

DEFORMATION BEHAVIOUR OF ORIENTED ELECTROSPUN PAN NANOFIBER MATS

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The research addresses the limited understanding of the deformation behaviour in mechanically loaded orientated electrospun nanofiber mats, which are crucial for applications such as filtration, catalysis, and sensing. Focussing on polyacrylonitrile (PAN) as a reference polymer, we investigated the mechanical properties of PAN nanofiber membranes with aligned fibre orientations, specifically examining their response to mechanical stresses introduced by notches and punch holes. Mechanical testing revealed that these membranes showed a consistent deformation pattern at the macroscale until fracture. In particular, we observed significant variations in key parameters such as elastic modulus, ultimate strength, and critical stress in different membrane samples, which were also compared with an analytical model. The presence of a notch in the nanofiber mat reduced the strength by 48 %, indicating a remarkable fracture resistance, even in pre-damaged membranes. Furthermore, elongation of fibres along the loading direction was observed to cause the tip of the crack to not grow, providing local reinforcement to the membrane by undamaged nanofibers and enhancing its overall mechanical robustness.

Keywords: Critical stress, deformation of nanofibers, hole, notch, tensile strength.

1. INTRODUCTION

Electrospinning emerges as a cost-effective method for the production of nanofiber mats. This technique facilitates the fabrication of a relatively new class of materials characterised by a non-woven assemblage of nanofibers, typically from 100 to 500 nm [1]. The diminutive fibre diameter, coupled

with the nonwoven structure of these mats, imparts them with distinct properties, such as an elevated internal surface area and significant porosity, whilst maintaining flexibility. Consequently, these materials have immense potential for application in areas demanding high performance, including

gas and water filtration [2], tissue scaffold engineering [3], [4], wound healing [5], [6], catalysis [7], composites [8], [9], antibacterial textiles [10] and food packaging [11]. However, the successful deployment of these materials often requires robust mechanical performance and durability.

Recent research has turned towards aligned nanofibers [12], [13] attributed to their improved strength and the consistency of their mechanical properties, yielding highly repeatable results. Although these are commonly classified as nanofiber mats in numerous studies, they are often evaluated against the standards of polymeric films [14]. This comparison is justified, given that the overall mechanical properties of nanofiber mats are calculated and these materials are treated as polymeric films in analytical and numerical calculations [8]. Fundamentally, a nanofiber mat usually has a large number of interconnected fibres.

In this context, the deformation behaviour of nanofiber mats is anticipated to diverge from that of conventional polymeric films. Notably, in the presence of an initial crack, the propagation within the nanofiber mat is expected to follow a different trajectory, influenced by the remaining nanofibers. Comprehending this deformation behaviour is crucial to understanding the performance of nanofiber mats in practical applications.

In the present study, the authors prepared nanofiber mats incorporating holes and notches, comparing them with their undamaged counterparts. The testing of these pre-damaged nanofiber mats aids in elucidating the deformation behaviour, particularly of orientated polyacrylonitrile (PAN) nanofiber mats, thereby contributing valuable insights into their structural integrity under various conditions.

2. MATERIALS AND METHODOLOGY

To investigate the deformation behaviour of orientated polyacrylonitrile (PAN) nanofibers, we used electrospun nanofibers employing PAN powder and N,N-Dimethylformamide (DMF). Polyacrylonitrile (average molecular weight: 150,000 (typical); CAS number: 25014-41-9) and N,N-dimethylformamide (DMF; ACS reagent grade, solvent; $\geq 99.8\%$ purity; CAS number: 68-12-2) were procured from Sigma-Aldrich Chemicals, Merck KGaA, Darmstadt (64287), Germany.

Following the production of nanofiber mats as mentioned in [12], [13], [15], samples measuring 10 mm in width and 50 mm in length were precisely incised in the centre using a sharp blade, resulting in a cut length of 5 mm (half the total width). To create holes in the samples, a 5 mm diam-

eter punch was used, ensuring precise puncturing in the centre of each sample. Figure 1 delineates the methodology for fabricating nanofiber mat samples with notches and holes.

Tensile properties were measured using a Mecmesin Multi-Test 2.5-i tensile testing machine equipped with a 250 N sensor (PPT Group UK Ltd., t/a Mecmesin, Newton House, Spring Copse Business Park, Slinfold, UK). The samples were conditioned at room temperature according to ISO 139:1973 ‘Standard Environments for Conditioning and Testing’, which stipulates a temperature of $21 \pm 1^\circ\text{C}$, a relative humidity of 60 %, and an atmospheric pressure of 760 mm Hg. The dimensions of the sample were conformed to ASTM D882-18, measuring 50 mm $\times$ 10 mm (length $\times$ width). To

determine the tensile properties, a quintet of measurements was conducted. The thickness of the nanofiber mats was determined using a digital micrometre (range: 0 to 25 mm; Digimatic micrometre, MDC-25PX, code No. 293-240-30, serial No. 71912410, Mitutoyo, Japan). For testing in the longitudinal direction, the specimens were cut parallel to the nanofiber orientation. A paper template was prepared, measuring 50 mm × 40 mm with an interior cut of

30 mm × 20 mm. Using double-sided thin Scotch tape (3M Scotch Magic Tape (Matte Finish) 3/4" × 36 yard desk dispenser refills), the specimen's ends were affixed to the paper template. Subsequent to attachment of the paper and sample to the tensile testing apparatus, the sides of the paper template were meticulously removed with scissors, according to the protocol detailed in [8], [12], [13].

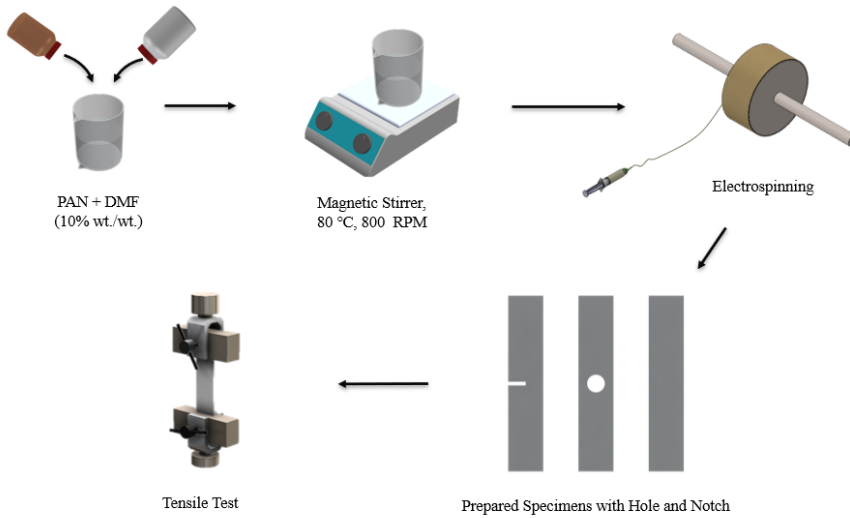


Fig. 1. Fabrication process of PAN nanofiber mats and specimens.

3. RESULTS AND DISCUSSION

Figure 2 presents representative of the stress strain curves: of the plain nanofiber mat, nanofiber mat with a hole, and nanofiber mat with a notch. The thickness found was 154 ± 8 μm of all specimens. The ultimate tensile strength on the plain nanofiber mat was 16.5 ± 2 MPa while for the nanofiber mat with a hole was 9.1 ± 1 and with a notch was 8.5 ± 1 . The elastic modulus of the PAN nanofiber mat was found 570 ± 18 MPa and for the nanofiber mat with a hole it was 357 ± 27 and for the nanofiber mat

with a notch it was 368 ± 21 MPa. The elongation at break for the entire specimen was obtained almost similarly. For the PAN nanofiber mat, the elongation at break was 15 ± 1 , for the nanofiber mat with a hole it was 13 ± 2 and for the nanofiber mat with a notch it was 15 ± 1 . The summary of the mechanical properties of the plain nanofiber mat, the nanofiber mat with a hole, and the nanofiber mat with a notch is shown in Table 1.

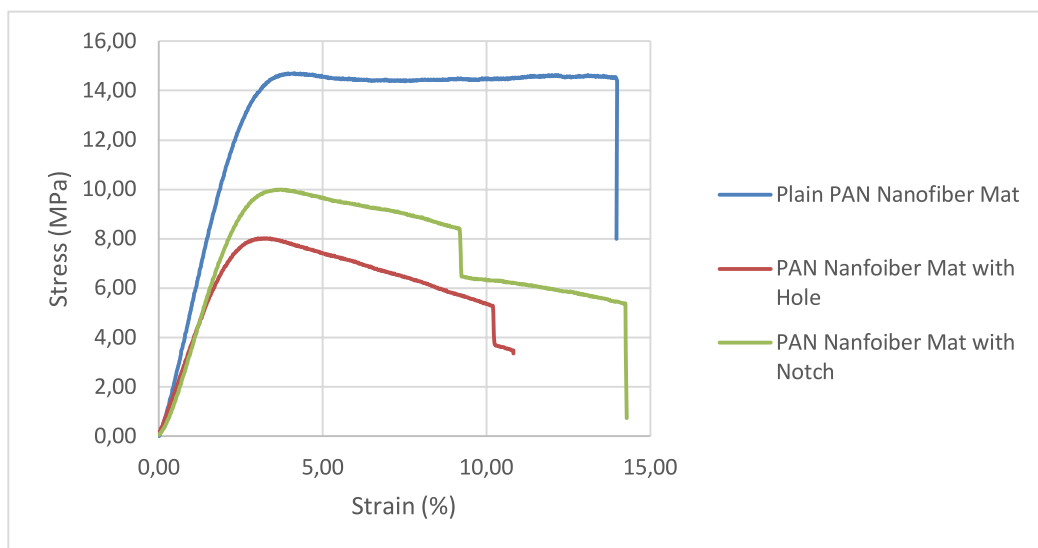


Fig. 2. Representative stress-strain curve of plain nanofiber mat, nanofiber mat with a hole, and nanofiber mat with a notch.

Table 1. Summary of the Mechanical Properties of the Plain Nanofiber Mat, the Nanofiber Mat with a Hole, and the Nanofiber Mat with a Notch.

Specimen	Thickness, t (μm)	Tensile Strength σ at Break (MPa)	Young's modulus, E (MPa)	Elongation at break, ϵ at Break (%)
Plain nanofiber mat	154 ± 8	16.5 ± 2	570 ± 18	15 ± 1
Nanofiber mat with hole	154 ± 8	9.1 ± 1	357 ± 27	13 ± 2
Nanofiber mat with notch	154 ± 8	8.5 ± 1	368 ± 21	15 ± 1

Figure 3 shows the deformation behaviour of the PAN nanofiber mats with a notch and a hole under loading conditions. It is

evident from the figure that only the undamaged nanofibers in the mat are subjected to the load, elongating until rupture.

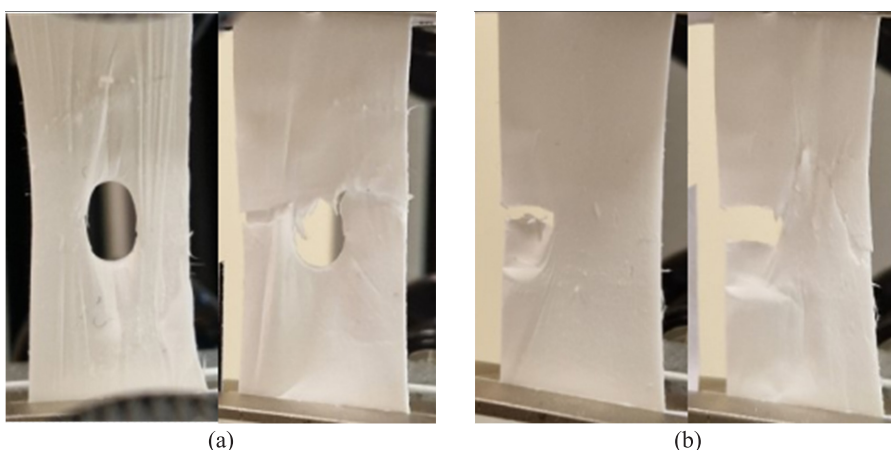


Fig. 3. Deformation behaviour of nanofiber mats with a hole and a notch under load.

The experimental results indicate a significant reduction in both the elastic modulus and the ultimate tensile strength, approximately halving in value. This suggests that regardless of the presence of a notch or hole, the undamaged nanofibers within the nanofiber mat carry the load, elongating and eventually breaking, which was observed when the nanofibers were aligned in a single direction [16].

Given that all nanofibers on the mat are aligned in one loading direction, the material does not conform to traditional crack propagation theories, where a crack grows leading to failure. Instead, when the fibres are

aligned in a singular direction, all undamaged nanofibers collectively sustain the load until failure. This finding also implies that, when the mechanics are at the individual nanofiber level, it cannot be equated to a thin polymeric film, where crack growth is typically expected. When considering the mechanical and numerical behaviour of nanofiber mats at the microscale, it is imperative to treat nanofibers as separate entities that do not behave analogously to a film, particularly in the context of fracture and plasticity, while considering at the macroscale when polymeric film is considered, it predicts elasticity very precisely [8], [17].

4. CONCLUSIONS

The research has comprehensively explored the deformation behaviour of orientated polyacrylonitrile (PAN) nanofiber mats, with a particular focus on understanding the impact of introduced defects such as notches and holes. The findings from this study are pivotal in elucidating the mechanical properties and response characteristics of these nanofiber mats under stress conditions.

It has been observed that the presence of holes or notches significantly influences the ultimate tensile strength and elastic modulus of the nanofiber mats. In particular, both of these mechanical parameters exhibited a marked reduction in defects in mats compared to plain mats. This reduction highlights the critical role of the structural integrity of the nanofiber network in determining the overall strength and flexibility of the material. However, the elongation at break remained relatively consistent across all samples, suggesting that the deformation capacity of the nanofiber mats is largely unaffected by the presence of small-scale damage.

Furthermore, the research findings challenge conventional notions in polymer science, particularly concerning crack propagation and failure in polymeric films. Unlike traditional polymeric films, where cracks tend to propagate, leading to failure, orientated PAN nanofiber mats demonstrated a different failure mechanism. In these mats, the undamaged nanofibers bear the load and elongate until rupture, indicating a unique interaction between the nanofibers within the mat. This behaviour underscores the need to consider each nanofiber as an individual entity in mechanical assessments, especially when considering the fracture and plasticity properties of nanofiber mats.

In conclusion, this investigation into the deformation behaviour of PAN nanofiber mats contributes valuable knowledge to the field of material science, particularly for applications where mechanical resilience and durability are paramount. The findings suggest potential for these materials in various high-demand applications, although further research is required to fully understand the long-term behaviour

and performance under diverse environmental conditions. Ultimately, this study lays the groundwork for future exploration and exploitation of the unique properties of

electrospun nanofiber mats, paving the way for innovative uses in various scientific and industrial domains.

ACKNOWLEDGEMENTS

This research/publication has been supported by the Doctoral Grant Programme of

Riga Technical University.

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