orientation on the mechanical properties of the mat.
Figure 14 shows the impact of porosity on the mechanical properties of the nanofiber mat.

Figure 15 elucidates those alterations in the $L : W$ ratio that significantly influenced the mechanical characteristics of mats with random fibre orientations, manifesting anisotropic tendencies as the ratio shifted. Conversely, mats comprised of oriented fibres exhibited stable mechanical properties, undisturbed by variations in the $L : W$ ratio.
Chapter 3 concludes by reflecting on the broader impact of the FE model within the field of materials science and engineering. It highlights the model's significance not only as a research tool that bridges empirical and theoretical realms but also as a practical asset for industries seeking to exploit the unique properties of PAN nanofiber mats. The development and validation of this FE model underscore the Thesis's contribution to advancing the understanding and application of nanofiber technology, setting a foundation for future explorations in the mechanical analysis and design of nanofiber-based materials.

**Chapter 4: Effect of Annealing on PAN Nanofiber Mats**

Chapter 4 delves into the transformative impact of annealing on the mechanical properties and thermal stability of polyacrylonitrile (PAN) nanofiber mats. This chapter is instrumental in elucidating how controlled thermal treatment can enhance or modify the intrinsic characteristics of PAN nanofibers, contributing to their suitability for a range of applications where mechanical integrity and thermal resistance are paramount. The content of this chapter is also available for reference in a published format (Sanchaniya, Lasenko, Kanukuntala, et al., 2023).

The chapter begins with a theoretical overview of the annealing process, explaining its role in polymer science as a method for relieving internal stresses, improving crystallinity, and
potentially altering the microstructure of polymeric materials. It sets the stage by detailing the specific objectives of annealing PAN nanofiber mats, such as increasing tensile strength, modifying elasticity, and enhancing thermal properties.

Figure 17 provides a visual comparison of PAN nanofiber mats before and after the annealing process. It was observed that untreated mats and those annealed at lower temperatures (70 °C and 140 °C) retained their original white coloration. However, as the annealing temperature increased, notable colour changes were observed. Mats annealed at 210 °C exhibited a pale-yellow hue, while those treated at 280 °C turned golden, indicative of the onset of degradation.

The relationship between nanofiber diameter and annealing temperature is depicted in Fig. 18. Statistical analysis, particularly the calculation of $p$-values, revealed a significant difference in the diameter of nanofiber mats annealed at 70 °C and 140 °C, with a threshold significance level set at 0.05.

The mechanical properties of annealed polyacrylonitrile (PAN) nanofibers are explored, focusing on their stress-strain behaviour. Figure 19 (a), (b) presents the stress-strain
curves for untreated and annealed PAN nanofiber mats in both the longitudinal and transverse directions.

![Stress-strain graphs](image)

(a) (b)

Fig. 19. Representative stress-strain graphs of oriented PAN nanofiber mats: (a) longitudinal direction; (b) transverse direction.

Figure 20 presents the TGA graphs for PAN powder, untreated nanofiber mats, and annealed nanofiber mats, illustrating their thermal degradation patterns. A notable, sharp decline in weight, indicating a mass loss of up to 30%, was consistently observed at approximately 290 °C across all samples. This mass loss points to the rapid degradation of PAN.

![TGA graphs](image)

Fig. 20. TGA of PAN nanofiber mats annealed at different temperatures.

The second heating cycle (Fig. 21) reveals the glass transition temperatures. PAN powder exhibited a glass transition temperature of 96.8 °C. The untreated and 70 °C annealed nanofiber mats showed similar glass transition temperatures of 97.0 °C and 96.7 °C,
respectively. However, mats annealed above the glass transition temperature displayed a marked decrease in this temperature: 90.1 °C, 92.3 °C, and 91.0 °C for mats annealed at 140 °C, 210 °C, and 280 °C, respectively.

Chapter 4 concludes by highlighting the practical implications of the annealing process for the application of PAN nanofiber mats. It explores the potential for annealed mats in industries requiring materials with precise mechanical specifications and thermal resistance, such as aerospace, automotive, and biomedical sectors. The chapter emphasizes how the insights gained from annealing experiments contribute to a deeper understanding of PAN nanofiber behaviour and open up avenues for material optimization and application development.

By providing a detailed investigation into the effect of annealing on PAN nanofiber mats, Chapter 4 not only advances the scientific knowledge of nanofiber treatment processes but also underscores the Thesis's contributions to enhancing the functionality and applicability of PAN-based nanomaterials.

**Chapter 5: Investigation of PVA Bonded PAN Nanofiber Mats**

Chapter 5 explores an innovative approach to enhancing the mechanical properties and functionality of polyacrylonitrile (PAN) nanofiber mats through the application of polyvinyl alcohol (PVA) bonding. This chapter is pivotal in presenting a non-conventional method that potentially opens new pathways for the development of nanofiber mats with improved
performance characteristics suitable for diverse applications. The content of this chapter is also available for reference in a published format (Sanchaniya, Lasenko, Vijayan, et al., 2024).

The chapter starts with an introduction to the concept of polymer bonding, specifically focusing on the use of PVA as a bonding agent for PAN nanofibers. It outlines the theoretical basis for selecting PVA, including its compatibility with PAN, its water solubility, and its ability to form hydrogen bonds, which can significantly impact the mechanical integrity and porosity of the nanofiber mats.

This delicate process of doping PAN nanofiber mats with PVA involved immersing PAN nanofiber mats into the PVA solutions, followed by a drying period to evaporate the solvent, thereby embedding PVA uniformly within the mat. The preparation, electrospinning conditions, and dip-coating methodology are visually encapsulated in Fig. 22, providing a step-by-step illustration of the fabrication process aimed at producing enhanced nanofiber mats capable of improved performance in various applications.

![Fig. 22. Fabrication process of PVA-doped PAN nanofiber mats.](image)

The development of a finite element (FE) model for PVA-doped PAN nanofiber mats was meticulously undertaken, leveraging methodologies previously established in Chapter 5. This advanced model integrates essential geometric parameters to precisely depict the structural nuances of the nanofibers post-PVA doping, as illustrated in Fig. 23. Key parameters such as domain length \( D_L \) and height \( D_H \) were defined to demarcate the spatial extents of the nanofiber mat model accurately.
The model is configured to simulate the tensile behaviour of nanofiber mats. Boundary conditions detailed in Fig. 24 were meticulously applied to emulate their response to displacement, focusing on the reaction force (RF) along the X-axis. Displacements (U1, U2, U3) were strategically imposed to reflect real-life stretching behaviours under tensile load, with particular constraints ensuring a faithful simulation of the material's deformation characteristics. The utilization of linear beam elements (B31) and shell elements (S4R) in Abaqus FEA software (2022) facilitates a nuanced representation of the nanofibers and the PVA dopant, respectively, ensuring a high-fidelity model of the nanocomposite material.
The scanning electron microscopy (SEM) analysis of PVA-doped PAN nanofiber mats unveils the intricate impact of the dip-coating process on their morphology, as vividly captured in Fig. 25. This figure showcases the nanofiber mats subjected to a 2.0 % PVA solution treatment, revealing three noteworthy morphological transformations: the formation of localized PVA agglomerations within the nanofiber mat, the emergence of thin PVA films bridging the gaps between PAN nanofibers, and a uniform PVA coating enveloping the surface of the PAN nanofibers. These morphological alterations are pivotal, enhancing the structural robustness of the mats by fostering additional interaction points between fibres, thereby augmenting the composite's mechanical attributes significantly.

Fig. 25. SEM images of a PAN nanofiber mat doped with a 2.0 % PVA solution: (a) localized agglomerations of PVA within the nanofiber mat (red) and coating on fibres (green); (b) cross-sectional image of the localized agglomerations of PVA.

The meticulous evaluation of the mechanical properties of PVA-doped PAN nanofiber mats, as delineated in Figs. 26 (a) and (b), provide a comprehensive insight into the enhancements achieved through the incorporation of PVA at various concentrations. The independent PVA films showcased a robust elastic modulus of (1254 ± 57) MPa, an ultimate tensile strength of (34 ± 2.4) MPa, and an exceptional plasticity with an elongation at break of 0.38 ± 0.03. Notably, the thickness consistency observed across both undoped and PVA-doped PAN nanofiber mats indicates that the incorporation of a low percentage of dopant meticulously maintained the mats' structural dimensions.
Fig. 26. Representative stress-strain graphs: (a) longitudinal direction, (b) transverse direction.

Figure 27 underscores the TGA and DTG analyses for PAN nanofiber mats infused with varying PVA concentrations. Remarkably, an increment in PVA concentration heralds a decrease in peak degradation temperature, suggesting an alteration in the composite's thermal stability. At a 0.5 % PVA concentration, the peak degradation temperature closely matched that of the undoped PAN nanofiber mat. However, at 1 % and 2 % PVA concentrations, a
discernible reduction to 288.2 °C and 288.0 °C, respectively, was noted. Concurrently, early mass loss up to 150 °C escalated with PVA concentration, marking a progression from 1.27 % at 0.5 % PVA to 1.67 % and 1.7 % at 1 % and 2 % PVA, respectively.

In the second DSC heating cycle, as presented in Fig. 28, the glass transition temperatures of the doped nanocomposites closely mirrored those of the pure PAN nanofiber mat, suggesting that PVA's inclusion does not significantly alter the composites' Tg.
Figure 29 vividly illustrates the normal stress distribution along the X-axis under loading, highlighting the dopant's role in augmenting the nanofiber mat's structural integrity. This enhancement in rigidity underscores the composite's fortified resilience against stress.

Fig. 29. Normal stress on the X-axis for nanofiber mat doped with 2% PVA.

The juxtaposition of the FE model's calculated elastic responses against the spectrum of experimental data, as delineated in Fig. 6.12, underscores the model's fidelity.

Fig. 30. Comparison of the elastic moduli obtained from the experiments and the FE model.

Chapter 5 concludes by reflecting on the practical applications and potential benefits of PVA-bonded PAN nanofiber mats. It explores their suitability for use in areas requiring materials with specific mechanical strengths, thermal resistances, and controlled porosity, such as in filtration, tissue engineering scaffolds, and wearable sensors. The chapter emphasizes how the novel approach of PVA bonding enriches the functional versatility of PAN nanofiber mats,
highlighting the contribution of this research to advancing materials science and nanofiber technology.

By presenting a detailed investigation into PVA-bonded PAN nanofiber mats, Chapter 5 not only broadens the scope of nanofiber mat enhancement techniques but also showcases the potential of polymer bonding as a viable strategy for material property optimization, underscoring the Thesis's role in pioneering new directions for nanofiber mat development.

Chapter 6: Non-Crimping Laminated Textiles Reinforced with PAN Nanofibers

Chapter 6 delves into the innovative integration of PAN nanofiber mats into textile structures to create reinforced laminated textiles without crimping. This chapter presents a significant advancement in the field of composite materials, offering a novel approach to enhancing the structural integrity and functional properties of textiles through the incorporation of nanofiber technology. The content of this chapter is also available for reference in a published format (Sanchaniya, Lasenko, Kanukuntla, et al., 2023).

The chapter begins by establishing the rationale behind the reinforcement of textiles with PAN nanofibers, highlighting the limitations of traditional textile reinforcement techniques that often lead to crimping and the associated mechanical weaknesses. The unique properties of PAN nanofibers, including their high tensile strength and thermal stability, are presented as solutions to these challenges, proposing a new paradigm in textile reinforcement that maintains the flexibility and drapability of the base textile while significantly enhancing its performance characteristics.

Figure 31 shows the fabrication process of the laminated textile composites via direct electrospinning on the textile fabric.
Fig. 31. The fabrication process of PAN nanofiber-laminated composite fabrics: (a) mixture of PAN and DMF; (b) magnetic stirrer; (c) electrospinning directly on woven fabric.

Figure 32 (a) displays the stress (σ) versus strain (ε) curves for the PAN nanofiber mat, plain fabric, and laminated composites. Notably, no failures occurred at the grips during tensile testing due to the effective gripping force. An enlarged view of these curves within a 5% deformation range (Fig. 32 (b)) reveals that the elastic modulus of the laminated composite fabric was higher than that of the plain fabric alone. This enhancement is attributed to the reinforcement provided by the nanofibers.
Fig. 32. (a) Representative stress-strain graph of the nanofiber mat, the fabric, and the laminated composite fabrics; (b) enlargement of the stress–strain curve in the low range of deformation (0–5 %).

Figure 33 visually represents the stress-strain behaviour of both the plain fabric and the nanofiber-laminated composite fabric. The plain fabric exhibited a transition in the crimping region under loading, aligning the woven structure of the yarns. The nanofiber-reinforced fabric, however, displayed a non-linear region due to the delamination and constant elongation of the PAN nanofibers under stress, leading to plastic deformation.

![Fig. 33. Typical stress-strain curve of the fabric and the nanofiber-laminated composite fabric.](image)

Figure 34 offers a visual representation of the fractured surfaces of both materials. The SEM images provided a detailed view of the fracturing patterns, highlighting the differences in fracture mechanisms between the two types of fabrics. The woven fabric's fractured surface predominantly exhibited broken fibres, aligning with a brittle fracture mechanism. The deformation was confined within the same plane, indicating a lack of multi-planar stress distribution. This behaviour is typical of traditional woven fabrics, where the failure occurs primarily along the fibre breaking points.
Figure 34 focuses on SEM images near the clamps and the ends of the warp fibres, shedding light on the fracture behaviour and shear stress presence within the laminated composite and woven fabric. Post-fracture, the SEM images revealed that the nanofiber-laminated composite fabric and the woven fabric separated, indicative of in-plane shear stress causing delamination. This stress resulted from the mismatched elastic regions between the layers, leading to their separation.
Chapter 6 concludes by reflecting on the broader impact of this research, considering the future possibilities for non-crimping laminated textiles reinforced with PAN nanofibers. The chapter underscores the versatility of this approach, suggesting avenues for further research and development, such as the incorporation of multifunctional nanofibers for added functionalities like antimicrobial properties or conductivity.

By the development of non-crimping laminated textiles reinforced with PAN nanofibers, Chapter 6 contributes a novel and impactful advancement to the field of materials science and engineering, showcasing the potential of nanofiber technology to create next-generation composite materials with unparalleled performance and versatility.
CONCLUSIONS

1. Introduction: The Thesis introduces the field of nanofiber technology, emphasising its significance due to the unique properties of nanomaterials. It sets the stage for the study by highlighting the potential of polyacrylonitrile (PAN) nanofiber mats in various applications, driven by their exceptional mechanical, thermal, and filtration capabilities. The introduction delineates the research gap and the necessity for a deeper investigation into the fabrication techniques, properties, and applications of PAN nanofibers.

2. Literature Review: This chapter provides an exhaustive review of the current state of nanofiber technology. It covers the evolution of nanofibers, focusing on fabrication techniques with a special emphasis on electrospinning, and exploring the mechanical and thermal properties critical to their performance. The review identifies the existing research gaps, particularly in the area of PAN nanofibers, and sets a clear direction for the study.

3. Fabrication of PAN Nanofiber Mats: Chapter 3 delves into the experimental procedures for fabricating PAN nanofiber mats. It examines different methods of electrospinning, assessing their impact on fibre orientation and mat structure. This chapter provides foundational work for understanding how fabrication techniques influence the physical properties of nanofiber mats. The nanofiber mat with the orientated structure has 128 % higher UTS and 298 % (~ four times) higher Young’s modulus compared to the random structure.

4. An FE Model for Determining the Mechanical Properties: Here, the development and validation of a finite element (FE) model for predicting the mechanical properties of electrospun nanofiber mats are presented. The model’s accuracy in simulating the behaviour of nanofibers under different conditions represents a significant step forward in the analytical capabilities of nanofiber research.

5. Effect of Annealing on PAN Nanofiber Mats: This chapter investigates the effects of annealing on the properties of PAN nanofiber mats. It provides critical insights into how thermal treatments can enhance the strength and stability of nanofibers, offering a pathway to improve their application potential. Annealing has a significant impact on PAN nanofibers when annealed at various temperatures, the diameter of nanofibers decreased by 20 %. Annealing at 70 °C increased UTS by 32 % and Young’s modulus by 6.5 %. However, annealing above 100 °C resulted in a decrease in tensile strength.
and Young’s modulus. In the transverse direction, the enhanced UTS increased by 23.5%, and Young’s modulus increased by 18.5%.

6. Investigation of PVA Bonded PAN Nanofiber Mats: Chapter 6 explores a novel approach to enhance the mechanical properties of PAN nanofibers through PVA bonding. This innovative strategy addresses the challenge of maintaining the structural integrity of nanofiber mats while enhancing their strength. Adding 2% PVA to the PAN nanofiber slightly reduced nanofiber porosity by 12.5%; with 1% PVA solution, it was reduced to 6.9% and with 0.5% PVA solution, it reduced to 4.1%. The thermal stability remained constant with the PVA dopant, with a slight change of 0.5%. The composite prepared with an added 2% PVA solution showed increased Young’s modulus by 78.3% and UTS by 84.3% in the longitudinal direction, whereas in the transverse direction, it was 159.5% and 200%, respectively. The nanofiber composite mat made with 2.0% PVA has a 563% higher Young’s modulus in the longitudinal direction and 22% higher Young’s modulus in the transverse direction compared to Young’s modulus of the random nanofiber structure.

7. Non-Crimping Textiles Reinforced with PAN Nanofibers: The final experimental chapter focuses on the application of PAN nanofibers in reinforcing non-crimping textiles. It highlights the potential of PAN nanofibers in the creation of composite materials with superior mechanical properties.
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Jaymin Vrajial Sanchaniya, born in 1992 in Rajkot, India, holds a Bachelor’s degree in Mechanical Engineering from Gujarat Technical University, India (2015), and a Master’s degree in Mechanics and Mechanical Engineering from Riga Technical University, Latvia (2020). Since 2020, he has been working as a research assistant at Riga Technical University. He has gained extensive experience through collaborations and training at renowned institutions such as KTH Royal Institute of Technology (Sweden), RWTH Aachen University (Germany), University of Technology of Compiègne (France), University of Rouen Normandy (France), and Tallinn University of Technology (Estonia). His research interests revolve around the fabrication, characterization, finite element modeling, and mechanics of nanofibers and nanofiber mats. His dedication to the field is reflected in his impressive publication record, with more than 20 journal and conference articles indexed in the SCOPUS database, spanning areas such as fabricating and characterizing nanofiber mats for the fields of environment and smart materials.