Direct measurement of the elasticity and fracture properties of electrospun polyacrylonitrile/halloysite fibrous mesh in water

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Abstract

The objectives of this research are to characterize the effects of hydration on the elasticity and fracture properties of electrospun polyacrylonitrile (PAN) and PAN/halloysite meshes and to use the information for design analysis for water filtration application. Electron micrographs of these meshes revealed pore diameters ranging 1-7 μm . Direct measurement of the mesh stiffness and strength in water revealed that PAN/halloysite meshes were stiffer and stronger than PAN meshes. Solution diffusion model predicted that PAN/halloysite mesh can support a water flux of 2.4 times higher than PAN mesh without breaking during desalination. However, wet meshes were weaker and less stiff than dry meshes. This was attributed to a reduced effectiveness for stress transfer between fibres, caused by the presence of water in (and swelling of) the inter-fibre space, as reflected by a reduction in the volume fraction of the respective PAN and halloysite components.

Keywords: electrospinning; polyacrylonitrile; halloysite nanotube; stress transfer; volume fraction; water flux

1 **1 Introduction**

2 We have used micromechanical testing to investigate the effects of hydration on the mechanical properties of
3 electrospun nanofibrous mesh made from blending halloysite nanotubes (HNTs) in polyacrylonitrile (PAN). PAN
4 is a polymer resin with the linear formula represented by $(C_3H_3N)_n$ [1]. Known for its high chemical resistant as
5 well as having a relatively hydrophilic chemistry [2], PAN can be processed to make fibrous membranes—with
6 pore sizes ranging from 0.1 to 0.001 micron—which can be used for ultrafiltration, such as water/wastewater
7 treatment and reverse osmosis pretreatment. The applicability of PAN fibrous membrane for water filtration
8 has generated a lot of research and commercial interests with regards to desalination, removing heavy metals
9 and bacteria from the water. A detailed literature survey of the results of the study of PAN fibrous membrane
10 and the significance of commercially available ones is out of the scope of this paper. For a recent review on
11 water purification system based on nanofibrous mesh, see Suja et al. [3]. For informational purpose, the reader
12 is directed to summaries of key findings from recent investigations as well as the performance of commercial
13 PAN fibrous membrane in Table 1.

14 In many applications, the PAN fibrous membrane may be subjected to fluid flow under unduly high pressure,
15 cyclic loading (hydration and dehydration) and chemical degradation associated with attack by radicals and
16 other reactive species, to name a few. To this end, significant research effort has been focused on enhancing
17 the mechanical properties of the PAN fibrous membrane, particularly where thin membranes are deployed
18 (Table 1), so as to increase the membrane resistance to failure and achieve better durability. Failure mechanics
19 of thin membrane dictates that the mechanical parameters, such as fracture strength and toughness, can be a
20 good indicator of the membrane lifetime as these parameters are sensitive to localized mechanical and chemical
21 degradation of the membrane [4]. While the mechanical stability of PAN fibres is attributed to the strong
22 interaction between the long molecular chains, underpinned by the electrostatic force between the dipoles of
23 the adjacent $-C\equiv N$ groups [5], failure occurs when these forces of interaction are disrupted.

24 There are various ways to improve the mechanical properties of the polymeric membrane, from chemical
25 methods (that are also intended to mitigate polymer degradation) such as cross-linking and chemical
26 stabilization, to physical reinforcement reinforcement such as using inorganic fillers [4]. With regards to the use
27 of inorganic fillers, various studies have shown how the mechanical properties of PAN fibres may be enhanced
28 by blending with high-strength and slender fillers [6]. Potential candidates are carbon nanotubes [7],
29 hydroxyapatite particles [8], organoclay particles, silica, titania [6] and even HNTs [9].

30 This study is concerned with the use of HNTs as fillers for the PAN fibres. HNTs are inorganic whisker-like
31 nanotubes (molecular formula $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$, similar to kaolinite) that resemble rolled-up aluminosilicate
32 sheets [9]. Between carbon nanotubes and HNTs, the latter shows greater potential as an alternative filler for
33 the following reasons: environmental friendliness, abundant availability and cost-effectiveness in production
34 [10]. Owing to the large surface- to-volume ratio, it is expected that ionic bonds between the HNT nanofiller and
35 matrix phases can result in a net increase in the composite modulus [11]. Additionally, a major advantage in
36 these nanotubular fillers is that the axis of the tubular structures can become align to the longitudinal axis of
37 the electrospinning jet [11]. This is expected to help enhanced the mechanical properties of the polymer-based

fibre by analogy to how short fibres reinforce composites [12]. Additionally, HNTs can be used as adsorbents for removal of several kinds of heavy metal ions (Cu(II), Pb(II), Cd(II), Zn(II), Cr(IV), and Co(II)) from the contaminated water [13]. On this note, the effectiveness of the removal of heavy metal ions from aqueous media by naturally occurring HNTs—free from any modification—depends on the physical and chemisorption mechanisms, site geometry, and metal speciation [13]. Blending polymeric material with HNTs can enhanced the barrier properties and thermal stability of the polymer composite material [10]. Thus, HNTs, as well as HNT-based materials, have been explored for useful applications in the treatment of contaminated drinking water or industrial wastewater [13].

While HNT has often been touted as a good candidate for reinforcement of polymers such as chitosan [14, 15], PLA [14-19] and ultrahigh molecular weight polyethylene [20], curiously PAN meshes processed by blending HNTs (from 1 to 3 % (w/w)) into the PAN matrix exhibit no significant enhancement to the mechanical properties [5]. This at first appears surprising because adhesion between the PAN and HNT can occur when HNT is blended in PAN. The adhesion was inferred from results from FTIR experiments which revealed shifts in vibrational bands of the C-N groups of PAN in the presence of HNT, attributing to the possibility of hydrogen bonding interactions between the C-N groups of PAN and O-H groups of HNT [5]. Adhesion between HNT and PAN can greatly facilitate stress transfer from the PAN to the HNT, by an analogy to short fibres reinforcement of composites [12].

One of the motivations of the present paper is to establish a comprehensive study of the mechanical properties encompassing the elasticity and fracture properties of the meshes and their relationships to the structure of the PAN-based fibre, underpinning the mechanics of HNT reinforcement in a single PAN fibre. Another motivation is to evaluate the structure-mechanical property relationship of the PAN-based fibrous mesh in a hydrated state in a consistent way both to allow for understanding how water interacts with the mesh (the transport phenomena) and for wider significance, i.e. predicting the critical performance of the mesh. This is relevant in the context of using PAN, as well as PAN/HNT, meshes for water filtration as it can inform the manufacturer about the key design parameters during process modelling [21]. Although the mechanical properties of PAN-based meshes have been widely reported [5, 14, 22-25], none of the studies have directly measured the mechanical properties of the hydrated fibrous meshes as well as relating to the structure of the PAN fibre. In addition, the arguments on the mechanical properties achieved has not been directly examined by analytical models of stress transfer between the HNT and PAN. On this note, the novelty of this study addresses a conceptual framework of the relationship between the mechanical properties of the PAN/HNT mesh and structure of the PAN-based fibre—in the respective dry and hydrated states—to allow for useful predictions of their expected performance. The significance of this study addresses fundamental understandings of the mechanical stability of the PAN/HNT mesh underpinning the influence of water within the fibre-fibre interspace during water permeation.

2 Theory

This section is concerned with a discussion of a conceptual framework that integrates the mechanical response of the nanofiltration membrane and the transport phenomena in water permeation. We begin with a simple mathematical model that leads to order-of-magnitude predictions of the relative composition (i.e. volume

fraction) of the PAN and HNTs in the hydrated PAN/HNT electrospun fibre. The PAN/HNT mesh may be considered as an example of a particle-reinforced composite material [12] in which the HNT particles provide tensile reinforcement to the individual fibre. Figure 1 A shows a schematic of the HNTs embedded in PAN fibres in the dry state, aligned along the fibre axis. Let L and D be the respective length and outer diameter of a HNT. When the mesh is loaded in tension, all fibres will be recruited into tension towards the direction of the applied load. Of note, E is used to represent the stiffness of the mesh, which is an elasticity-related property, and σ_u to represent the ultimate tensile strength, which relates to the fracture property. At the length scale of the mesh, it is expeditious to apply the rule-of-mixture to estimate, to order of magnitude, the contribution of the HNT and PAN components to the σ_u , i.e.

$$\sigma_u = \sigma_{HNT}V_{HNT} + \sigma_{PAN}V_{PAN}, \quad (1)$$

[12, 26] where

$$V_{PAN} + V_{HNT} = 1, \quad (2)$$

and σ_{HNT} and σ_{PAN} the fracture strength of HNT and the corresponding average stress in the PAN material, respectively. Equation (1), which originates from a continuous fibre-reinforced composite system, is applied to the PAN/HNT by assuming that the cross section is homogeneous through the composite material. This assumption is expected to be valid for the PAN/HNT system where the randomness of the HNT particle distribution means that the PAN/HNT fibre can be regarded as quasi-homogeneous and quasi-isotropic throughout the fibre length scale, which is much larger than the HNT size and spacing [12].

Based on a well-known modified Halpin–Tsai model presented by Ramakrishna et al. [11] and Yu et al. [10] to predict the Young's modulus of clay reinforced electrospun polymer nanofibres, the stiffness of an electrospun HNT reinforced PAN fibrous mesh may be described by

$$E = \zeta E_{PAN}, \quad (3)$$

where ζ is a modifying factor given by

$$\zeta = c[(1+q\eta V_{HNT})/(1-\eta V_{HNT})], \quad (4)$$

E_{HNT} and E_{PAN} represent the stiffness of HNT and PAN, c is a scale factor which may be determined by fitting to experimental data, q is related to the aspect ratio ("slenderness") of HNT, i.e.

$$q = 2L/D, \quad (5)$$

and

$$\eta = (E_{HNT}/E_{PAN}-1)/(E_{HNT}/E_{PAN}+q). \quad (6)$$

In fact, this is not an unrealistic description of E, because if HNTs were absence, $V_{HNT} = 0$ and $c = 1$, giving $\zeta = 1$, leading to the result of $E = E_{PAN}$.

The pores of PAN and PAN/HNT meshes can act as small capillaries. The surface tension associated with the hydrophilicity of PAN can help to facilitate the flow of water into the pores, when the PAN material comes into contact with water. HNTs are hydrophobic materials and when they are in contact with water, the direction of the surface tension will cause the water to be repelled from the HNT. With regards to PAN/HNT mesh, while most HNTs will reside within the PAN matrix, a number of HNTs could also be found just beneath the surface or on the surface as illustrated in Figure 1 A, and these HNTs could act to repel the water. On the other hand, the capillary action of the lumen could also lead to water flowing into the lumen. Thus, when water uptake occurs, this results in a three-component system (Figure 1 B). The amount of water accommodated in the fibre-fibre interspace can be estimated to order of magnitude by equating the sum of the V_{HNT} and V_{PAN} , weighted respectively by the coefficients, α_{HNT} , and α_{PAN} , and the volume fraction of water, V_{H_2O} , to unity, i.e.

$$\alpha_{HNT}V_{HNT} + \alpha_{PAN}V_{PAN} + V_{H_2O} = 1. \quad (7)$$

The following arguments are used to connect the values of α_{HNT} , α_{PAN} , and V_{H_2O} , to σ_U and E, which are expected to be valid to order of magnitude. Assuming that when subjected to tensile loading, water has negligible contribution to the respective E and σ_U , it is then expedient to use the rule-of-mixture to estimate, the contribution of HNT and PAN to the σ_U as follows,

$$\sigma_U \approx \sigma_{HNT}\alpha_{HNT}V_{HNT} + \sigma_{PAN}\alpha_{PAN}V_{PAN}. \quad (8)$$

With regards to E, equation (3) becomes,

$$E \approx \zeta' E_{PAN}, \quad (9)$$

where

$$\zeta' = c'[(1+\eta\alpha_{HNT}V_{HNT})/(1-\eta\alpha_{HNT}V_{HNT})], \quad (10)$$

and c' is another scale factor. Consequently, $\alpha_{HNT}V_{HNT}$ and $\alpha_{PAN}V_{PAN}$ may be regarded as the effective volume fractions of the HNT and PAN, respectively, in the presence of water in the fibrous mesh.

The mechanical properties are related to the performance of the membrane during the filtration process. When an external applied pressure is used to force water through the membrane, the membrane will attempt to resist the pressure exerted by the water on the membrane. The ability of the membrane to resist and not fracture must be related to the strength of the membrane in tension. To better understand the performance of the membranes for, e.g. desalination and oil-water separation, transport through the membrane may be described

by the solution diffusion model. The application of the solution diffusion model has been described elsewhere for desalination [27] and oil-water separation [27, 28]. For further insights into the solution diffusion model, the reader is referred to a detailed explanation concerning the solution diffusion equation developed by Paul and Ebra-Lima [29]. In this model, water flux (J_w , i.e. volume of water passing through the mesh per unit mesh area) is related to membrane thickness (h_0), molecular volume of water (v_w), membrane water permeability (p_w = product of water diffusivity and solubility), driving pressure (Δp_{DP}), osmotic pressure ($\Delta\pi$), and thermal energy (which is parameterized by RT). Since some of the parameters (i.e. v_w , h_0 , p_w) may present practical difficulties for measurement, for convenience, the RT , v_w , h and p_w are grouped together, parameterized by a constant of proportionality (A_0) known as the apparent water permeability coefficient. It follows that for the PAN mesh,

$$J_{w,PAN} \approx (\Delta p_{DP} - \Delta\pi)A_0, \quad (11)$$

where the driving pressure (Δp_{DP}) is greater than the osmotic pressure ($\Delta\pi$) of the NaCl solution, and

$$A_0 = (v_w/RT)p_w/h_0 \quad (12)$$

[30]. Similarly, the flux through the PAN/HNT mesh is described by

$$J_{w,PAN/HNT} \approx (\Delta p_{DP} - \Delta\pi)A_0', \quad (13)$$

where A_0' may not be equal to A_0 . In all cases, flux is proportional to the difference in Δp_{DP} and $\Delta\pi$.

The PAN-based mesh may be designed to withstand high water flux for as long as Δp_{DP} does not exceed the σ_U of the mesh. By identifying the upper bound of Δp_{DP} with the σ_U of Eq. (8), the upper limit of the respective J_{ws} can be estimated to order of magnitude as the J_w is directly proportional to the mechanical and physical properties of the membranes, namely σ_{HNT} , σ_{PAN} , V_{HNT} , V_{PAN} , α_{HNT} and α_{PAN} .

In the following sections, we described the experimental method (section 3 and 4) and results (section 5) of the direct measurement of the mechanical properties of the PAN-based mesh in a hydrated environment. Thereafter, we discussed how the conceptual framework developed in this section was applied to evaluate the findings (section 6) to help gain further insights into the mechanical response of the PAN-based mesh.

3 Materials

PAN (Mw = 150 kDa) was purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO), for the purpose of dissolving the PAN, was purchased from Fischer Scientific. The HNTs were obtained as a “processed product”, donated by Applied Minerals Inc. from its Dragonite operation.

The preparation method of the solutions for electrospinning PAN-based fibrous mesh follows from a previous report [5] which formed a part of an on-going study on the design, fabrication and applicability of PAN/HNT meshes. To make 8% (w/w) PAN solution, 0.86 g of the PAN polymer pellets were dissolved in 10 mL of 99.6% DMSO based on a method described elsewhere[31]; the mixture was stirred for 6 h until the solution became homogeneous. The solution was divided into two portions. One portion was used directly to produce neat PAN

fibrous meshes by electrospinning. The other portion was blended with 1 % (w/w) HNTs. Here, the HNTs were added into the solution and stirred for 12 h, before introducing the solution into the electrospinning device.

4 Experimental

4.1 Electrospinning

We used the electrospinning method to process PAN fibres to obtain very slender and long fibres with diameters on order of micrometer to nanometer length scale. (For ultrafiltration application, it was important that the individual fibres were adequately thin, in addition to the presence of a good number of fibres, in order to present a high surface area to volume for separating and retaining the unwanted particles and bacteria [3, 6, 32, 33].) Neat PAN and PAN/HNT meshes were processed using an electrospinning device (NB-EN1, NanoBond). Spinning was carried out using a solution flow rate of 1.4 mL/h; the distance between the spinneret and collector was set at 15 cm; a voltage of 13 to 14 kV was applied. A plane collector was used to collect the PAN fibres as they landed randomly on the collector surface. Six such meshes were fabricated in this way (neat PAN = 3 meshes; PAN/HNT = 3 meshes). Each mesh featured a size of 100 mm by 100 mm.

Test specimens were prepared from each mesh by dividing the mesh into several rectangular parts (using a surgical scalpel), with dimensions 10 mm by 5 mm, for microscopy and mechanical testing. The thickness of the mesh specimens ranged 0.01 to 0.05 mm. To account for possible variability in the inherent non-uniformities in the distribution of the fibres throughout a mesh, a randomized procedure was used to identify and allocate specimens from the meshes to each treatment, i.e. dry and hydrated states. For electron microscopy, five specimens from each of the three respective (PAN and PAN/HNT) meshes were used. For mechanical testing in dry condition, five PAN and PAN/HNT specimens were used; similarly, five PAN and PAN/HNT specimens were used for testing in hydrated condition.

4.2 Electron microscopy

The morphology of the mesh was observed under an ultra-high resolution field emission scanning electron microscope (FESEM, Hitachi SU8010). A thin layer of platinum was coated onto the specimens to minimize the accumulation of electrostatic charge on the specimens during observation. The voltage was set to values ranging from 3 kV to 5 kV depending on the magnification (ranging 5.0k to 10.0k) of the SEM image to be achieved.

Five specimens were randomly selected from each mesh for imaging. Several SEM images acquired were subjected to a randomized procedure to select the images for the measurement of fibre thickness and pore size. The measurements were carried out using ImageJ software. Individual fibres at different depths were identified and the thickness (D_f) was measured. To order of magnitude, we can identify the D_f with the fibre diameter, assuming that each fibre had a circular cross section. Pores at different depths were identified by the region enclosed by adjacent fibres. Each pore was carefully outlined to determine the pore perimeter. To order of magnitude, by modelling each pore by an equivalent circle, we can identify the pore size with the diameter of the circle. From the value of the pore perimeter, the pore diameter, D_p , was found by dividing the perimeter ($= \pi D_p$) by π .

Further analysis was performed to evaluate the structure and dispersion of HNTs in the fibers under the transmission (STEM) mode of the same FESEM instrument.

Data derived for the structural properties, i.e. fibre diameter and pore diameter, can be found in Table 1 and 2 in Ref [34].

4.3 Micromechanical testing

A high-throughput small-scale environmental mechanical tester (developed in-house) was used to determine the tensile properties of the mesh (Figure 2). The method for preparing a specimen for testing was reported in previous papers [15, 35]. Briefly, the specimen first had to be mounted across a rectangular aluminum frame (known as the 'template'; Figure 2). After securing the specimen onto the template using cyanoacrylate adhesive, the template was mounted on the grips of the tester. Before the test commenced, the borders of the template adjacent to the specimen were severed using a pair of scissors. The tester was mounted onto the stage of a conventional microscope for real-time monitoring of the specimen during testing. The microscope was also used for measuring the thickness and width of each specimen to derive the cross-sectional area (α), which was used in the calculation for the nominal stress generated in the mesh. During mechanical testing, the test specimen was stretched to rupture at a displacement rate of 3.6 mm/min, i.e. 0.06 mm/s [8, 35, 36]. For the hydration test, the mounted specimen would be submerged in water held in a petri dish.

Force (F) and grip-to-grip displacement (Δ) were recorded for each specimen by the loadcell and the strain transducer. From these data, the corresponding nominal stress ($= F/\alpha$) and strain ($= \Delta/L_g$) were determined. Here, L_g is the gauge length of the specimen which corresponds to the initial grip-to-grip distance (adjusted until just before the specimen became taut). A straight line was fitted to the points along the initial part of the stress-strain curve where the region featured a linear stress-strain response. The yield strength and yield strain were identified at the point beyond the limit of proportionality, which was defined as the yield point. The gradient of the linear region was used to parameterize the stiffness of the mesh, E . In addition, the area under the curve from the origin to the yield point was determined to parameterize the elastic strain energy density, u_v , until yielding (otherwise known as resilience). The strain energy density to fracture (otherwise known as toughness) u_f , of the mesh was determined from the area under the curve from the origin to the point of rupture.

Data derived for the mechanical properties can be found in Table 3 in Ref [34].

4.4 Statistical analysis

We tested the null hypotheses that (1) hydration has no effect on the mechanical properties, (2) HNT has no effect on the mechanical properties and (3) no interaction between the factors, i.e. the effect of the state of hydration does not differ between HNT concentrations, or equivalently the effect of HNT concentration does not differ between the state of hydration, versus the alternative hypotheses. A two-factor ANOVA, using commercial software (Minitab, version 17, Minitab Inc.), was carried out to evaluate the hypotheses. The two factors referred to hydration (levels: hydrated, dry) and HNT concentration (levels: 0, 1%) treatments. Five specimens were tested for each treatment level. Further analysis by two-sample t-test were carried out to

determine the level of significance of the state of hydration for each level of HNT concentration and vice versa. Differences were considered statistically significant at $p < 0.05$.

5 Results

5.1 Microscopic morphological analysis

HNTs appeared as whisker-like particles with blunt ends as shown in the SEM image in Figure 3 (A). At higher magnification, it was possible to discern the lumen (lighter shade along the tube's axis) of the HNT as pointed out by the arrows shown in the STEM image (Figure 3 B). The HNT in Figure 3 (B) has a length of about 800 nm and outer diameter of 100 nm. According to Eq. (5), this gives an aspect ratio, q , of 16. With regards to the dispersion of HNTs, some HNTs were found, possibly, within very thin PAN fibres as shown in the STEM images (Figure 3 C and D); the examples shown here revealed that these HNTs were aligned along the fibre axis. HNTs were also found on the surfaces of PAN fibres, and particular attention is drawn to the those circled as shown in the SEM images (Figure 3 E and F).

Figure 4 shows SEM images of PAN and PAN/HNT meshes at two different magnification levels. It was observed that the PAN and PAN/HNT meshes shared some common geometrical features: (1) a randomly oriented arrangement of fibres; (2) fibres aligning side-by-side, suggesting that fusion occurred between these fibres. No textural differences were observed between the fibres of the PAN and PAN/HNT meshes (Figure 4 A and B). At low magnifications, the surface of the fibres appeared to be somewhat smooth; at higher magnification (Figure 4 C and D and inset), the finer structure revealed granular features on the surface of the fibres, and certain sections along the fibres appeared thicker than others. These granular structures did not occur with a periodicity and did not all run parallel.

Figure 5 A and B show the histograms of the normalized frequency of D_f and D_p for the respective PAN and PAN/HNT meshes. The profiles of the D_f distribution for the PAN and PAN/HNT meshes overlapped considerably and followed a somewhat normal distribution with a mean of 0.5 μm and 0.6 μm (identified by the highest frequency). The mean D_f of the PAN/HNT meshes were larger than that of the PAN mesh. The PAN mesh exhibited wider variability about the mean value (0.30 μm to 0.75 μm) than the PAN/HNT mesh (0.45 μm to 0.75 μm). With regards to the pore size, the D_p distribution profiles of the PAN and PAN/HNT meshes featured a left-skew shape (Figure 5 C and D); in both cases the peak frequency occurred at 2 μm . With regards to the PAN mesh, the D_p distribution profile revealed a long (right) tail of large D_p s although the number was relatively small compared to the peak at 2 μm . On the other hand, the D_p distribution profile of the PAN/HNT meshes revealed an absence of a long (right) tail.

5.2 Stress versus strain relationships

In all specimens, the stress reached a maximum value, followed by a decrease in the stress until rupture occurred. Of note, the dry specimens were more brittle than the wet specimens. For the dry specimens this brittle nature was consistent with a higher rate of change of stress with respect to strain in the region beyond

the maximum stress, compared to the wet specimens. Consequently, fewer data points could be acquired in this region.

The overall profile of the stress-strain curves from the dry PAN mesh and dry PAN/HNT mesh appeared to deviate little from one another (Figure 6 A), suggesting that the presence of HNT did not lead to drastic change in the mechanical response of dry meshes. On the other hand, the curves of the respective hydrated PAN and PAN/HNT meshes showed an appreciably differentiated mechanical response (Figure 6 B), suggesting that the presence of HNT and the hydration of PAN-based fibrous meshes could result in a drastic change in the mechanical properties of the mesh.

5.3 Main effects and interactions

The bar-charts in Figure 7 show that the magnitudes of the elasticity-related properties, namely E , σ_Y and u_Y , of the hydrated specimens appeared somewhat less scattered about the mean value, compared to those of the dry specimens. On the other hand, the magnitudes of the ε_Y of the hydrated and dry specimens appeared to scatter over a similar range of values. The bar-charts show that the means of E , σ_Y and u_Y , of the dry specimens were higher than those of the hydrated specimens. However, the means of ε_Y of the dry and hydrated specimens revealed no significant differences.

Only the E (Figure 7 A) and σ_Y (Figure 7 B) of the hydrated specimens were sensitive to the presence of HNT. In particular, the mean E and σ_Y of the hydrated PAN/HNT meshes were higher than those of the PAN mesh. Accordingly, Figure 7 shows that the mean values of other parameters revealed no significant differences between PAN and PAN/HNT. In other words, the magnitudes of the E , σ_Y , ε_Y , and u_Y of the dry specimens and the magnitudes of the ε_Y and u_Y of the hydrated specimens were not influenced by the presence of HNT.

With regards to the fracture parameters, the bar-charts in Figure 8 A and C show that the magnitudes of the σ_U and u_F of the hydrated specimens appeared somewhat less scattered about the mean value, compared to those of the dry specimens. On the other hand, the extent of the scatter in the magnitudes of the ε_U in both the hydrated and dry specimens appeared similar (Figure 8 B).

As illustrated in the bar-chart in Figure 8, the magnitudes of the mechanical properties, namely ε_U , σ_U and u_F , of the dry specimens were generally higher than those of the hydrated specimens, with the exception of the ε_U of the PAN/HNT mesh (Figure 8 B) which showed no significant difference between dry and hydrated specimens. Only the ε_U , σ_U and u_F , of the hydrated specimen were sensitive to HNT; the ε_U , σ_U and u_F , of the dry specimen were not affected by the presence of HNTs.

For the hydrated specimens, the magnitude of the σ_U of the PAN/HNT mesh were higher than that of the PAN mesh (Figure 8 A). However, the magnitudes of the ε_U (Figure 8 B) and u_F (Figure 8 C) of the PAN/HNT mesh were lower than those of the PAN mesh.

Finally, with regards to the possible effects arising from the interaction between the two factors (hydration and HNT) on the mechanical parameters of the PAN meshes associated with elasticity and fracture properties, in all cases, it was observed that there was no significant interaction between the two factors ($P > 0.05$).

This study has shown that hydration affects the elasticity and fracture properties of the PAN mesh significantly. Hydrated electrospun PAN/HNT meshes at 1 % w/w (HNT) resulted in significant increases in E , σ_v , and σ_u but yielded significant decreases in u_f and ε_u as compared to the hydrated PAN meshes. Of note, the E , σ_u and ε_u of the dry specimens tested using the environmental micromechanical tester yielded similar order of magnitudes to those obtained from previous study which employed the TA XT Plus Texture Analyzer [5]. While both the micromechanical tester and Texture Analyzer tester are of comparable accuracy with respect to the displacement rate, load and displacement measurements, the choice of the micromechanical tester (which possessed a horizontal test frame) allowed for sensitive testing of the specimen when submerged in water which would otherwise be less straight-forward to implement with the Texture Analyzer tester (which possessed a vertical column test frame).

6 Discussion

6.1 Effects of electrospinning on fibre size

Our estimate of the fibre diameter (D_f) yielded a mean value of 0.5 μm and 0.6 μm for the PAN and PAN/HNT meshes, respectively (section 5.1). The larger D_f associated with the latter meshes is attributed to the alteration of the flow dynamics of the exudate by the HNTs during the electrospinning process. Neglecting the effect due to evaporation of the solvent and solution, assuming that the exudate exhibited a Newtonian flow and the PAN and HNT possessed negligible charge carrying capacity, the D_f derived from the electrospinning process could be estimated to order of magnitude by

$$D_f = [\gamma\mu\{Q^2/I^2\}[2/\pi]/(2\ln(L/D_0-3))]^{1/3} \quad (14)$$

[6, 37], where γ is the surface tension of the solution, μ the dielectric constant, I the electric current in the jet, Q the flow rate of the solution, L the initial jet length, and D_0 the nozzle diameter, for processing the PAN fibres, the key factors that control the dynamics of the whipping jet and henceforth the D_f , are Q , I and γ . Given all things being equal, i.e. Q , I , L and D_0 , as well as the μ of PAN and PAN/HNT, to order of magnitude, the surface tension of the PAN solution and the PAN/HNT could be estimated by substituting the values of the diameter of the PAN and PAN/HNT fibre at peak frequency into Eq. (14). Numerically, the ratio of the surface tension of PAN to PAN/HNT solution is equal to $(0.50 \mu\text{m}/0.60 \mu\text{m})^3 = 0.58$. (In other words, the surface tension of the solvent for the PAN is about one-half that of the PAN/HNT.) Surface tension of solvent has a positive effect on the fibre diameter[38]. From a structure-property relationship perspective, it is often argued that the mechanical properties of the meshes is dependent on the fibre diameter: the larger the fibre diameter, the lower is the σ_u and E [6]. Thus, it is not surprising that the electrospun PAN meshes with smaller D_f (0.03 to 0.30 mm) yielded a higher σ_u (= 265 MPa), and higher E (= 4.5 GPa) [39] with respect to our results. The sensitivity of the mechanical properties of the meshes to D_f could outweigh that of the molecular weight of the PAN. The PAN molecular weight used in this study was higher than that used in the study carried out by Ge and co-worker [39]. The lack of difference in the respective mechanical properties between dry PAN and PAN/HNT meshes is also not

surprising as there was no appreciable difference in the mean D_f between the PAN and PAN/HNT and there was also an extensive overlap in the spread of the D_f values about the (peak) value.

What advantage can a small D_f confer on the efficiency of water filtration mesh? With regards to filtration application, the efficiency of a filter increases with decrease in D_f [6, 33]. The design of an efficient filter requires that the pores and structure of the fibre of a filter to be of comparable length scale to the particles or droplets [33]. Our pore size measurement (Figure 5 C and D) revealed pore diameter (D_p) ranging 1 μm to 15 μm ; thus the PAN and PAN/HNT fibrous meshes may be effective at filtering out tiny particles of the order of $> 1 \mu\text{m}$. Small D_f may have another advantage: it can result in high surface area to volume ratio and this could generate high surface cohesion [33]. Further discussion about the performance of the mesh for water filtration is found in section 6.4.

6.2 *Effects of water uptake on mechanical properties*

As pointed out in section 2, the "nanotubes in the nanofibres" of the PAN/HNT meshes may be considered as an example of particles reinforcing composites [12] in which the HNTs provide tensile reinforcement to the PAN-based composite fibre. What could have resulted in the diminution in the E and σ_U of both PAN and PAN/HNT meshes in the presence of water as shown in section 5.3? (Of note, this could not be attributed to water being a solvent for PAN because water only becomes a solvent for PAN at temperatures of around 210 $^{\circ}\text{C}$ [40].) We examine more fundamentally why this should be so in the following paragraphs.

To begin, according to equation (7), the parameters governing the structural changes are namely α_{HNT} , α_{PAN} and $V_{\text{H}_2\text{O}}$. To predict the values of these parameters, first, using representative values, namely density of HNT = 2.53 g/cm^3 and PAN = 1.184 g/cm^3 (Sigma Aldrich material data sheet), it follows that a 1% (w/w) HNT concentration corresponds to a volume fraction, $V_{\text{HNT}} = 0.0047$. Consequently, one finds that $V_{\text{PAN}} = 1 - V_{\text{HNT}} = 0.9953$. Assuming that the α_{PAN} will be comparable to the ratio of the σ_{US} of wet to dry PAN meshes, $[(\sigma_U)_{\text{wet}}/(\sigma_U)_{\text{dry}}]_{\text{PAN}}$, it is predicted that, to order of magnitude, $\alpha_{\text{PAN}} = (\sigma_U)_{\text{wet,PAN}}/(\sigma_U)_{\text{dry,PAN}} = 0.1532$, based on the mean values of σ_U taken from Table 2. Similarly, assuming that the α_{HNT} will be comparable to both the ratio of σ_{US} of wet to dry PAN/HNT meshes, $(\sigma_U)_{\text{wet,PAN/HNT}}/(\sigma_U)_{\text{dry,PAN/HNT}}$, it is found that, to order of magnitude, $\alpha_{\text{HNT}} = (\sigma_U)_{\text{wet,PAN/HNT}}/(\sigma_U)_{\text{dry,PAN/HNT}} = 0.1453$, based on the mean values of σ_U taken from Table 2. The presence of water will change the relative amount of the HNT and PAN, so that the effective volume fractions of HNT and PAN become $\alpha_{\text{HNT}}V_{\text{HNT}} = 0.0007$ and $\alpha_{\text{H}_2\text{O}} = 0.1525$, respectively. One can use Eq. (7) to estimate proportion of water trapped in the mesh: one then finds that $V_{\text{H}_2\text{O}} = 1 - \alpha_{\text{PAN}}V_{\text{PAN}} - \alpha_{\text{HNT}}V_{\text{HNT}} = 0.8468$. The predicted value of $V_{\text{H}_2\text{O}}$ is not an unrealistic estimate because this is in good agreement with the results from SEM which we will explain as follows. We note that the parameters associated with volume fraction in Eq. (3), (1), (9) and (8) are essentially extensions of the cross-sectional area fraction [12]. Thus, the volume fraction of the pore (V_p) observed in SEM (Figure 4) is of the order of $(D_p)^2/(D_p^2 + D_f^2)$. Since the $D_p = 2.0 \mu\text{m}$ (peak) and mean D_f is $0.5 \mu\text{m}$ for PAN fibres (or $0.6 \mu\text{m}$ for PAN/HNT fibres), one finds that $V_p \approx 0.9$, which is in good order-of-magnitude agreement with the predicted value of $V_{\text{H}_2\text{O}}$. For informational purpose, the predicted volume fractions are tabulated in Table 4.

This paragraph is concerned with a technical discussion addressing the extent to which the σ_U and E predicted using the derived values of α_{HNT} , α_{PAN} and V_{H_2O} , are consistent with the micromechanical test results derived from the current study. We compare the predictions from the models described by Eq. (1), (3), (7) and (9) with the experimental results. With regards to Eq. (1) we note that the $\sigma_{HNT} = 2000$ MPa [41] (Table 3). The average stress (σ_{PAN}) in the PAN material is identified with the mean $\sigma_U (= (\sigma_U)_{dry,PAN})$ associated with the PAN mesh derived from our experimental study (Table 2), i.e. $\sigma_{PAN} \approx (\sigma_U)_{dry,PAN} (= 25$ MPa, Table 2). Substituting these values of σ_{HNT} (Table 3), σ_{PAN} (Table 2), V_{HNT} and V_{PAN} (Table 4), into Eq. (1), we find that the predicted fracture strength of the dry PAN/HNT mesh, $\sigma_U = 34.1$ MPa, which is in close agreement with the experimentally derived mean value of $\sigma_U (= 35.8$ MPa, Table 2). We next examined the consistency with regards to the prediction of E for the dry PAN/HNT mesh. According to studies on the direct measurement of the bending stiffness of HNT, E_{HNT} may be set to 130 GPa [42] (Table 3). The structural stiffness of neat PAN mesh, E_{PAN} , is identified with the mean $E (= (E)_{dry,PAN})$ derived from our experimental study, i.e. $E_{PAN} \approx (E)_{dry,PAN} (= 275$ MPa, Table 2). This is not unrealistic given that E_{PAN} is clearly more compliant than single PAN nanofibres, which has a stiffness of about 26.8 GPa [43]. Substituting these values of E_{HNT} (Table 3), E_{PAN} (Table 2), q (Table 3), V_{HNT} (Table 4), into Eq. (3) and setting the scale factor $c = 1.66$, it follows that the predicted stiffness of the dry PAN/HNT mesh is given by $E = 491$ MPa, which is in close agreement with the experimentally derived mean value of $E (= 492.0$ MPa, Table 2). For the hydrated PAN-based mesh, with regards to fracture strength, substituting $\sigma_{HNT} = 2000$ MPa (Table 3), $\sigma_{PAN} \approx (\sigma_U)_{dry,PAN} (= 25$ MPa, Table 2), and $\alpha_{HNT}V_{HNT}$ and $\alpha_{PAN}V_{PAN}$ (Table 4), into Eq. (8), it follows that the predicted fracture strength of the hydrated PAN/HNT mesh is given by $\sigma_U = 5$ MPa, which is also in close agreement with the experimentally derived mean value of $\sigma_U (= 5.2$ MPa, Table 2). Finally, with regards to the stiffness of hydrated PAN/HNT mesh, substituting the values of E_{HNT} (Table 3), E_{PAN} (Table 2), q (Table 3), and $\alpha_{HNT}V_{HNT}$ (Table 4), into Eq. (9), and setting $c = 0.22$, numerically it follows that the $E = 61$ MPa, which is in close agreement with the experimentally derived mean value of $E (= 61.6$ MPa, Table 2).

To examine more fundamentally why the PAN/HNT mesh exhibited higher stiffer and strength than the PAN mesh when both were hydrated, we shall examine the ratio, V_{HNT}/V_{PAN} . In previous paragraph, it was argued that for dry PAN/HNT meshes, $V_{HNT} = 0.047$ and $V_{PAN} = 0.9935$ (Table 4); numerically we find that $(V_{HNT}/V_{PAN})_{dry} \approx 0.0047$. for hydrated PAN/HNT meshes, $V_{HNT} = 0.007$ and $V_{PAN} = 0.1525$ (Table 4); numerically we find that $(V_{HNT}/V_{PAN})_{wet} \approx 0.0045$. Since $(V_{HNT}/V_{PAN})_{wet} < (V_{HNT}/V_{PAN})_{dry}$, it is concluded that the presence of water in the mesh resulted in a reduction in the effective volume fraction of PAN than HNT. These differences are small and not based on a detailed experimental study, but they indicate that when water is present the relative HNT concentration increases and the relative PAN concentration decreases.

The mathematical arguments in previous paragraphs have provided insights into the effects of the interplay between the HNT and PAN on the σ_U and E in the presence of hydration. To what extent do these arguments apply to the other mechanical properties? It is impossible to answer this question with any certainty because no similar mathematical model exists for these mechanical parameters, e.g. ϵ_U and u_F ; the rule-of-mixture argument does not lend readily to these parameters. Entangled fibres could hinder extensive relative displacement in the

absence of water; when the PAN/HNT mesh is soaked in water, the presence of water, i.e. within the inter-fibre spaces, may facilitate the sliding action of the fibres. Thus, the extensibility (a strain-related parameter) of the meshes was enhanced when the mesh was hydrated. On the other hand, the u_F of the hydrated mesh was lower than the dry mesh suggesting that changes in the extensibility did not parallel changes in fracture toughness. One might argue that since u_F is proportional to the product of stress and strain, the result was that the stress-related component in both hydrated and dry meshes predominated the strain-related component and thus masked any effects that could be caused by the strain-related component.

6.3 Validity of the model

As a test of the validity of the model for predicting the water flux through a given membrane—described by equations (11) to (13)—we considered an earlier investigation on oil-water separation experiment using the PAN and PAN/HNT (1 % w/w HNTs) fibrous meshes [5]. In this study, a dead-end filtration module (Syringe Filter Holder 25 mm, Sartorius) was used to separate water from an emulsion of vegetable oil (1350 ppm) in water (stabilised by Tween20 surfactant at 125 ppm) at a constant flow rate of 0.4 mL/min, at $T = 300$ K. Results from ultraviolet visible light spectroscopy to evaluate the solute concentrations in the feed and permeate solutions revealed that the oil concentration of the filtrate was less than 7 ppm. Thus, the PAN/HNT fibrous mesh exhibited an oil rejection of 99%. Whereas the PAN fibrous mesh yielded a flux rate of 81 L/m²h, the PAN/HNT fibrous mesh yielded a flux rate of 86 L/m²h, which was marginally higher (1.06 times) than that the former.

Let us consider more fundamentally why this should be so. To begin, the water permeability of the mesh (equation (12)), namely $p_{w,PAN}$ and $p_{w,PAN/HNT}$, depends on a number of factors: the presence of nanochannels and the concentration of hydroxyl groups in the HNTs [5]. The water flux (equation (13)) may increase if there is an overwhelming increase in the number of internal nanochannels, translating to an increase in the net surface area of the PAN/HNT fibrous mesh and higher water permeability. The water flux (equation (13)) may also decrease depending on the available hydroxyl groups in the HNT lumen. Of note, a large proportion of the aluminols of the halloysite is located inside the HNT structure while a small proportion of the aluminols and silanols are confined to the edge of the HNT sheet, and siloxanes dominate the outer surface of the HNT [14]. Comparing HNTs with other nanoclays and nanosilica, one may argue that the relatively lower content of hydroxyl groups on the HNT surface implies that HNT is relatively hydrophobic [14]; this feature would not be advantageous for water filtration. On the other hand, the lumen of the tubular structure of HNTs can facilitate water uptake and accommodate water in the lumen by the nanotube capillarity [44]. If water is intercalated in the lumen, this would terminate the flow of water through the HNT lumen and the entire HNT becomes predominantly hydrophobic. Thus, this could decrease the water permeability (i.e. p_w) of the PAN-based meshes when HNTs are present. In this simplified treatment, if one assumes that both factors result in comparable effects which negates one another, to order of magnitude estimate, it seems reasonable to take $p_{w,PAN/HNT} \approx p_{w,PAN}$, which is of the order of 10⁻⁹ m²/s [30]. The nature of this assumption can also be understood by noting that the flux rate of electrospun PAN mesh containing 1 % (w/w) HNTs is somewhat marginally higher (=1.06 times) than PAN mesh [5], suggesting that water permeability of the membrane is somewhat altered in the presence of HNTs.

Noting that v_w is of the order of 0.018×10^{-3} mL/mol, we thus predict that v_w/RT (equation (12)) will be of the order of 7.2×10^{-6} L/J. The solution diffusion model has been applied to study membranes for oil-water separation [27, 28]. To evaluate the performance of the PAN-based mesh, with a practical value of $\Delta\pi = 2400$ Pa for the osmotic pressure [45], the realistic upper bound of $J_{w,PAN}$ (equation (11)) can be estimated to order of magnitude by replacing Δp_{DP} by $[\sigma_U]_{PAN}$ ($= 3.8$ MPa, equivalent to 551 psig); one finds the upper bound $J_{w,PAN} = p_{w,PAN}(v_w/RT)([\sigma_U]_{PAN} - \Delta\pi)$. Similarly, the realistic upper bound of $J_{w,PAN/HNT}$ (equation (13)) can be estimated to order of magnitude by replacing Δp_{DP} by $[\sigma_U]_{PAN/HNT}$ ($= 5.2$ MPa, equivalent to 754 psig); one finds the upper bound $J_{w,PAN/HNT} = p_{w,PAN/HNT}(v_w/RT)([\sigma_U]_{PAN/HNT} - \Delta\pi)$. Assuming all things being equal, numerically one finds that the upper bounds $J_{w,PAN/HNT} = 135$ L/m²h and $J_{w,PAN} = 99$ L/m²h. These estimates are not unrealistic as they are clearly higher than the J_w values (namely 86 L/m²h and 81 L/m²h) derived experimentally for normal applied pressures. We can use the ratio $J_{w,PAN/HNT}/J_{w,PAN}$ to estimate the theoretical performance of the PAN/HNT mesh relative to the PAN mesh. We then find that $J_{w,PAN/HNT}/J_{w,PAN} = 1.3$. We thus conclude that the PAN/HNT mesh can support water flux to 1.3 times higher than that of PAN mesh without breaking apart during the oil-water separation process. The theoretical performance was parameterized by $J_{w,PAN/HNT}/J_{w,PAN}$, where the respective water flux was determined in terms of the fracture strength of the mesh—amongst other factors namely the volume fraction reduction ratio, fibre diameter and pore size—to show the nature of the HNT for reinforcing the PAN in oil-water separation application.

6.4 Predicting the performance of the PAN/HNT mesh for desalination

To further demonstrate the versatility of the model just presented, let us next consider how the model can be used to evaluate the performance of the PAN/HNT mesh during desalination. Our goal is to develop simple order-of-magnitude predictions that describe the theoretical performance of the mesh parameterized by $J_{w,PAN/HNT}/J_{w,PAN}$. With a practical value of $M = 1.13$ mol L⁻¹ for the total ionic concentration in sea water [46], the osmotic pressure that must be applied to prevent osmotic flow of pure water into sea water—through a membrane permeable only to water molecules—is given by $\Delta\pi = MRT = (1.13 \text{ mol L}^{-1})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = 27.6 \text{ atm}$ or 2.8 MPa. In this simplified treatment, the water permeabilities (namely $p_{w,PAN/HNT}$, $p_{w,PAN}$) will be of the order of 10^{-9} m²/s [30] (section 6.3). Recall in section 2, the upper bound of Δp_{DP} is identified with the fracture strength of the mesh (σ_U) described by Eq. (8). To estimate the performance of the PAN mesh for maximum flux during desalination, according to equation (13), the realistic upper bound of $J_{w,PAN}$ should be $\propto p_{w,PAN}([\sigma_U]_{PAN} - \Delta\pi)$ (where $\Delta\pi = 2.8$ MPa); similarly, with regards to the PAN/HNT mesh the realistic upper bound of $J_{w,PAN/HNT}$ should be $\propto p_{w,PAN/HNT}([\sigma_U]_{PAN/HNT} - \Delta\pi)$. Recall that the means $[\sigma_U]_{PAN} = 3.8$ MPa (551 psig) and $[\sigma_U]_{PAN/HNT} = 5.2$ MPa (754 psig)—these estimates suggest that the PAN/HNT mesh is viable for ultrafiltration because the typical ultrafiltration PAN membrane is expected to perform at an operating pressure of about 50 psig (Table 1). Assuming all things being equal, it follows that the $J_{w,PAN/HNT}/J_{w,PAN} = p_{w,PAN/HNT}([\sigma_U]_{PAN/HNT} - \Delta\pi)/[p_{w,PAN}([\sigma_U]_{PAN} - \Delta\pi)] \approx 2.4$. This has an important and immediate consequence for the water passing through the mesh, per unit mesh area: the theoretical performance of the PAN/HNT mesh is such that it can support a water flux of 2.4 times higher than that of PAN mesh during the desalination process without breaking apart.

7 Conclusions

This study has assessed the effects of water on the mechanical properties of electrospun PAN mesh and PAN/HNT mesh to address the significance of this study, i.e. the fundamental understandings of the mechanical stability of the PAN/HNT mesh underpinning the influence of water within the fibre-fibre interspace during water permeation. The novelty of our study addresses a conceptual framework for the relationship between the mechanical properties of the PAN/HNT mesh and structure of the PAN-based fibre to allow for useful predictions of their expected performance.

Our findings are summarized as follows.

(1) The mechanical properties of both dry PAN and PAN/HNT meshes were not significantly different.

(2) The mechanical properties of the hydrated mesh were lower in magnitude compared to the dry meshes, with exception of yield strain and strain at rupture which showed no significant differences between the hydrated and dry meshes.

(3) In the hydrated state, PAN/HNT mesh possessed higher yield strength, and was stiffer and stronger than the PAN mesh but possessed lower strain to rupture and fracture toughness than the PAN mesh.

(4) Based on a solution diffusion model that considers the mesh fracture strength argument with implicit dependence on volume fractions of the respective components in the mesh, estimates of the theoretical performance of the PAN/HNT mesh revealed that it could support water flux of 2.4 times higher than that of PAN mesh during the desalination filtration process without breaking apart.

(5) The water-related effects are attributed to the filling up (and possibly the swelling) of the fibre-fibre interspace, which decreases the effectiveness for load transfer between fibres during load uptake owing to differential reduction of the volume fractions of the respective PAN and HNT phases.

There have been many studies on electrospun PAN-based fibrous mesh since the early works of, e.g. Fennesey and Farris [47]. Indeed several different PAN-based meshes have been used to investigate the same problem: water filtration [6]. It is likely that the results of this study, and the underpinning arguments, will be adapted to enable a wider variety of PAN-based meshes to be designed, such as the thin film composite design consisting of crosslinked polyamide layer on a microporous PAN support [48], and to be explored, making it possible to draw more general conclusions and leading to meshes with enhanced mechanical properties.

8 Declaration of Conflicting Interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and publication of this article.

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10 Data availability

The raw data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study. The processed data required to reproduce these findings are found in Ref [34].

11 References

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12 Figure captions

Figure 1. Schematics of the local environment of the PAN/HNT fibrous meshes in the (A) dry state and (B) hydrated state. When water enters the fibre-fibre interspace, the hydrostatic pressure acts on the fibre and results in a net increase in the overall volume of the occupied space, as the fibres are spaced further apart.

Figure 2. Schematics of the synthesis of PAN-based meshes by electrospinning. (A) PAN-based fibres emerges from a spinet and is collected by a rotating drum. (B) Sectioning the PAN-based meshes into rectangular specimens for testing. For the respective PAN and PAN/HNT meshes, a randomized process was used to select the specimens for testing; for the respective PAN and PAN/HNT meshes, the selected specimens were divided equally into two groups, i.e. one group was tested in the hydrated state while the other group was tested in the dry state.

Figure 3. Electron micrographs of HNTs. (A) HNT agglomerates (SEM). (B) An isolated HNT (STEM). (C)-(D) HNTs along PAN fibres (STEM). (E)-(F) HNTs on PAN fibres (SEM).

Figure 4. Scanning electron micrographs of PAN-based meshes. Panels A and C show neat PAN meshes at low and high magnifications (scale bar 10 and 5 μm) respectively. Panels B and D show PAN/HNT meshes at low and high magnifications (scale bar 10 and 5 μm) respectively.

Figure 5. Structural properties. Histograms of normalized frequency of fibre diameter of the respective (A) PAN and (B) PAN/HNT meshes and pore diameter of the respective (C) PAN and (D) PAN/HNT meshes. Data used for the respective fibre diameter and pore diameter histograms represent the mean $\pm$ SE (standard error of the mean), derived by evaluating the normalized frequency values from three neat PAN (panels A, C) and three PAN/HNT (panels B, D) meshes.

Figure 6. Typical stress versus strain curves of PAN-based meshes in the (A) dry and (B) hydrated states.

Figure 7. Elasticity-related properties of PAN-based meshes. Graph of (A) stiffness, E , (B) yield strength, σ_y , (C) yield strain, ε_y , and (D) strain energy density to resilience, u_y . Symbol * represents $p < 0.05$; NS represents not significant.

Figure 8 Fracture properties of PAN-based mesh. Graph of (A) maximum stress, σ_u , (B) strain at maximum stress, ϵ_u , and (C) strain energy density to rupture, u_f . Symbol * represents $p < 0.05$; NS represents not significant.

13 Figures

Figure 1

Figure 2

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Figure 4

Figure 5

Figure 8

14 Tables

Table 1. PAN-based membranes for ultrafiltration: findings from some research studies and performance of commercially available ones

Membrane construct	Features of significance	Ref.
PAN mesh	<ul style="list-style-type: none"> Desalination performance (e.g. life-time and efficiency) was enhanced by preoxidation of PAN in high temperature environment and oxidative atmosphere (oxygen, air, carbon dioxide and NH₃) to facilitate crystallization through efficient chain packing-by adjusting the charged moieties of mesh surface and microstructure in mesh-in PAN amorphous phase Results showed rejection rate of 98% after 5 minutes; the rejection rate could be maintained at this level for up to 20 minutes 	[49]
PAN/Nafion mesh	<ul style="list-style-type: none"> Sulfonated tetrafluoroethylene based fluoropolymer-copolymer (Nafion), improves absorption of heavy metal ions by providing a net negatively charged surface on PAN fibre Absorption rate of Cr (III) ions by neat PAN (5% at 20 minutes, 25% at 180 minutes) improved dramatically when blended with nafion (30% at 20 minutes, 45% at 180 minutes) 	[25]
PAN/HNT mesh	<ul style="list-style-type: none"> HNT features a negatively charged surface Capable of absorbing heavy metal ions in contaminated water (for a recent review, see Yu et al. [13]); exhibits removal efficiency of 10-31% for Cu(II) ions Capable of oil-water separation (oil concentration of the filtrate was less than 7 ppm) to 99%, resulting in a highly transparent water permeate Exhibits enhanced water flux rate 	[5]
PAN laminate	<ul style="list-style-type: none"> Two-layer laminated mesh, comprising PAN fibrous mesh and chitosan/ZnO layer Capable of removing heavy metal ions, such as Cr(III); exhibited removal efficiency of about 34% for Cr(III) ions Useful for bacteria filtration; a bacteria filtration test revealed that the laminated mesh yielded a log reduction value = 6 for E. coli and E. faecalis Exhibited antibacterial action, i.e. able to resist biofouling; exhibited a log reduction value = 6 on the 4th hour (a measure of the time of kill) 	[50]
PAN laminate	<ul style="list-style-type: none"> Three-layer laminated mesh, comprising PAN fibrous layer sandwiched between non-woven PET and PAN layers For arsenate removal from contaminated water; rejection rate of 100 % for 8 hours at a pressure of 2 bars 	[32]
Laminate	<ul style="list-style-type: none"> Two-layer laminated mesh, comprising PAN mesh on polyethylene terephthalate substrate Membrane thickness = 180 to 200 µm. Average bubble point of more than 4.1 bar Traps particulates down to 0.2 µm in diameter Capable of withstanding temperatures below 100 °C Log retention value (=6) for bacteria, namely E.coli, R.Terrigena, B.Diminuta 	Steritech, www.steritech.com
PAN laminate	<ul style="list-style-type: none"> Can trap particulates down to size of 0.01 µm Capable of withstanding pressures of about 200 psig (equivalent to a differential pressure of 13.8 bar or 1.4 MPa) at 25 °C or lower than 200 psig if the membrane is subjected to higher temperatures, e.g. 50 °C (NB: typical ultrafiltration membrane operating pressure is around 50 psig) 	Applied Membranes www.appliedmembranes.com

Table 2. Descriptive statistics (mean $\pm$ SE) of the mechanical properties of the PAN and PAN/HNT meshes in the dry and wet states.

Mesh	State	E (MPa)	σ_Y (MPa)	ε_Y	u_Y (MPa)	σ_U (MPa)	ε_U	u_F (MPa)
PAN	Dry	274.0 $\pm$ 92.3	12.5 $\pm$ 7.1	0.050 $\pm$ 0.019	1.06 $\pm$ 0.45	24.8 $\pm$ 10.0	0.127 $\pm$ 0.015	1.92 $\pm$ 0.86
PAN	Wet	24.6 $\pm$ 3.0	0.6 $\pm$ 0.3	0.049 $\pm$ 0.025	0.07 $\pm$ 0.03	3.8 $\pm$ 0.1	0.334 $\pm$ 0.032	0.80 $\pm$ 0.11
PAN/HNT	Dry	492.0 $\pm$ 143.6	17.1 $\pm$ 5.7	0.069 $\pm$ 0.012	0.71 $\pm$ 0.08	35.8 $\pm$ 10.4	0.156 $\pm$ 0.015	3.07 $\pm$ 1.09
PAN/HNT	Wet	61.6 $\pm$ 2.2	1.8 $\pm$ 0.4	0.045 $\pm$ 0.011	0.10 $\pm$ 0.01	5.2 $\pm$ 0.3	0.144 $\pm$ 0.020	0.47 $\pm$ 0.09

E – Stiffness, σ_Y – Yield Strength, ε_Y – Yield Strain, u_Y – Resilience Energy, σ_U – Fracture Strength, ε_U – Strain at Fracture Strength, u_F – Fracture Toughness, SE – standard error of the mean

Table 3. Input parameter values used for mathematical modelling of PAN/HNT mesh

Parameter	Value	Reference
Fracture strength of HNT, σ_{HNT} (MPa)	2000	[41]
Fracture strength of PAN mesh, $\sigma_{U,PAN}$ (MPa)	24.8	This study
Young's modulus of HNT, E_{HNT} (GPa)	130	[42]
Young's modulus of PAN, E_{PAN} (MPa)	274.6	This study
Density of HNT (g/cm ³)	2.53	Sigma Aldrich material data sheet
Density of PAN (g/cm ³)	1.184	Sigma Aldrich material data sheet
Coefficient associated with HNT volume fraction, α_{HNT}	0.1453	This study
Coefficient associated with PAN volume fraction, α_{PAN}	0.1532	This study
HNT aspect ratio ("slenderness"), q	16	This study

Table 4. Predicted volume fractions of HNT, PAN and water in the PAN/HNT mesh.

State of mesh	Volume fraction		
	HNT	PAN	Water
Dry	0.0047	0.9953	-
Wet	0.0007	0.1525	0.8468