Multifunctional air filtration for respiratory protection using electrospun nanofibre membrane

A thesis submitted in fullfilment of the requirements for the degree of Doctor of Philosophy

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August 2018
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

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Signed: Vinod Kadam

Date: August 2018
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Dedication

This thesis dedicated to my beloved late father and my two little angels.
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller principle</td>
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<tr>
<td>BTCA</td>
<td>1,2,3,4-butane tetracarboxylic acid (BTCA)</td>
</tr>
<tr>
<td>ACGIH</td>
<td>American Conference of Governmental Industrial Hygienists</td>
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<tr>
<td>Al₂O₃</td>
<td>Aluminium oxide</td>
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<tr>
<td>CAAA</td>
<td>Clean Air Act Amendments of 1990, USA</td>
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<tr>
<td>CO</td>
<td>Carbon monoxide</td>
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<td>CO₂</td>
<td>Carbon dioxide</td>
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<td>cPs</td>
<td>Centipoise</td>
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<tr>
<td>DMF</td>
<td>N-Dimethylformamide</td>
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<tr>
<td>DP-MS</td>
<td>Direct pyrolysis mass spectrometry</td>
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<td>EDX</td>
<td>Energy dispersive X-ray</td>
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<td>ENM</td>
<td>Electrospun nanofibre membrane</td>
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<td>FAPs</td>
<td>Fly ash particles</td>
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<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<td>g</td>
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<td>GC-MS</td>
<td>Gas chromatography mass spectrometry</td>
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<td>HEPA</td>
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<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<td>m</td>
<td>Meter</td>
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<td>MERV</td>
<td>Minimum efficiency reporting value</td>
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<td>mL</td>
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<td>MPPS</td>
<td>Most penetrating particle size</td>
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<td>NaCl</td>
<td>Sodium chloride</td>
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<tr>
<td>NIOSH</td>
<td>National Institute for Occupational Health and Safety</td>
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<td>nm</td>
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<tr>
<td>NMR</td>
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<tr>
<td>NOₓ</td>
<td>Oxides of nitrogen</td>
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<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
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<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
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<tr>
<td>REL</td>
<td>Recommended exposure limit</td>
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<tr>
<td>SHP</td>
<td>Sodium hypophosphite monohydrate</td>
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<td>SiO₂</td>
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<td>SOx</td>
<td>Oxides of sulphur</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>TiO₂</td>
<td>Titanium dioxide</td>
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<tr>
<td>TLV</td>
<td>Threshold limiting value</td>
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<tr>
<td>ULPA</td>
<td>Ultralow-penetration air</td>
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<tr>
<td>UV</td>
<td>Ultraviolet spectrophotometry</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>β–CD</td>
<td>β cyclodextrin</td>
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<tr>
<td>μg</td>
<td>Microgram</td>
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<td>Micrometre</td>
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ABSTRACT

The ubiquitous presence of air pollutants and its consequences on human health is a global concern. Air pollutants, comprised of particulate matter (PM) and gaseous pollutants, differ in size and volatility. The microfibre based filter media is commonly being used to capture PM. The conventional air filter media does not capture aerosols smaller than 0.3 μm efficiently. They have limited surface area and requires high basis weights (10–200 g/m²) to attain desired filtration efficiency. In addition, protection against volatile organic compounds (VOCs) of the conventional media is negligible. Electrospun nanofibres have been efficient in capturing PM$_{2.5}$ at small basis weights (0.5–5 g/m²), however, at the expense of high pressure drop (breathing resistance) which is not desirable for respiratory filtration. This research presents the design and development of electrospun nanofibre membranes (ENMs) for capturing PM and VOCs simultaneously at a minimum pressure drop.

Two novel approaches are studied to reduce the pressure drop of ENMs. The method of the bead (200 nm) on string (55 nm) formation in sequential bilayer successfully decreased the pressure drop (137 Pa) with excellent filtration efficiency (>95%). In another approach, the sequential layering of coarse (400 nm) and fine (200 nm) nanofibres further reduced the pressure drop to 87 Pa and showed comparable filtration efficiency at a basis weight of 1 g/m². ENMs in this study meet the requirement of respirator mask recommended by the National Institute for Occupational Health and Safety (NIOSH). The filtration performance is at par with commercial P1 and P2 type masks along with lower pressure drop.

ENMs and the textile substrate functionalised with β-cyclodextrin were found useful in capturing model VOCs: formaldehyde, xylene and benzene. The VOC adsorption performance of ENMs was found many folds higher than the functionalised textile substrate and commercial P2 type masks. The ENM comprised of gelatin biopolymer showed multifunctional air filtration properties capturing PM and VOCs simultaneously. Gelatin/β-cyclodextrin composite ENMs were found most efficient for formaldehyde adsorption. Overall, ENMs in this study would be handy for personal and occupational safety as an advanced material for respiratory protection.
Chapter 1

Introduction: Electrospun nanofibre membrane

“There is plenty of room at the bottom”, a famous talk by Richard Feynman in 1960 [1], that introduced the concept of nanoscience to the world. Later in 1990, Eric Drexler coined the term Nanotechnology in his book “Engines of Creation” [2]. Nanotechnology is defined as science and engineering about materials, structures and devices with at least one of the dimensions of 100 nm or less [3]. In polymer nanofibres, this definition has been broadly expanded up to 1000 nm, and the size is associated with fibre diameter. Several nanofibre fabrication techniques are available such as conjugate spinning (sea-island method), chemical vapour deposition, phase separation (sol-gel process), drawing, self-assembly, melt-blowing and electrospinning [4]. Among them, electrospinning has the edge mainly because of scalability, reproducibility, convenience, and controllable morphology [3]. Therefore, electrospinning has been widely accepted for polymer nanofibre production.

1.1 Preface of electrospun nanofibres

The electrospinning concept to produce synthetic filaments using electrical charge was first patented by Cooley and Morton in 1902 [5]. In 1934, Anton Formhals [6] patented an improved version. Anton applied electric field (5–10 kV) to cellulose acetate polymer which was dissolved in alcohol acetone mixture and produced silk-like fine filaments. However, he neither named the apparatus as electrospinning nor the filaments as nanofibres. Sometime in the 1940s, the electrospinning principle was employed to prepare respiratory filter media by Petrynov in the USSR (now Russian Federation) [7], and it remained a trade secret for several decades.

viscosity and distance range for successful electrospinning to fabricate nanofibres without beads. Electrospinning has got real momentum after 1990’s mainly due to the know-how of nanoscience and variety of its potential applications. Electrospinning is a simple, easy and versatile process to produce nanofibres and control their shape [12-14]. **Figure 1-1** shows a simple setup of the electrospinning process comprised of three components, namely, a high voltage supply, a capillary tube and metal collector [15]. The high electric voltage is applied to a capillary tube or to a metal collector to produce a strong electric field between tube and collector. The capillary tube contains a viscoelastic polymer solution which is prepared using a suitable solvent. A metal needle is connected to the capillary tube to draw the solution at the desired flow rate using a syringe pump. The electrically charged fluid at the needle tip overcomes its surface tension, forms a cone shape (Taylor cone) [15] and elongates in a jet from towards the collector forming thin fibres. The continuous web of thin fibres is referred to as electrospun nanofibre membrane (ENM).

*Figure 1-1* Electrospinning principle set up for nanofibre production [16] (with permission from Sage).

The nanosize formation is due to the simultaneous effect of jet stretching and evaporation of the solvent during the jet travel. The jet stretching reduces its diameter thus increases the surface charge density and the repulsive forces. These high repulsive forces further split the first
jet into smaller secondary jets. This process may repeat several times to create many small jets which dry rapidly to form fibres with a small diameter [11].

The electrospinning process produces diameter ranging from tens to few hundred nanometres [17-19]. Electrospun nanofibres can be 800 times smaller than conventional microfibres. The smaller diameter increases the surface area to volume ratio (specific surface area) of the nanofibres. Nanofibres have more than 100 times larger specific surface area compared to microfibres [15, 20]. This increase in specific surface area is attributed to micropores (less than 2 nm) and mesopores (2–50 nm) generation in the nanofibres [20]. Moreover, the pore size of nanofibres is 4–100 times smaller than that of the microfibre nonwovens [15].

The properties of ENM such as small fibre diameter, high specific surface area and small pore size make them suitable for wide range of applications including filtration [20], biomedical (tissue engineering and drug delivery) [21], protective textiles [22, 23] and environment protection [7]. In environment protection, nanofibres have been explored in areas such as air filtration, dust capture, building filters, vehicle cabin filters and personal and respiratory protection from biological and chemical agents.

1.2 Rationale

Air pollution remains the largest environmental and public health issue affecting urban life [24]. Exposure to air pollution claims millions of lives every year across the world [16]. The mortality due to air pollution is estimated to reach 6.5 million by 2050 [25]. Air pollution, due to Particulate Matter (PM) and gaseous pollutants including Volatile Organic Compounds (VOCs) such as formaldehyde, can cause respiratory and cardiovascular diseases [26-28]. Air pollutants also cause asthma, nausea, skin irritation, high blood pressure, cancer, and congenital disabilities [29, 30]. The severity of the health hazard depends on the nature of the air pollutants and their exposure levels.

Air pollutants are classified as either solid/liquid aerosols, as PM, or gaseous contaminants. Indoor air is typically two to five times more polluted than the outdoor air [31]. Indoor smoking, cooking, heating and cooling elevate PM concentration in the indoor environment [32, 33]. Outdoor industrial activities such as petroleum processing expel PM and gases into the atmosphere [34-36].
The solid/liquid aerosols, i.e. PM and gaseous pollutants vary in their size and chemical composition. Based on inhalable particle size, PM is classified into coarse (2.5–10 μm), fine (0.1–2.5 μm) and ultrafine (<0.1μm) known as PM 10 [37], PM 2.5 [38] and PM 0.1 [39] respectively. Gaseous air pollutants such as NOx, SOx and VOCs are determined by their concentration levels (ppm) in the air. At present, PM and gas filters give negligible protection against each other’s hazard [40]. Hence different filter materials are being used to filter PM and gaseous pollutants. PM filters are made up of fibrous materials and are thinner, lighter and more porous than gas filters [40]. Gas filters are manufactured from granules of activated carbon, which have an extremely high surface area [40], but they are not good against small volatile gases such as formaldehyde. Gas filters are being used in military and heavy-duty industrial applications.

Fibre based nonwoven High-Efficiency Particulate Air (HEPA) and Ultra-Low Particulate Air (ULPA) filters capture tiny PM with ≥99.97% and ≥99.999% filtration efficiency, respectively [41, 42]. However, they suffer from high pressure drop (high air resistance) compared to microfibre based nonwoven media and clog quickly due to the limited specific surface area. The high air resistance not only consumes high energy for air filtration but also obstructs the breathing of a wearer in respiratory filtration. Moreover, the high grammage (mass coverage or basis weight) of HEPA/ULPA filters and their lack of VOC adsorption limits their use in respiratory applications. Certainly, there is a need for a lightweight filter media which provides efficient and simultaneous protection against PM and VOCs with lower resistance to air flow.

1.3 Research concept and hypothesis

ENM can be potentially employed to filter a variety of pollutants. ENM can capture PM due to a combination of small diameter, small pore size and high specific surface area. Moreover, the surface of ENM can be functionalized to adsorb different VOCs. Electrospun nanofibres can also be engineered to reduce the pressure drop which is immensely desirable for respiratory filter media. Carefully engineered ENMs can simultaneously extract harmful aerosols and gases from the air with minimum air resistance. This hypothesis is tested in various experiments involving different approaches, viz. beaded nanofibres, bilayer nanofibres, use of specific additives, and surface modification of electrospun nanofibres.


1.4 **Scope of the work**

The work in this thesis is directed towards understanding the requirements of ENMs for making multifunctional respiratory filters with minimum air resistance. ENMs are produced by electrospinning polymer solutions with and without additives. The morphology is engineered to obtain a beaded bi-layer structure. The study includes morphological and chemical characterisation of the ENMs. The ENMs are evaluated for air filtration performance against PM of different sizes and selected VOCs. This study focuses on creating materials which will simultaneously entrap PM and gaseous pollutants from the ambient air. The study is not intended for chemical, biological, radiological and nuclear (CBRN) warfare protection for defence or first responders. However, the research work will provide an opportunity to develop effective protective materials for urban life and industrial use such as in painting and carpentry where VOC emission is high.

1.5 **Aim and objectives**

This research is aimed at studying ENM as a protective material against different air pollutants while minimising breathing resistance in respiratory applications with the following objectives:

1. To reduce pressure drop (air resistance) across the ENM while maximising PM filtration efficiency;
2. To functionalize ENM with specific additives to adsorb gaseous pollutants;
3. To fabricate ENM for simultaneous PM capture and gaseous pollutants adsorption.

1.6 **Contribution of this research**

This thesis studies the design and development of ENMs for capturing of aerosols and VOCs while minimising air resistance. At the moment, such ENMs are not available. There is a high demand for more effective materials and devices for personal and occupational safety to combat ever-increasing hazardous air pollutants.

This research employs different approaches to reduce the pressure drop of ENMs. Consistent formation of beaded structures is one approach. Effect of beaded ENM on air
filtration is studied for the first time. Further, the placement of beads in bilayer ENM highlights the importance of sequential stacking in reducing the pressure drop.

Following the results of the above study, a bilayer ENM consisting of coarse and fine bead-free nanofibres was prepared from a single polymer (polyacrylonitrile). This is a new approach to improve the air filtration performance of ENMs. The optimised electrospinning parameters and bilayer structure arrangement reduce the pressure drop significantly without compromising filtration efficiency.

It is observed that ENMs in the study are thin, soft and compressible. Hence ENM thickness measurement is delicate and not precise using conventional techniques such as micrometre and SEM cross-section. This study used a non-contact laser microscopy method to measure the thickness. The laser microscopy technique is quick and relatively new for ENM thickness measurement.

β-cyclodextrin (β–CD), a renewable material, has truncated cone-shaped cavities. The cavities can accommodate a range of VOCs. This study used β–CD as an additive for fabrication of composite PAN/β–CD ENM. The composite ENM captured aerosols and VOCs in one step. Use of β–CD for aerosol filtration is novel. The cytotoxicity analysis of composite PAN/β–CD ENMs, important regarding respiratory applications, is reported for the first time.

ENMs because of the small basis weight invariably require a support substrate which is often a porous nonwoven. β–CD was cross-linked with the nonwoven to enhance VOC adsorption capacity. β–CD cross-linked nonwovens effectively adsorbed target VOCs and also displayed good air permeability. This approach is new to the air filtration field.

The concept of sustainable ENM for multifunctional air filtration is investigated. Gelatin, naturally occurring protein polymer, is inexpensive and abundantly available. Gelatin ENM commonly used in biomedical and food applications. However, this research work employed gelatin for multifunctional air filtration. The air filtration performance of gelatin is rarely reported. Gelatin ENM also showed an affinity towards certain VOCs.

1.7 Thesis outline

This thesis is divided into eight chapters. Chapter 1 introduces the electrospinning concept followed a summary of the pros and cons of ENM properties for specific applications. This chapter also includes the research hypothesis, rationale, aim, objectives of this investigation and
highlights the contribution to the existing knowledge of air filtration and VOC adsorption using ENMs.

Chapter 2 provides a literature review which includes air pollutants classification, air filtration theory, particle capture mechanism and air filtration performance measurement. Polymers, additives, and solution parameters used in electrospinning and design of air filter media are reviewed. It also covers techniques used in the characterisation of ENMs such as scanning electron microscopy, capillary flow porometry, laser microscopy and infrared spectroscopy. This work has been published in the Journal of Industrial Textiles [16]. This chapter also reviews β–CD as an adsorbent to capture pollutants and identifies research gaps. β–CD as an additive in electrospinning is the simplest forms of use for air filtration and VOC adsorption. Previously the majority of the publications concerning β–CD were conducted in water filtration. The adsorption performance of β–CD modified fabrics/nanofibres can be studied for different VOCs such as xylene, benzene and HCHO.

Chapter 3 explains experiments conducted using PAN solution to produce ENMs and to quantify airflow through ENMs. It includes the basic setup used in electrospinning, the rotating collector assembly for obtaining large format sized ENMs, and the effect of different deposition times and collector speeds on air permeability. This work is reported in the Journal of Fiber Bioengineering and Informatics [43].

Chapter 4 investigates the approach of fabricating beaded PAN nanofibres in bilayer structures for enhanced air filtration. The electrospinning process parameters are optimised to obtain consistent and uniform sized beads. Further, the importance of the bilayer structure formation and its hierarchical positioning is investigated. Engineering beaded bilayer structures significantly reduce the pressure drop. This research is under review with a journal.

Chapter 5 follows on from the previous one expanding on the bilayer structure approach. Experimental results on bilayer alternate coarse-fine bead-free PAN ENMs are presented. The changes in morphology and filtration performance due to the difference in the stacking order of the nanofibres in the bilayer ENM are shown and explained. This work was awarded best oral paper at the 3rd World Congress on Nanotechnology at Rome, Italy (2017) [44].

Chapter 6 uses β–CD as an additive during PAN electrospinning to prepare composite ENMs for multifunctional air filtration. PAN/CD ENMs were characterised using infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS). The results of filtration test and
gas adsorption showed that β–CD is useful in VOC adsorption. The composite ENMs showed simultaneous filtration of aerosols and gas molecules at less breathing resistance. These findings have been recently published in ACS Applied Nanomaterials [45].

Chapter 7 explores the use of an electrospun protein (gelatin) for air filtration. Gelatin ENMs was modified with additives such as β–CD and saponin. The effect of additives on fibre morphology is investigated. The aerosol filtration and VOC adsorption performance of the ENMs are quantified. The chapter ends with a short discussion on the advantages and limitations of the materials used in this approach.

Chapter 8 covers the concluding remarks and indicates a possible future direction for this research.

Appendices show the calculations used in the main body of the thesis.
Chapter 2

Literature review: air pollution, air filtration and ENM

2.1 Health effects of air pollution

Until 1960, people did not realise air pollution is a nuisance despite a major incident in 1948, Pennsylvania, the USA where air pollution caused 6000 residents to become sick and 18 to die [46]. Over the last five decades, air pollution becomes a serious global concern with the exponential rise in health consequences and death toll. Exposure to air pollution caused 3 million premature deaths across the globe in 2012 (World Health Organization)[47]. The premature mortality attributed to air pollution is estimated to raise more than 6.5 million by 2050 [25]. At present, a strong association between air pollution and mortality rate has been found in countries like USA [48, 49], UK [50, 51], Australia [52], Japan [53], China [26-28] and India [54, 55].

Air pollution can cause asthma, nausea, skin irritation, hypertension, cancer and congenital disabilities [33, 56]. Air pollution can have adverse effects on the respiratory system, cardiovascular system, nervous system, urinary system and digestive system [30]. The severity of the health hazard depends on the exposure level and nature of the air pollutants. Long-term exposure to air pollutants can cause cardiopulmonary mortality and lung cancer [53]. However, a strong correlation is also found between mortality and short-term exposure to air pollution [56]. Short-Term exposure refers to an acute effect over several days whereas long-term exposure has a chronic impact over many years.

Table 2-1 tabulates several studies on the health effects of different air pollutants. Both short term and long term exposure to air pollutants are harmful to human health. Major air pollutants include particulate matter (PM) in the aerosol format of different sizes, oxides of nitrogen (NOx), oxides of sulphur (SOx), carbon monoxide (CO), carbon dioxide (CO2), ozone and volatile organic compounds (VOCs). A simple classification of air pollutants would assist in deriving a meaningful conclusion towards designing efficient air filter media.
Table 2-1 Human health effects of air pollution.

<table>
<thead>
<tr>
<th>Air pollutant</th>
<th>Exposure time</th>
<th>Health effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>Long-term</td>
<td>Lung function, bronchitis, Lung cancer and cardiopulmonary disease</td>
<td>[48, 56]</td>
</tr>
<tr>
<td>SO₂, PM2.5, PM10, NO₂, Co²+</td>
<td>Short term</td>
<td>High blood pressure, Impaired lung function</td>
<td>[29, 57]</td>
</tr>
<tr>
<td>NO₂, PM10</td>
<td>Long-term</td>
<td>High blood pressure</td>
<td>[57]</td>
</tr>
<tr>
<td>PM10, PM2.5, SO₂, NO₂, CO</td>
<td>Short term</td>
<td>Coronary heart disease</td>
<td>[27]</td>
</tr>
<tr>
<td>Formaldehyde (VOC)</td>
<td>Short term</td>
<td>Skin irritation, respiratory tract, Death (&gt; 100 ppm)</td>
<td>[29]</td>
</tr>
</tbody>
</table>

2.2 Classification of air pollutants

In 2004, Bernstein [33] grouped air pollutants, based on their source, chemical composition, and mode of release into the atmosphere (Figure 2-1). Primary air pollutants are defined as those that are directly emitted into the atmosphere and can be either natural or human made. Hydrogen sulphide from volcanos, carbon dioxide from grassland fires and carbon monoxide from automobiles are the examples of primary pollutants. Whereas, secondary pollutants are generated when two or more primary pollutants react with each other to produce another species.
The indoor and outdoor air pollutants had received considerable attention from the scientific community since 1999 when the adverse health effects of indoor air pollutants were realised. The term indoor refers to residential and office areas while outdoor air refers to the industrial workplace and ambient air outside the buildings. The general perception is that poor outdoor air quality is significantly more dangerous than the poor indoor air. However, indoor air is usually two to five times more polluted than the outdoor air [31]. Indoor smoking, cooking, heating and cooling elevate PM concentration [32, 33]. In developed countries like the USA, an individual spends 88% time of the day inside buildings [29]. Hence environmental protection agencies such as the US–EPA have designed specific standards for indoor air quality (IAQ) centred on PM. It should also be noted that furniture, paints on the wall inside a building, also emit VOCs such as formaldehyde which can cause acute health effects. Therefore, gaseous pollutants need also be taken into account for clean air.

Air pollutants have been classified into PM (solid/liquid aerosols) and gas molecules based on chemical composition and size. This grouping is invariably linked with the other two groups since primary–secondary and indoor-outdoor pollutants either comprised of aerosols or gaseous compounds. The industrial activities such as petroleum processing expel aerosols and chemicals into the atmosphere. Aerosols are a mixture of solid and liquid droplets suspended in the air [56].
They vary in size, shape, surface area, chemical composition, solubility and origin [48, 49]. Aerosols size in the ambient air ranges from a few nanometres to tens of micrometres (Figure 2-2). Lungs can inhale aerosols of this scale with adverse effects; hence the US-EPA’s national ambient air quality standards (NAAQS) are based on the size and concentration of aerosols.

Figure 2-2 Examples of PM and their relative size [58, 59].

NAAQS evolved over the last fifty years with a fundamental understanding of particle size and its adverse effects on health. In the early 1970’s the air quality standards were expressed as total suspended particles concentration per cubic metre of air. In 1987, PM10 was defined as coarse particles having an aerodynamic diameter from 2.5 μm to 10 μm which can penetrate the lower respiratory system. PM10 are derived from soil dust, road dust, construction debris and aggregation of smaller combustion particles while PM2.5 and PM0.1 are primarily formed during combustion of fossil fuel [33]. PM2.5 is fine particles with diameters ranging from 0.1 μm to 2.5 μm. PM2.5 can penetrate the gas-exchange region of the lung [56] and hence more toxic than large particles. PM0.1, which denotes ultrafine particles of aerodynamic diameter less than 0.1 μm, was defined in 2002; however, their effect on health is still unknown. PM0.1 ultrafine particles are the most abundant with large specific surface areas capable of a higher degree of lung penetration compared to PM10 and PM2.5 [56]. Thus, the smaller particles are potentially more hazardous to health. In fact, there is no threshold concentration is determined below which no health effects are expected. However, relative risk estimates are identified to
help policymakers to quantify air quality standards. NAAQS specified threshold concentration of 150 µg/m$^3$ for PM10 and 60 µg/m$^3$ for PM2.5 upon 24 h exposure.

Smog (a mixture of smoke and fog) in London and Los Angeles are classic examples of secondary pollutant formation. PM particles react with primary gaseous pollutants in the air to form smog. The primary gaseous contaminants in air include oxides of nitrogen, oxides of carbon, oxides of sulphur, VOCs and chlorofluorocarbons (CFCs). Combustion processes typically at high temperature emit NOx. This toxic gas has a robust biting odour and is a significant contributor to ground-level ozone (O$_3$) formation. The primary source of emission for oxides of carbon is vehicle exhaust, incomplete fuel combustion such as natural gas, wood, coal and petroleum gas (carbon monoxide is more poisonous than carbon dioxide). Sulphur compounds in fossil fuels creating sulphur dioxide which reacts with water, oxygen in the atmosphere resulting in “acid rain”.

VOCs denote the entire set of vapour phase atmospheric organics excluding CO and CO$_2$ [60] having boiling points from $<$0°C to 240–260°C [61]. Since VOCs are used in many consumer related products and industrial manufacturing processes, they can be found indoors as well outdoors. Some of the examples VOCs are formaldehyde, n-heptane, benzene and xylene, n-hexane and tetrachloroethylene.

Formaldehyde is categorised as a human carcinogen [62] by the agencies such as International Agency for Research on Cancer (IARC) and the U.S. National Toxicology Program [63]. Acute exposure to formaldehyde can cause a headache, irritation and asthma whereas chronic exposure can cause neurotoxicity, pulmonary function damage, hematotoxicity [64] and male reproductive impairment [65]. The National Institute for Occupational Health and Safety (NIOSH) Recommended Exposure Limit (REL) is set at 0.016 ppm (0.019 mg/m$^3$) for 15 min [66]. American Conference of Governmental Industrial Hygienists (ACGIH) specified the Threshold Limit Value (TLV) of 0.3 ppm (370 mg/m$^3$) for formaldehyde. The sources of formaldehyde are building materials such as particle board, medium-density board, plywood and carpeting [29] due to the widely accepted use of formaldehyde as resin, adhesive (binder) and cross-linker. Formaldehyde VOC continues to come off from these household items over the life period. Brown [67] found elevated formaldehyde emission rates (>1 mg/m$^3$) in newly constructed buildings of Melbourne. Rovira et al. believed the indoor formaldehyde concentration in China and USA are alarming (>100 µg/m$^3$) [63].
Benzene is carcinogenic VOC and may cause leukaemia through prolonged exposure. The TLV for benzene is 31 mg/m$^3$ (NIOSH). The sources of benzene include automobile service stations and exhaust, industrial emissions, tobacco smoke and fumes from benzene containing consumer products such as paints, furniture wax and detergents [68].

Xylene is hazardous VOC which can be found in many consumer products such as inks, paints, cement, varnishes and cleaning agents [69]. It is used in the manufacturing of plastics, leather goods and insecticides. Xylene is a clear, colourless liquid that has a characteristic pungent odour. It is hazardous and toxic VOC under Clean Air Act Amendments (CAAA) of 1990, USA. NIOSH specified TLV for xylene is 434 mg/m$^3$. Zuraimi et al. [70] conducted a study where residents complained about eye and skin irritation due to surrounding VOCs including xylene despite their lower concentration.

Eventually, all air pollutants, irrespective of classification, are either PM or gaseous pollutants including VOCs. Both are different from each other regarding size and chemical composition. Consequently, filtration principles of PM and VOCs vary to a large extent.

### 2.3 Particulate matter filtration

The key development in PM filtration is the discovery of Brownian motion in early 1800 which is still the basis of air filtration theory. During the past two centuries, research contributions of Brown, Stokes, Tyndall, Hansen, Kaufman, Kuwabara, Fuchs, Brown and Hinds progressively developed filtration theories to our current level of understanding [58, 59, 71-75] which is discussed in the following section.

Aerosol filters, based on their structural design, can be classified as fibrous filters, screen filters, granular filters, sintered metal filters, and membrane pore filters [76]. Table 2-2 describes the structure and application of each filter system. Among these filters, the fibrous filter is superior in terms of filtration efficiency for particles less than 1 µm particles for the lowest pressure drop [72]. The filtration mechanism, performance and development of electrospun materials discussed in this thesis are related to fibrous filters.
Table 2-2 Aerosol filter classification based on structural design.

<table>
<thead>
<tr>
<th>Filter type</th>
<th>Structure</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibrous filter</td>
<td>Woven or nonwoven fibrous assembly as a membrane or fabric form</td>
<td>A broad range of uses from the respiratory filter to industrial filter</td>
</tr>
<tr>
<td>Screen filter</td>
<td>The polymer or metal screen</td>
<td>Cake (dust loading) filtration</td>
</tr>
<tr>
<td>Granular filter</td>
<td>Packed bed consisting of large particles</td>
<td>High temperature (850°C) air filtration</td>
</tr>
<tr>
<td>Sintered metal filters</td>
<td>Sintered metals with uniform porosity</td>
<td>The silver metal filter is stable in the temperature range of -130–370°C</td>
</tr>
<tr>
<td>Membrane/ pore filters</td>
<td>Perforated polyethylene or polyurethane foam</td>
<td>Semiconductor industries</td>
</tr>
</tbody>
</table>

2.3.1 Filtration mechanism

The filtration mechanism can be used to understand a particle’s retention on the filter and its removal from air. Straining or sieving is one of the capture mechanisms of high efficiency particulate air (HEPA) and ultra-low particulate air (ULPA) filters [77]. Straining occurs in a filter when the particles enter passages between two or more fibres that have dimensions less than the particle diameter. The mechanism of particle capture is influenced and tuned by fibre assembly, single fibre theory, filtration mode, the design of filter and operating conditions [78]. Particle capture through the single fibre is the most crucial mechanism since the fibrous filter can retain particles much smaller than its pore size which is beyond simple sieving.

As illustrated in Figure 2-3, particle capture by the single fibre is tuned by diffusion, interception, inertial impaction and electrostatic interaction, gravitation, van der Waals interaction and straining [40, 78]. Among those, diffusion and interception are important filtration mechanisms in providing a theoretical basis for explaining the mechanisms involved in electrospun nanofibre membrane (ENM) filtration. Simulation results from Maze et al. [73] indicated that nanofibres increase the collection efficiency for particles in size range from 50 to 500 nm mainly due to the Brownian diffusion and interception mechanisms.
Before discussing the mechanism, it is essential to consider the airflow pattern which dominates the filtration performance. The Reynolds Number, Re (Eqn 2-1) determines the flow regime [79].

\[
Re = \frac{\rho u L}{\mu}
\]  

(2-1)

Where, \(\rho\) is the density of air (1.20 kg/m\(^3\)); \(u\) is the air velocity inside the filter; \(\mu\) is the coefficient of viscosity (1.81x10\(^{-5}\)) at room temperature and pressure (20\(^\circ\)C and 1 atm), and \(L\) is the characteristic length which can be equivalent to pore diameter (\(\mu\text{m}\)). A low Reynolds number (< 1) indicates laminar flow whereas a high Reynolds number (> 1) shows turbulent flow.

Diffusion explains the capture of fine particles below 0.5 \(\mu\text{m}\) that move randomly due to Brownian motion [42, 78]. Aerosol particles which are suspended in the gas phase continuously collide with other gas molecules and tend to diffuse from high concentration to low concentration. During this random movement, small particles get captured by the fibres [78]. Diffusion predominantly occurs for fine particles at low flow velocity, and at high temperature.

**Figure 2-3** Particle capture mechanism of a single fibre [16] (with permission from Sage).
due to high collision probability [7]. The Peclet number, Pe (Eqn 2-2) is used in determining the contribution of diffusion in filtration efficiency in comparison to interception.

\[
Pe = \frac{ud_f}{D}
\]  

(2-2)

Where \( u \) is the air velocity inside the filter; \( d_f \) is the fibre diameter, \( D \) is the diffusion coefficient.

In the interception mechanism, a particle intercepts with fibre when the distance between the fibre surface and the particle centre is equal to or less than the particle radius [80]. Interception occurs when particles of small mass and low inertia come close to a fibre surface [78]. The probability of interception is higher with an increase in the particle size. Interception is the only mechanism which is not influenced by the face velocity. The face velocity is defined as the undisturbed air velocity at the surface of the filter medium.

According to the inertial impact model, the high inertia of a massive particle makes it unable to adjust with the air stream near the surface. Thus, the massive particle crosses the air stream before colliding the filter surface [59]. The ratio of particle stopping distance to fibre diameter is termed as Stokes number (Eqn 2-3) [59]. If Stokes number, \( Stk \gg 1 \), the particle will continue in a straight line and obstructed by fibre surface along the air stream [58]. In the case of, \( Stk \ll 1 \), particles will follow the air stream correctly without inertia impact. When the air stream is more than 1 m/s, the inertia capture mechanism is dominant [7].

\[
Stk = \frac{\tau V}{d_f}
\]  

(2-3)

where \( V \) is face velocity, \( d_f \) is the fibre diameter, and \( \tau \) is the relaxation time of particle which is expressed as

\[
\tau = \frac{\rho_p d_f^2 p C_c}{18 \mu}
\]  

(2-4)
Where $C_c$ represents Cunningham slip correction factor. The Cunningham factor describes the molecular movement (drag force) of a particle moving in an air stream [59]. This slip correction factor is relevant to nanofibres where no-slip condition at the fibre surface is invalid [59].

Knudsen number, $\text{Kn}$ (Eqn 2-5) is the ratio of the mean free path of air molecules in the flow to the fibre diameter.

$$\text{Kn} = \frac{2\lambda}{d_f} \tag{2-5}$$

where $\lambda$ is mean free path of the gas molecule (Eqn 2-6) and $d_f$ is the fibre diameter.

$$\lambda = \frac{R \ T}{\sqrt{2} \ L \ \pi \ d^{2}_m \ P} \tag{2-6}$$

where $R$ is the gas constant, $T$ is the temperature (K), $L$ is Avogadro’s number, $d_m$ is the collision diameter of air molecules ($3.7 \times 10^{-10}$), and $P$ is pressure ($\text{Nm}^{-2}$).

Four flow regimes identified with a range of Knudsen number. They are free molecule regime ($\text{Kn} > 10$); Transient regime ($10 > \text{Kn} > 0.25$); slip flow regime ($0.25 > \text{Kn} > 0.001$) and continuum regime ($\text{Kn} < 0.001$) [58]. Higher Knudsen number suggests strong diffusion. However, with high flow regime, aerosol retention time on nanofibres gets reduced making the diffusion ineffective [16]. These changes in the particle capture mechanisms strongly influence the air filtration performance of the filter media.

### 2.3.2 Filtration performance

The filtration performance of a filter medium can be described by filtration efficiency, penetration, pressure drop, quality factor, minimum efficiency reporting value (MERV) and most penetrating particle size (MPPS). Filtration efficiency is the ability of a filter medium to capture different size aerosols. The required filtration efficiency varies with the desired application and dependant on particle size. HEPA and ULPA filters are defined as filters with $\geq 99.97\%$ efficiency for $0.3 \ \mu\text{m}$ aerosols and $\geq 99.999\%$ efficiency for $0.1–0.2 \ \mu\text{m}$ aerosols, respectively [42]. Filtration efficiency ($E$) (Eqn 2-7 and Eqn 2-8) can be based on particle count or particle
mass. Count efficiency is, generally, lower than mass efficiency [58]. The term specific filtration efficiency referred to the filtration efficiency normalised with basis weight [81].

\[
E = \frac{N_{\text{In}} - N_{\text{Out}}}{N_{\text{In}}} \tag{2-7}
\]

\[
E = \frac{M_{\text{In}} - M_{\text{Out}}}{M_{\text{In}}} \tag{2-8}
\]

Where, \( N \) and \( M \) are the particle number and mass concentration respectively at the inlet (upstream, \( N_{\text{In}} \) and \( M_{\text{In}} \)) and the outlet (downstream, \( N_{\text{Out}} \) and \( M_{\text{Out}} \)) of the filter.

The penetration (\( P \)) (Eqn 2-9) can be defined as the fraction of particles that penetrate into the filter and can be either count or mass based.

\[
P = 1 - E \tag{2-9}
\]

The pressure drop (\( \Delta P \)) (Eqn 2-10) is the difference between the inlet (upstream, \( P_{\text{In}} \)) and the outlet (downstream, \( P_{\text{Out}} \)) air pressure at a given air velocity during the filtration.

\[
\Delta P = P_{\text{In}} - P_{\text{Out}} \tag{2-10}
\]

Minimising the pressure drop is always desirable for maximum airflow across the filter. For respirator filters, the pressure-drop must be below 147 Pa [82]. However, high filtration efficiency is usually associated with a high pressure drop [83, 84]. While high filtration efficiency is excellent, the simultaneous increase in pressure drop is unfavourable.

The quality factor (\( Q \)) (Eqn 2-11) is a function of pressure drop and filtration efficiency, and also known as a figure of merit [85]. It is the ratio of the negative natural logarithm of penetration over pressure drop. A quality factor is, in general, independent of thickness and basis weight of filter media [7]. A high quality factor indicates better performance which yields high filtration efficiency and low pressure drop [86].
Filter resistance \( R_f \) (Eqn 2-12) can be used to determine the breathability of the filters and related to pressure drop [87].

\[
Q = \frac{-\ln (1 - E)}{\Delta p}
\]  

(2-11)

\[
R_f = \frac{\Delta P}{\nu}
\]  

(2-12)

MERV is minimum fractional particle size efficiency in three different particle size ranges. It is expressed as E1, E2 and E3 for very fine particles to coarse particles in the range of 0.3 to 1.0, 1.0 to 3.0, and 3.0 to 10.0 µm, respectively. MERV numbers are usually expressed on a scale from 1 to 20 representing an increasing order of efficiency for decreasing size of particles [58]. While MPPS is the minimum particle size that cannot be filtered by any capture mechanism of the filter media. MPPS mainly depends on fibre diameter and packing density of filter media. A typical MPPS value for most filters is between 0.1 to 0.3 µm.

TSI 8130 air filter testers and Hauda filter testers are commonly employed for measurement of filtration performance. A standard air filtration setup is comprised of optical particle counters, pressure transducers and an atomiser. Table 2-3 illustrates the performance values required for respiratory filter media set by various standards.
Glass fibres have been used in HEPA filters [90]. However, glass fibres have the drawback of high pressure drop (at least 20 mm of H$_2$O (196 Pa)) [91]. They also exhibit depth loading characteristics and clogs over time, reducing air flow through the media [92]. Moreover, the conventional melt-blown and spun-bonded fibres have limited surface area due to a larger fibre diameter which adversely affects the filtration efficiency, especially for fine particles [93]. The small diameter of nanofibres results in the higher surface area to volume ratio. Hence, more dust particles get captured at the surface, and the saturation can be delayed. Therefore, nanofibres are desirable for better filtration performance [15, 93].

2.4 Gas molecules adsorption

The use of toxic chemicals, especially for warfare, has a long history from the days of Ancient Greek and Roman times to modern times [94, 95]. However, rapid industrialisation
during the last century has resulted in the emission of many toxic gases into the atmosphere which is harmful to human health and the environment in general.

The earliest report that recommends charcoal as an adsorbent for gas filtration found in 1919 [96]. Charcoal with different degrees of activation could affect the adsorption. Therefore, charcoal samples were rated based on breakthrough time (service time) determined by the accelerated chloropicrin test (amount of time taken for a concentration of chloropicrin to break through the filter at a defined flow rate). In the definition, it is the time taken for a 7000 ppm of chemically inert chloropicrin in dry air at a flow rate of 1000 cc/cm² passed through a 10 cm layer of a charcoal sample. In 1921, the mixture of manganese, copper and silver metal oxides was used for catalytic oxidation of carbon monoxide at room temperature.

The most common gas adsorbents studied are carbon (activated), zeolite (alumina-silicate crystal structure) and organic polymers [97]. Activated carbon is made by the pyrolysis of materials such as coal, wood, bark and coconut husk to remove all other gas vapours and removal of organic molecules leaving only carbon. Activated carbon has been employed in gas filtration to remove VOCs due to its high efficiency. However, it has some shortcomings such as short service life and poor chemical functionality in terms of non-selectivity. The activated carbon filters require proper care and handling since a person can inhale loose activated carbon particles.

There are 118 types of zeolites in nature [97], mostly hydrophilic. Zeolites are dealuminated by chemical replacement of the aluminium with silicon without changing the crystal structure. Zeolites have a uniform pore size which can be reduced through synthesis. However, synthesis is expensive.

Organic polymers in the form of granules, beads or fibres, usually have large pores and small surface area compared to activated carbon. They can desorb faster than activated carbon. Electrospinning of polymers can produce nanofibres with reduced pore size and can increase the specific surface area. Although electrospun polymeric nanofibres cannot match the specific surface area of activated carbon, the gas adsorption capacity can be improved by blending different additives along with the polymer during electrospinning. The choice of additive depends on the affinity and chemistry between the additive and the target gas pollutant. The polymer–additive system is discussed later in the chapter.
2.4.1 Adsorption mechanism

In 1916, Langmuir first postulated the theory of gas adsorption onto homogeneous surfaces attributed to physisorption and chemisorption [98]. The removal of gas molecules from the air through a fibrous structure may involve one or more of the following mechanisms: (a) diffusion (mass transfer) of the gas to the gross surface of sorbent, (b) adsorption of gas into the large pores of the structure, (c) adsorption of the gas molecule into the interior of the surface and (d) the chemical reaction between the gas molecule and the structure which may be treated as absorption and not adsorption [99].

Physical adsorption refers to the capturing of molecules at the surface pores of the fibre structure due to intermolecular attraction, i.e. Van der Waals forces [100]. The US-EPA [97] have documented the adsorption process which is as follows. A molecule is placed near the adsorbent surface, for instance, polymer surface at a certain distance normal to the surface (Figure 2-4a). There is repulsion between electron clouds of the molecule and the surface, but there is also a Van der Waals nuclear attraction force which has relatively less radius of influence. The difference between the attraction forces creates a “well” in the potential energy curve for a very short distance (Figure 2-4b). Molecules get adsorbed in the well and require kinetic energy to desorb.

Chemisorption is defined as converting pollutants into simpler compounds by chemical action. The chemical action may be a nucleophilic attack, acid-base reaction, catalytic/non-
catalytic oxidation and reduction, or polymerisation. Chemisorption is more selective than physisorption.

2.4.2 Gas adsorption performance

Two ways can be used to evaluate gas adsorption performance of ENM, adsorption capacity and breakthrough time. The adsorption capacity is defined as the amount of target chemical adsorbed per unit of mass of the filter as a function of pressure and temperature (adsorption isotherm). While in breakthrough experiments, the efficacy of sorbent to remove a target chemical is evaluated, which is often expressed as a function of time [95].

The quantification of gas adsorption capacity is relatively complex compared to the measurement of PM filtration efficiency. Figure 2-5 shows a typical setup for VOC adsorption. A fibre mat is placed in an airtight container where a known amount of VOC injected on the fibre surface and allowed to evaporate for one hour. After the exposure, unabsorbed residual VOC was fed to the Tenax-GR absorber and subsequently analysed using gas chromatography. The experiment without any fibre mat was also performed to calculate VOC adsorbed on a fibre mat. In such experimental setups, VOC concentration and exposure time can be controlled. The residual air, after VOC exposure, can be analysed using different analytical methods such as gas chromatography and mass spectroscopy [87, 100-104].

![Figure 2-5 VOC adsorption setup](103) (with permission from Elsevier).
The VOC adsorption capacity of filter media can be determined in two ways. One is to determine the residual concentration of VOC in the air by gas chromatography as discussed above. However, gas chromatography is complex and may not be appropriate for VOCs like formaldehyde [29]. Another way, extract the VOC adsorbed by the filter media in a suitable solvent and analyse through techniques such as high performance liquid chromatography (HPLC) [105, 106], UV-VIS spectrophotometry [13, 87, 107] and BET adsorption isotherm [108]. For instance, the fibre sample after formaldehyde exposure treated with 2,4-dinitrophenylhydrazine (2, 4-DNPH) according to US-EPA 8315 method and the mixture analysed using HPLC to determine formaldehyde hydrazone concentration [105]. HPLC equipped with UV detector is used to measure aniline vapour adsorbed by the sample after immersion in acetonitrile [106]. In BET isotherm [108], a known amount of VOC is injected into the nitrogen stream under controlled temperature. The sample is challenged against the stream. The increase in sample weight and equilibrium is recorded. The adsorption capacity is expressed as:

\[ \eta = \left( \frac{M}{M_0} \right) - 1 \]  

(2-13)

where \(M\) and \(M_0\) are the equilibrium and initial masses of the sample.

UV spectroscopy is a relatively simple technique which can be used to evaluate VOC adsorption capacity and also applicable to a range of VOCs including xylene and benzene. The characteristic absorbance of a specific VOC in a suitable solvent can be determined and calibrated. The adsorbed VOC by the filter sample can be extracted in the same solvent. UV spectrum of the samples can be compared with the calibration, and VOC adsorption per mass unit of the filter can be calculated. On the other hand, UV spectroscopy can also be used to determine the change in absorbance when the sample is immersed in the solution containing gaseous pollutant [13, 87, 107].

Although UV spectroscopy applies to xylene and benzene, formaldehyde (HCHO) is hard to detect. Instead, commercial Formaldemeter™ (PPM technology) [100, 109] is used to determine formaldehyde concentration in air. This digital meter shows the HCHO concentration in 0.01 ppm increments. The formaldemeter is work on the principle of the electrochemical sensor. The sensor is comprised of two metal electrodes and an electrolyte. When air is drawn
into the sensor, a small voltage is generated which is directly proportional to the HCHO concentration in the sample.

2.5 ENMs for air filtration and gas adsorption

Polymers and ceramics are the materials that can be electrospun. The choice of materials in electrospinning depends on the application. For instance, ceramic nanostructures can be used in chemical and biological sensors, microelectronic devices and drug delivery [3]. Polymeric electrospun nanofibres have a broad range of applications from filtration to tissue engineering [3, 4, 110]. It is worth to mention that air filtration is the first commercially successful application of electrospun nanofibres based on polymers. Although polymer is a generic name given to a vast number of materials which have high molecular weight, the discussion henceforth is referred to in the context of organic polymers.

2.5.1 Polymers

The molecular weight, concentration and solubility are the critical parameters of polymer for electrospinning. These parameters determine the solution characteristics such as viscosity, surface tension and conductivity. The solution characteristics along with electrospinning process parameters have a strong influence on resultant fibre morphology. Mostly all polymer types can be electrospun through the versatility of the electrospinning process. For air filtration applications, synthetic polymers preferred in electrospinning (Table 2-4) owing to their high strength, excellent abrasion resistance, thermal stability, chemical stability and low cost [12, 14, 83, 111-113].
Table 2-4 Examples of synthetic polymers electrospun for air filtration application reported in the literature.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular weight (g/mol)</th>
<th>Concentration (%)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>90,000 120,000</td>
<td>7–13</td>
<td>DMF</td>
<td>[12, 112, 114, 115]</td>
</tr>
<tr>
<td>Nylon 6 and</td>
<td>18,000 63,000</td>
<td>10–17.5 25</td>
<td>Formic acid, 2,2,2-tri-fluoro ethanol</td>
<td>[14, 83, 91, 111, 116-118]</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PU</td>
<td>65,000</td>
<td>10, 13</td>
<td>DMF, DMF:MEK, THF:DMF</td>
<td>[19, 23, 93, 103, 108]</td>
</tr>
<tr>
<td>PVA</td>
<td>85,000–150,000</td>
<td>6–10</td>
<td>Water</td>
<td>[13, 82, 119]</td>
</tr>
</tbody>
</table>

Among synthetic polymers, PAN and nylon are widely electrospun for air filtration applications. PAN nanofibre is more efficient in capturing PM and gaseous pollutants as compared to the nanofibres prepared using nylon [120], polyvinyl pyrrolidine (PVP), polystyrene (PS), polyvinyl alcohol (PVA) and polypropylene (PP) [114]. Figure 2-6 shows that PAN has a higher dipole moment (3.6 Debye (D) units) than other polymers such as PVA and PP. The high dipole moment indicates the strong polarity of PAN polymer. Thus, PAN tightly binds the smoke particle around itself which is different from mere surface attachment (Figure 2-7). PAN can capture pollutants ten times of its self-weight owing to higher dipole moment and efficient single fibre capture mechanism [114].
Figure 2-6 Molecular model and formula of different polymers including PAN, PVP, PS, PVP and PP with calculated dipole moments of the repeating units of each polymer [114] (with permission from Springer Nature).

PAN-based nanofibre filter showed a 95–100% efficiency over 100 h in Beijing field test [114] under hazardous air quality conditions (PM 2.5 index > 300). The electrospun fibres produced using nylon showed small diameter, narrow diameter distribution [111] and high electrostatic charge [14]. Nylon nanofibre filters exhibit excellent filtration efficiency, 250% higher as compared to cotton cloth [83]. Nylon ENM also showed five times reduced areal density and almost three times less pressure drop than the commercial glass filter media [117].

Figure 2-7 FE-SEM image showing PM tightly wrapped around the PAN nanofibre. Scale bar, 1 µm [114] (with permission from Springer Nature).

Besides PAN and nylon, polymers such as polyvinyl alcohol (PVA) [82, 119], polyurethane (PU) [19, 103, 108], polyvinylidene fluoride (PVDF) [87], polymethyl methacrylate (PMMA) [121], polyester [106], polyethylene oxide (PEO) [75], polyvinyl chloride (PVC) [93] and
polystyrene [107] have been electrospun for air filtration applications. The filtration efficiency and pressure drop of PVA ENM are better than conventional cotton based respirator [82]. PU ENM employed for VOC absorption [108] was developed as a protective textile against chemical and biological threats in the air [113]. PS was chosen as a matrix for adsorption of organic compound in the air since it does not form inclusion complexes with chemicals used in electrospinning [107].

With increasing concerns for sustainability, researchers recently employed organic and semi-organic polymers in electrospinning for air filtration. Examples include PLA [122, 123], silk, chitosan [124] and keratin (extracted from wool) [100]. Biopolymers blend, PLA/PHB [125] and bio-based PA-56 [126] showed good mechanical strength, high filtration efficiency, low pressure drop and high dust loading capacity.

The protein-based biopolymers have the potential for active filtration. For instance, keratin absorbs and removes toxic substances in the air including aerosols [127], formaldehyde [128, 129] and other hazardous VOCs [130] due to electrostatic attraction forces, three-dimensional complex proteins structure and general reactivity towards aldehydes. However, electrospinning of keratin is difficult due to the low molecular weight. Hence, keratin as an additive blended with nylon for ease of electrospinning [131, 132]. Similarly, many other additives can be employed for VOC adsorption.

### 2.5.2 Additives

Additives can be used to modify polymer solution properties such as viscosity, surface tension and conductivity to enhance the electrospinning ability of a solution. For example, sodium chloride electrolyte improves the conductivity of the melt during electrospinning [133]. Additives can also be used to increase the absorption capacity of the ENMs towards VOCs. In this thesis, an additive is employed to improve VOC adsorption. Table 2-5 shows different additives used in electrospinning for preparation of composite ENMs for gaseous pollutants adsorption. Additives studied so far include metal oxides like titanium dioxide (TiO$_2$) [13, 134], aluminium oxide (Al$_2$O$_3$) [87], silicon dioxide (SiO$_2$) [112], starch product like β–cyclodextrin (β–CD) [101, 107, 121] and mineral compounds such as fly ash particles (FAP’s) [103]. This additive imparted functionality to composite ENMs along with morphological modifications.
Table 2-5 Examples of additives used in electrospinning to adsorb gaseous pollutants.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Polymer</th>
<th>Pollutant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>PVA</td>
<td>Acetone</td>
<td>[13]</td>
</tr>
<tr>
<td>Al$_2$O$_3$ and silver</td>
<td>PVDF</td>
<td>Paraoxon</td>
<td>[87]</td>
</tr>
<tr>
<td>β-Cyclodextrin</td>
<td>PMMA</td>
<td>Styrene, Toluene</td>
<td>[101]</td>
</tr>
<tr>
<td>β-Cyclodextrin</td>
<td>Polyester</td>
<td>Aniline</td>
<td>[106]</td>
</tr>
<tr>
<td>β-Cyclodextrin</td>
<td>PS</td>
<td>Phenolphthalein</td>
<td>[107]</td>
</tr>
<tr>
<td>Keratin</td>
<td>Nylon</td>
<td>Formaldehyde</td>
<td>[100]</td>
</tr>
<tr>
<td>FAP</td>
<td>PU</td>
<td>Chloroform, Benzene, Toluene, Xylene, Styrene</td>
<td>[103]</td>
</tr>
</tbody>
</table>

Metal oxide additives can enhance the specific surface area and surface roughness of the ENM. TiO$_2$ presence in PSU [134] and PVA [13] solution reduced the fibre diameter, due to reduced viscosity and created “nano” protrusions (Figure 2-8a) in the membrane with micro and nanoscale roughness that enhanced filtration. TiO$_2$ creates free radicals in the presence of UV light which degrades the concentration of acetone VOC by photocatalysis [13]. The metal oxides can purify toxic gases by catalysing them to less harmful chemical species. Al$_2$O$_3$ enabled PVDF–silver ENM efficiently captured PM, biological contaminants and chemical pollutants in a single step air filtration [87].
It has been observed that β-CD assisted in preparing bead-free PMMA and PET nanofibres at low polymer concentrations [121]. PMMA/β–CD ENMs nanofibres [101] trapped styrene, toluene and aniline. The addition of β-CD into PET [106] and PS [107] entrapped aniline vapour and phenolphthalein respectively. Inclusion complexes are formed with the small organic compounds trapped in β–CD cavities. PU/FAP composite ENMs (Figure 2-8b) have been found to remove VOCs from the air [103]. FAPs possess physicochemical properties such as bulk density, particle size, porosity and surface area which make them suitable for air filtration [103].

As mentioned above additives used in electrospinning also affect fibre diameter, pore size and thickness of composite ENM. Additives such as TiO₂, BTEAC, FAP and FPU tend to decrease the nanofibre diameter. Whereas, the addition of Al₂O₃ [87] and PU [93] in composite ENM caused to increase the nanofibre diameter. FPU decreased the pore size from 4.3 to 1 μm as its concentration in the solution rose from 0.25 to 1% [115]. Al₂O₃ (8%) reduced pore size of PVDF ENMs from 0.56 to 0.36 μm [87]. Silica reduced the fibre diameter and decreased the contact area among nanofibres resulting in small pore size [135]. Sometimes additives such as Al₂O₃ and BTEAC also contribute to increasing the thickness [87, 136] of ENMs.

All the above additives reported in the literature are aimed at gas adsorption of composite ENMs. However, limited information is available on aerosol filtration of such composite ENMs. Also, additives modified the morphology of composite ENMs which may affect the aerosol filtration performance.
2.6 PM filtration performance of ENMs

PM filtration performance varies with morphology (fibre diameter, pore size), properties (thickness, basis weight, packing density) and structure (single/multilayer, composite) of ENMs. The following section provides further information about the effect of the various parameters.

2.6.1 Effect of morphology

Fibre diameter affects filtration efficiency. The filtration efficiency of PAN filter increased from 48.21 to 98.11% as the fibre diameter was reduced from 1000 nm to 200 nm [114]. Table 2-6 shows air filtration performance of ENMs for various fibre diameters and different polymer types. Nanofibre diameters up to 300 nm can be suitable to attain more than 99% filtration efficiency for particles of size 300 nm. However, smaller fibre diameter increases the pressure drop of ENMs.

Table 2-6 Air filtration performance of electrospun polymers along with fibre diameter and basis weight.

<table>
<thead>
<tr>
<th>Material</th>
<th>Fibre diameter (nm)</th>
<th>Weight (g/m²)</th>
<th>PM size (nm)</th>
<th>Filtration efficiency (%)</th>
<th>Pressure drop (Pa)</th>
<th>Quality factor (1/Pa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>273</td>
<td>5.18</td>
<td>260</td>
<td>99.997</td>
<td>165.3</td>
<td>0.065</td>
<td>[122]</td>
</tr>
<tr>
<td>PA6</td>
<td>150</td>
<td>1.5</td>
<td>300</td>
<td>99.5</td>
<td>500</td>
<td>0.01</td>
<td>[83]</td>
</tr>
<tr>
<td>PA/PAN</td>
<td>272</td>
<td>2.94</td>
<td>300</td>
<td>99.99</td>
<td>100</td>
<td>0.1163</td>
<td>[137]</td>
</tr>
<tr>
<td>PAN</td>
<td>200</td>
<td>NA</td>
<td>&lt; 100</td>
<td>96.12</td>
<td>133</td>
<td>0.024</td>
<td>[114]</td>
</tr>
<tr>
<td>PAN/SiO₂</td>
<td>650</td>
<td>2.04</td>
<td>300–500</td>
<td>99.989</td>
<td>117</td>
<td>0.02–0.14</td>
<td>[112]</td>
</tr>
<tr>
<td>PAN/PU</td>
<td>175</td>
<td>24</td>
<td>300–500</td>
<td>99.98</td>
<td>120</td>
<td>0.07</td>
<td>[115]</td>
</tr>
<tr>
<td>PU</td>
<td>120</td>
<td>0.4–0.9</td>
<td>20–400</td>
<td>99.66</td>
<td>96–190</td>
<td>0.059–0.029</td>
<td>[19]</td>
</tr>
<tr>
<td>PVC/PU</td>
<td>960</td>
<td>20.72</td>
<td>300–500</td>
<td>99.5</td>
<td>144</td>
<td>0.036</td>
<td>[93]</td>
</tr>
<tr>
<td>PSU/TiO₂</td>
<td>760</td>
<td>7.75</td>
<td>300–500</td>
<td>99.997</td>
<td>45.3</td>
<td>0.07–0.1</td>
<td>[134]</td>
</tr>
</tbody>
</table>
ENMs have different pores such as closed pores, blind pores and through pores as a result of the ways the nanofibres laid over each other during the electrospinning process [138]. Closed pores are not accessible, and blind pores terminate inside the ENM structure itself and are therefore no use for filtration application. It is the through pores that form open passageways through the ENM thickness and hence critical for air filtration. Generally, the pore size is not identical, but instead there is a distribution in their size which determines through pore characteristics.

The pore size of ENM largely depends on electrospinning time at the same deposition area. PA6 ENM electrospun for 5 min showed pore size of 0.24 μm. The electrospinning time of 15 min reduced the pore size to 0.15 μm [14]. It is essential to determine the electrospinning time at which the desired average pore size is produced which satisfies the filtration requirement. Due to the small pore sizes, compared to glass microfibre, ENMs can capture dust particles on its surface [92]. ENMs with smaller pore sizes can increase filtration efficiency but adversely affects both air permeability and pressure drop, i.e. decreases permeability and increases the pressure drop [117]. The combination of pore sizes 0.2 μm and 0.098 μm from PU ENM of average diameter (120 nm) alters the tortuous path of air flow thereby reduce the pressure drop from 123 Pa to 96 Pa [19].

As mentioned above, PM size can influence filtration efficiency and pressure drop which eventually effects quality factor (Figure 2-9). For PM less than 0.1 μm, ENM with nanofibre diameter of 185 nm were found to be more efficient than those with 94 nm due to the natural diffusion of small PM [139]. However, for particles of the size range 0.1–0.4 μm, ENM with fibre diameters of 94 nm showed a higher quality factor than ENMs with NF diameters of 185 nm which is due to the dominance of the interception mechanism over the diffusion mechanism. The smaller fibre diameter reduces the pore size by decreasing the pore aperture and enhancing the direct-interception mechanism for particle capture [82].
Nanofibre diameter effect on (a) filtration efficiency and (b) on quality factor. Small fibre diameters show higher filtration efficiency and a more significant pressure drop at the same mass coverage and face velocity. However, smaller fibre shows lower quality factor for particles (0.3 μm) and tends to improve with an increase in particle size (0.3 μm to 1 μm) (49) (with permission from Elsevier).

2.6.2 Effect of basis weight and thickness

ENM basis weight and thickness are directly proportional to each other and linearly dependent on electrospinning time [140]. The basis weight is directly proportional to pressure drop and inversely proportional to air permeability [141]. A small change in basis weight of ENMs can have a significant effect on filtration efficiency and pressure drop (Figure 2-10). The basis weight of 0.5 g/m² with 100 nm fibre diameter yielded maximum benefit to filtration efficiency at least expense of pressure drop [111].
ENMs of a few micron thicknesses restrict the air flow of the membrane to a great extent [14]. ENM of comparable thickness, if arranged in layers instead of one thick coat, can improve filtration efficiency [19]. ENM thickness does not improve PM filtration beyond a certain limit, but the pressure drop does increase thus deteriorating the quality factor [111]. ENM thickness reported from several studies ranges from 2.3 to 71 µm [14, 19, 82, 111, 119]. ENM thickness is invariably linked with basis weight and packing density. In general, basis weight increases with ENM thickness while packing density reduces with higher ENM thickness. It is important to balance between ENM thickness, basis weight and packing density to achieve desirable filtration performance at reduced pressure drop. The determination of ENM thickness presents a challenge since ENMs are soft and easily compressible. Conventional micrometre measurement may not be an accurate representation of thickness as the force applied would be too high for the thin and soft ENMs. Instead, alternative options such as non-contact laser microscopy could be used for thickness measurement.

**Figure 2-10** Effect of mass coverage on filtration efficiency and pressure drop at constant face velocity and same fibre diameter [139] (with permission from Elsevier).
Higher ENM thickness invariably reduces the packing density of the nanofibres. Packing density is often derived theoretically calculations of which are explained in subsequent chapters at relevant places. Although the volumetric fraction of fibre and the packing density is small, the pressure drop can significantly increase due to small fibre diameter and small pore size.

2.6.3 Effect of structure fabrication

The electrospinning technique offers versatile ways to produce ENMs with different structures which consequently improve quality factor. Innovative structures such as hybrid [142, 143], bead on a string [122] and multilayered [112] have been studied to maximise quality factor. In the case of a composite coarse-fine nanofibre structure, the fine fibres contribute to filtration efficiency while the coarser fibre contributes to rigidity. Thus, an integrated ENM comprised of coarse and fine nanofibres with alternate stacking could be useful in achieving high filtration efficiency at minimum pressure drop.

Beads on string structure have been prepared [122] using a low concentration of PLA on the continuous matrix of PLA ENM. The beads in the fibre structure were formed due to the low viscosity and insufficient stretching of the polymer solution in the electric field. The beaded structure increased the distance between the nanofibres and reduced the volume fraction of the membrane allowing more natural air flow through the filter. Beads on string structure exhibited higher filtration efficiency and a relatively lower pressure drop compared to a composition without beads. However, it is not known that the beads were uniformly distributed in the ENM and made up of the same size.

A twinjet electrospinning system was used to form a multilayer composite structure consisting of pristine PAN and PAN/SiO₂ blend [112]. The heterogeneous nature of the solutions created micro pockets bonding with base ENM at different places. This structure eventually, yielding a filter with a high quality factor. Recently, the composite ENM of PAN/PA with 2/2 jet ratio showed excellent filtration efficiency (> 95%) and high quality factor (0.11/Pa) at small basis weight (2.94 g/m²) [137]. The twinjet spinning of two different polymers produced an excellent blend of fibre diameters and pore sizes. However, adjustments of jet ratios and complexity of electrospinning system could be an issue for bulk processing.

In another study [144], five layers of polyether sulphone ENM were arranged in a reducing pore size order (29.6 µm to 4.6 µm) to mimic cocoons tree-like structure. The hierarchical pore
sizes were obtained by varying the electrospinning time from 5 min for the first three layers and 20 min for the last two. This multilayer arrangement showed a dramatic increase in filtration efficiency (38% to 96%) with good air permeability (106 mm/s).

Multiple thin layers of ENMs, instead of a single thick layer, deposited for shorter times with similar basis weight showed improvement in quality factor [139, 145]. PEO nanofibres sandwiched between two nonwoven microfibre structures showed consistent pore size, filtration efficiency and pressure drop when subjected to repeated filtration tests [138]. Electrospun structures such as core-shell, hollow and porous nanofibre structures [146] have shown to be useful in preparing combined ultra-filtration materials for the PM and gaseous pollutants.

2.6.4 Effect of filter test conditions

Figure 2-11 shows a typical experimental setup used to measure air filtration performance of ENMs. In addition, commercial filter testers such as TSI 8130 filter tester (USA) and Huada filter tester (China) are also used in many reports. These filtration setups use an atomiser to generate aerosols from the salt solutions. Most commonly used aerosols are sodium chloride, potassium chloride and methylene blue.

Aerosol size, air flow rate and ENM sample size are the variables in the filter test which influence air filtration results. Mostly, air filtration performance of ENMs against 0.3 μm aerosols is reported while limited studies described filtration performance for a broad range of particles (0.3–5 μm). Air flow rate and ENM sample size together determine the face velocity of the test. The air flow rate varies from 10 L/min to 95 L/min. The smallest sample size could be 36 mm in diameter and maximum could be 109 mm.

The choice of face velocity depends on the intended application of the filter media. For respiratory filtration, a smaller face velocity (5.3 cm/s), which resemble the breathing rate, is preferred. At higher face velocity, for instance, 15 cm/s, pressure drop elevates by two times or greater. The face velocity and pressure drop are linearly proportional.

It is difficult to compare the filter performance of ENMs due to variations in the filter test protocols [147]. The differences include the type of aerosol, aerosol size, sample size, flow rate, face velocity, temperature and RH. This study followed the AS NZ 2012 standard as a benchmark to evaluate the performance of ENMs.
Experimental set up used for air filtration performance measurement [123] (with permission from Elsevier).

2.7 Gas adsorption performance of ENMs

The commonly used ambient air cleaning technologies are catalytic oxidation, plasma, ozone, adsorption, filtration and ultraviolet disinfection [90]. Among those, filtration is good for PM while sorption is useful for gaseous pollutants. The catalytic oxidation, plasma, ozone, and ultraviolet disinfection are also suitable for degradation of gaseous pollutants. However, these technologies may produce a relatively high amount of secondary pollutants [90]. Sometimes, the two techniques can be used sequentially to improve the gas adsorption performance of ENM. Porous carbon nanofibres were prepared by oxidation and carbonisation of PAN electrospun nanofibres for NO removal at room temperature [148]. The removal mechanism follows the sequence of adsorption, catalytic oxidation of NO into NO2 and reduction of N to N2.

The high specific surface area of ENMs makes them potentially suitable for removal of PM and gaseous air pollutants, along with biological contaminants [149]. The specific surface area of the electrospun polymeric material varies between 5 to 200 m²/g [103, 122] which is, lower than activated carbon granules (>800 m²/g). The relatively smaller surface areas of polymeric
nanofibres may be a limiting factor to adsorb gaseous pollutants. To overcome this limitation, the ENM must be more efficient and selective. In this context, the chemical absorption and choice of selecting materials for specific pollutants would be useful. Chemically modified ENMs can efficiently capture gaseous pollutants without producing any harmful by-products [149], although the chemistry will vary depending upon the GM pollutant.

Nanofibres made from PU and containing metal oxide particles showed excellent photocatalytic activity to neutralise NOx and CO [150]. Tin oxide/chromium oxide (95/5) particles with 3% concentration in PU showed 70–80% catalytic efficiency (ratio of emission before and after the filter) towards NOx, CO and CO₂ [150]. These chemical species have been oxidised over the tin oxide/chromium oxide photocatalyst.

2.7.1 VOC adsorption

Additives such as metal oxides and biomaterials during electrospinning of synthetic polymers have been found effective in VOC pollutants filtration. Table 2-7 shows different ENM materials that have been used to adsorb various VOCs. ENMs have adsorbed VOC pollutants such as formaldehyde [100], acetone [13, 108], aniline [101, 106], toluene [103, 108], chloroform [103] xylene and benzene [103].
Table 2-7 Electrospun polymers and pollutants used for detoxification study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter (nm)</th>
<th>VOC pollutant tested</th>
<th>Concentration (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keratin/PA6</td>
<td>150</td>
<td>Formaldehyde</td>
<td>0.6</td>
<td>[100]</td>
</tr>
<tr>
<td>PU</td>
<td>2000</td>
<td>Toluene, acetone, chloroform and hexane</td>
<td>Not available</td>
<td>[108]</td>
</tr>
<tr>
<td>PU/ FAP</td>
<td>267</td>
<td>Chloroform, benzene, toluene, o-xylene and styrene</td>
<td>4</td>
<td>[103]</td>
</tr>
<tr>
<td>PET/CD</td>
<td>150–2740</td>
<td>Aniline vapour</td>
<td>500-4000</td>
<td>[106]</td>
</tr>
<tr>
<td>PMMA/CD</td>
<td>800–1000</td>
<td>Styrene, toluene and aniline vapour</td>
<td>Not available</td>
<td>[101]</td>
</tr>
<tr>
<td>PVDF/Ag/Al₂O₃</td>
<td>1850</td>
<td>Paraoxon</td>
<td>30</td>
<td>[87]</td>
</tr>
</tbody>
</table>

Protein-based keratin ENMs proved effective against formaldehyde [100, 151]. This is due to the porous network within the membrane and a large number of functional groups on the keratin protein. The functional groups include polar side chains of amino acid which offer active chemical sites to entrap VOCs. The keratin/PA ENM reduced formaldehyde concentration by 70% in relatively quick time as compared to pristine polyamide [100] materials. Currently, keratin use for air filtration is limited to one or two reports in the open literature [100, 151]. Gelatin is another protein polymer, which can be readily electrospun, is used in this thesis.

TiO₂ nanoparticle-enabled ENM degraded 98% of acetone (250 ppm) in 10 seconds [13]. However, at higher acetone concentrations (1500 ppm) loss in degradation efficiency is observed. [13]. PU ENM absorbed toluene, chloroform, acetone, and hexane [108]. The VOC absorption capacity of pure PU ENM is significantly enhanced using FAPs [13]. The composite ENM can form a π-complex with VOCs. The PU/FAP ENM was effective against styrene followed by xylene, toluene, benzene and chloroform [13].
Use of cyclodextrin in ENMs effectively entrapped aniline vapour [106] due to the formation of an inclusion complex and their large surface area. ENMs of pristine PET, PET/α-CD, PET/β-CD and PET/γ-CD captured approximately 1300, 2600, 2600 and 3400 ppm of aniline respectively, in an exposure time of 12 h [106]. The high adsorption of γ-CD was attributed to the bigger cavity size of γ-CD that allowed greater amounts of aniline to form a complex. The choice among α, β and γ CD depend on the size of target pollutant to be captured. However, β-CD may be preferred in many studies due to less solubility in water compared to the other two which makes it suitable for a broad range of applications. β-CD modifies fibre surface and catalytically cleaves reactive esters or phosphates [152].

2.8 β–Cyclodextrin (β–CD)

Cyclodextrins (CD) are cyclic oligosaccharides obtained from starch [153]. The well-known industrially produced cyclodextrins are α–CD, β–CD and γ–CD [154]. CD is produced from the enzymatic conversion of starch [155-157]. The manufacturing process of β–CD has four stages: (i) preparation of microorganism culture to produce the cyclodextrin glucosyltransferase enzyme (CGT-ase); (ii) separation and purification of enzyme from the fermentation medium; (iii) enzymatic conversion of pre-hydrolyzed starch; and (iv) separation β–CD from the mixture. The enzyme degrades the starch and initiates intermolecular attractions without precipitating the water [154]. The glucopyranose units’ link together through glycosidic oxygen bridges by α-(1,4) bonds to form CD. The α–CD, β–CD and γ–CD have six, seven and eight such units linked together respectively. However, the purification of α–CD and γ–CD elevates the production cost multiple times. β–CD has been commercially the most attractive one due to availability, simple synthesis, good reactivity and lower price [158, 159]. Hence, more than 95% of the CD used in the industry are β–CD.

2.8.1 Structure and properties of β–CD

Figure 2-12a shows the chemical structure of β–CD which is seven repeating glucose units linked via α-1,4-glucosidic bonds [153, 155-157, 160]. β–CD is a torus-shaped crystalline substance isolated from starch digestion and is homogenous and non-hygroscopic [153, 154]. β–CD is non-toxic nature, biodegradable and has a macrocyclic structure [161]. β–CD has a cyclic molecule with a cone-shaped structure (Figure 2-12b) with a hydrophilic exterior and a
hydrophobic interior cavity capable of forming host-guest complexes with organic molecules [162, 163]. Table 2-8 tabulates properties of β–CD.

![Figure 2-12](image)

**Figure 2-12** (a) glucopyranose units linked by α (1–4)-glycosidic linkages forming β–CD structure, (b) truncated cone-shaped β–CD, (c) inclusion complex of a drug with β–CD. (with permission from Elsevier [164].

**Table 2-8** Properties of β–CD [159].

<table>
<thead>
<tr>
<th>Property</th>
<th>β–CD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>1135</td>
</tr>
<tr>
<td>Solubility in water at 25°C (%)</td>
<td>1.85</td>
</tr>
<tr>
<td>The outer diameter (Å)</td>
<td>15.4</td>
</tr>
<tr>
<td>Cavity diameter (Å)</td>
<td>6.0</td>
</tr>
<tr>
<td>The height of torus (Å)</td>
<td>7.9</td>
</tr>
<tr>
<td>Cavity volume for 1 mol β–CD (ml)</td>
<td>262</td>
</tr>
</tbody>
</table>

Bhaskara et al. [165] compiled different techniques adopted to attach β–CD to textile fabrics such as cotton, wool and polyester. The techniques include cross-linking, grafting, reactive fixation, disperse dyeing method, a basic dyeing method, sol-gel process, enzymatic coupling and polymer extrusion.

β–CD has been successfully cross-linked to cotton fabrics using epichlorohydrin and the polycarboxylic acids [166]. Among cross-linking agents, 1,2,3,4-butane tetracarboxylic acid (BTCA) is preferred as it is less toxic than epichlorohydrin. BTCA with four carboxyl groups
per molecule reacts with the hydroxyl groups of cellulose and form stable ester bonds [167]. The cross-linked fabrics did show better anti-wrinkle properties and better adsorption of dyes.

β–CD has limited water solubility due to the intramolecular hydrogen bonds within the β–CD which prevents their attachment to surrounding molecules [157]. The hydrogen bonds of β–CD need to be substituted by methyl or hydroxypropyl groups which require a chemical modification. Often the chemical modification involves a toxic preparation method [168] and also implies costly manufacturing [169]. For instance, a typical randomly methylated β–CD, heptakis (2,6-di-O-methyl)-β-CD (DIMEB) showed excellent water solubility at lower temperatures and found favourable for separation. However, the manufacturing process is toxic and adds cost [168]. For example, the toluene adsorption of unmodified β–CD (0.506 mg/g) was higher than hydroxypropyl β–CD (0.314 mg/g) and randomly methylated β–CD (0.366 mg/g) [170].

2.8.2 β–CD for pollutant adsorption

β–CD has a hydrophilic outer surface and a hollow hydrophobic interior which forms a truncated cone-shaped cavity both in diameter and height [171]. This typical cavity structure of β–CD can accommodate a variety of complex guest molecules. Thus, it is one of the simplest encapsulation systems [160]. β–CD can adsorb VOCs in the air and forms an inclusion complex with them (Figure 2-12c) [160, 171]. Mostly, the complex is stable and remain unchanged after many regeneration cycles [169]. The advantage is that β–CD can be used in their dissolved or solid, native or modified forms for pollutant adsorption.

Literature indicates that β–CD has been used either in solid or liquid form for adsorption of VOCs, polycyclic aromatic hydrocarbons, organic molecules, dye molecules and metal ions. The micro-pollutants adsorbed by β–CD can be grouped based on the two target applications: air filtration and water filtration. Table 2-9 shows examples of β–CD for air filtration to adsorb different air pollutants. β–CD captured pollutants such as HCHO, toluene, aniline and styrene. Two different types of gaseous pollutant adsorption studies reported in the literature. One is direct adsorption or release from the air, and another is adsorption from aqueous solution. For measurement from the air, gas chromatography is commonly used while UV spectroscopy is used for analysis from aqueous solutions. The nanofibre samples exposed to the target air
pollutant. The adsorbed contaminant is extracted using a suitable solvent and quantified using UV-vis spectroscopy.

**Table 2-9** Different air pollutants adsorbed by β–CD.

<table>
<thead>
<tr>
<th>β–CD form</th>
<th>Measurement medium</th>
<th>Measurement principle</th>
<th>Pollutant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN/β–CD composite nanofibre (432–647 nm)</td>
<td>Air</td>
<td>US-EPA 8315; Extraction using 2,4 dinitrophenylhydrazine (DNPH)</td>
<td>HCHO</td>
<td>[105]</td>
</tr>
<tr>
<td>β–CD; hydroxypropyl β–CD; Methylated β–CD; Sulfo-butyl-ether β–CD</td>
<td>Air</td>
<td>Gas chromatography with flame ionising detector</td>
<td>Toluene (0.3–0.5 μg/mg)</td>
<td>[170]</td>
</tr>
<tr>
<td>Solid β–CD</td>
<td>Aqueous</td>
<td>UV-spectrophotometry</td>
<td>Naphthalene</td>
<td>[172]</td>
</tr>
<tr>
<td>PET/β–CD nanofibres (300–2200 nm)</td>
<td>Aqueous</td>
<td>After 12 h exposure of aniline, the web was immersed in two mL acetonitrile to extract aniline using HPLC</td>
<td>Aniline</td>
<td>[106]</td>
</tr>
<tr>
<td>β–CD modified zeolite</td>
<td>Air</td>
<td>Gas chromatography;</td>
<td>Toluene;</td>
<td>[173]</td>
</tr>
<tr>
<td>β–CD cross-linked cotton fabric</td>
<td>Aqueous</td>
<td>UV-spectrophotometry</td>
<td>Styrene</td>
<td>[174]</td>
</tr>
<tr>
<td>Monochlorotriazinyl CD attached to the cotton fabric</td>
<td>Air</td>
<td>Electronic nose equipment</td>
<td>Third-hand cigarette smoke</td>
<td>[175]</td>
</tr>
<tr>
<td>β–CD powder; β–CD solution in water and KI solution</td>
<td>Aqueous</td>
<td>Sodium thiosulphate titration</td>
<td>Iodine</td>
<td>[176]</td>
</tr>
<tr>
<td>β–CD/polymethyl methacrylate (675-816 nm)</td>
<td>Air</td>
<td>Styrene, toluene and aniline</td>
<td>Direct pyrolysis mass spectroscopy</td>
<td>[101]</td>
</tr>
<tr>
<td>Polyvinyl chloride/β–CD nanofibres</td>
<td>Aqueous</td>
<td>UV-spectrophotometry</td>
<td>Paraoxon (organophosphorous agent)</td>
<td>[177]</td>
</tr>
</tbody>
</table>

Recently, β–CD was used as an additive in electrospinning to produce useful ENMs to adsorb VOCs [107, 155, 178-181]. However, β–CD tends to increase fibre diameter (more than 500 nm) and pore size (more than 2 μm) of the ENM consequently reducing surface area and air filtration efficiency. β–CD containing electrospun nanofibres having fibre diameter less than 500 nm and pore size less than 2 μm would be useful for filtration of solid/liquid aerosols and volatile organic compounds in the air.

Most of the adsorption studies of β–CD [155, 156, 181-183] devoted to aqueous solutions since quantification of VOC adsorption using liquid adsorbent is relatively easy and also water plays a vital role in host-guest complexion. Table 2-10 shows different water pollutants adsorbed using β–CD. The micropollutant such as phenolphthalein and dye molecule like methylene blue has been separated from water.
Table 2-10 β–CD for adsorption of water pollutants.

<table>
<thead>
<tr>
<th>β–CD form</th>
<th>Measurement principle</th>
<th>Pollutant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN–PAA/β–CD nanofibres (231–510 nm)</td>
<td>UV-spectrophotometry</td>
<td>Phenolphthalein</td>
<td>[184]</td>
</tr>
<tr>
<td>BTCA cross-linked hydroxyl propyl β–CD nanofibres (480 nm)</td>
<td>Dead-end filtration system using nitrogen gas stream</td>
<td>Methylene blue (96.79 mg/g)</td>
<td>[185]</td>
</tr>
<tr>
<td>PAN/β–CD composite nanofibre (465–580 nm)</td>
<td>UV-spectrophotometry</td>
<td>Methylene blue; Methylene violet</td>
<td>[186]</td>
</tr>
<tr>
<td>Chitosan/β–CD composite film</td>
<td>UV-spectrophotometry</td>
<td>Methyl orange</td>
<td>[187]</td>
</tr>
<tr>
<td>β–CD cross-linked PET nanofibres using citric acid (cross-linking agent) and SHPI (catalyst)</td>
<td>High-performance liquid chromatography</td>
<td>Phenanthrene</td>
<td>[106]</td>
</tr>
<tr>
<td>PAN/β–CD nanofibre</td>
<td>UV-spectrophotometry</td>
<td>Copper (II) ion</td>
<td>[188]</td>
</tr>
<tr>
<td>CMC β–CD</td>
<td>Inductively coupled plasma-optical emission spectrometry</td>
<td>Ba, Ca, Cd, Ni, Pb, Sr, and Zn</td>
<td>[189]</td>
</tr>
<tr>
<td>β–CD modified zeolite</td>
<td>UV-spectrophotometry; Methyl orange</td>
<td></td>
<td>[173]</td>
</tr>
<tr>
<td>β–CD cross-linked cotton fabric</td>
<td>UV-spectrophotometry</td>
<td>Bisphenol A</td>
<td>[174]</td>
</tr>
<tr>
<td>PES/ β–CD nanofibres (518 nm)</td>
<td>Gas chromatography</td>
<td>Steroid hormone estradiol; pesticide chlorpyrifos</td>
<td>[190]</td>
</tr>
<tr>
<td>PS/β–CD nanofibres</td>
<td>UV-spectrophotometry and Direct Pyrolysis mass spectrometry</td>
<td>phenolphthalein</td>
<td>[178]</td>
</tr>
<tr>
<td>β–CD cross-linked 4,4 difluorodiphenylsulfone</td>
<td>UV-spectrophotometry</td>
<td>2 napthol, propranolol hydrochloride,</td>
<td>[182]</td>
</tr>
<tr>
<td>Material</td>
<td>Method</td>
<td>Dyes/Reagents</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------------</td>
<td>----------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PS/polydopamine/β–CD</td>
<td>UV-spectrophotometry</td>
<td>bisphenol A, 2,4 dichlorophenol</td>
<td>[156]</td>
</tr>
<tr>
<td>Water-insoluble β–CD polymer cross-linked by a citric acid</td>
<td>UV-spectrophotometry</td>
<td>phenolphthalein</td>
<td>[183]</td>
</tr>
<tr>
<td>β–CD/PAA/citric acid</td>
<td>UV-spectrophotometry</td>
<td>Phenol and methylene blue</td>
<td>[155]</td>
</tr>
<tr>
<td>PVA/β–CD/sericin</td>
<td>UV-spectrophotometry</td>
<td>Methylene blue and methyl orange</td>
<td>[181]</td>
</tr>
</tbody>
</table>

### 2.9 Concluding remarks

Exposure to air pollutants causes acute and chronic effects on human health and is also strongly associated with mortality. Aerosols (PM) and gaseous pollutants are, ultimately, the primary and simplified classification of air pollutants. Aerosols and gaseous pollutants differ from each other regarding size and chemical composition. Consequently, the filtration mechanisms are entirely different. Diffusion and interception are the best mechanisms to describe aerosol filtration using ENMs whereas physical adsorption is the primary mechanism of gas molecules entrapment.

Filtration performance measurement of ENMs for PM and VOCs also vary to a large extent. Altogether different performance evaluation techniques are required for PM and VOCs. PM filter performance is commonly determined by filtration efficiency, pressure drop and quality factor. On the other hand, gas adsorption performance mainly expressed as adsorption capacity of a particular pollutant per unit mass of adsorbent or adsorption per unit time.

ENMs prepared from polymeric materials are established as successful PM filter media. However, high pressure drop even at a small basis weight of ENM is a drawback, especially in respiratory filtration. The morphology, basis weight, thickness and structure fabrication of ENM are the factors which influence the filtration result. The tunable morphology of ENM provides opportunities to prepare innovative compositions to reduce pressure drop. The reproducible beaded structure and hierarchical layering of coarse and nanofibres can be useful to achieve less pressure drop in ENMs.
Limited information is available on simultaneous filtration of aerosols and VOCs using ENMs. Nearly no study is focused on multifunctional air filtration at reduced air resistance which would be most suitable for respiratory filtration applications. The additive such as β-CD can be employed for multifunctional air filtration. The VOC adsorption analysis can be determined using a relatively quick method through a small in-house fabrication.

The majority of the published literature on β–CD is in the area of water filtration. Adsorption studies of β–CD have been limited to toluene, styrene and aniline air pollutants. Limited data are available on the adsorption of formaldehyde (HCHO), benzene and xylene VOCs.
Chapter 3

Air permeability of ENMs

3.1 Introduction

Electrospun nanofibre membranes have received considerable attention in air filtration owing to the high filtration efficiency attributed to the nanoscale diameter and small pore size [20, 82, 92]. However, as a consequence of small fibre diameter, ENMs restrict air flow which is not desirable in air filtration [16, 83, 120, 191]. For a respiratory filter, less air permeability elevates breathing resistance, which has been identified as the cause of fatigue, impaired physical work capacity and exhaustion [192]. The air resistance of an industrial air filter medium requires higher energy to overcome, which increases the cost of air filtration [41].

ENM to be useful as an air filter the resistance to air flow or pressure drop across the filter must be minimum. The term air permeability refers to the rate of air flow through a porous material under a specified differential pressure across the material, usually 0.5 inches of water (approximately 125 Pa) [117]. A small change in the electrospinning parameters can have a substantial effect on the air permeability and therefore the air filtration [16, 193]. An increase in applied voltage and flow rate elevates the fibre diameter [3, 15, 16, 142] whereas the electrospinning time modifies the basis weight and thickness [139]. Even a small increase in thickness and basis weight at similar fibre diameter can affect the air permeability.

This chapter describes the effect of electrospinning parameters, including collector speed and collection time on fibre morphology (fibre diameter, fibre diameter distribution) and ENM properties such as air permeability. In this study, PAN ENMs were fabricated using a laboratory scale electrospinning set up and in-house built collector assembly. The association between porosity, air permeability and ENM thickness is evaluated statistically.

3.2 Experimental

3.2.1 Materials

Polyacrylonitrile polymer (Mw 110 000 g/mol) was purchased from Goodfellow Cambridge Limited, England. N, N-dimethylformamide (DMF) was obtained from Merck,
Australia. Both polymer and solvent were used without further purification. Wool/polyamide (40:60) fabric was obtained from Bruck textiles and used as a support to ENMs. The wool/polyamide fabric (basis weight-130g/m², ends/inch-53 and picks/inch-48) also served as a control fabric for the experiment.

3.2.2 Electrospinning

Figure 3-1(a) shows the laboratory electrospinning setup comprised of a high voltage power supply (ES30P5W, Gamma High Voltage Research, USA), a syringe pump (KDS 100, KDS scientific) and in-house built collector assembly. The power supply was adjustable from 0 to 30 kV. The syringe pump had an adjustable holder for a syringe and controllable flow rate. The assembly (Figure 3-1b) comprised of a smooth metallic surfaced cylinder, wooden frame, electrical connection with the metal surface, variable speed motor and adjustable pulleys. The cylinder was fitted in the wooden frame and grounded. The adjustable pulleys were connected with variable speed motor so that the cylinder rpm can be controlled from 3–30 rpm.

Polyacrylonitrile (8% w/w) was dissolved in dimethylformamide. The solution was filled in a 5 ml plastic syringe attached with a blunt needle (18 gauge). The syringe was mounted on a pump to dispense the solution at a flow rate of 1 ml/hr. The voltage of 8 kV was applied at the tip of the needle. The distance between the needle tip and collector was fixed to 14 cm. The ENM was obtained in continuous form on the cylindrical collector.

The ENMs were obtained at three, six and nine rpm. The electrospinning (deposition) time varied from 20–60 min as indicated in the results section. The ENMs were collected on a support
substrate (wool/polyamide fabric). All the experiments were performed at ambient conditions (temperature 20 ± 2°C, relative humidity 45–55%). After electrospinning, the samples were air-dried overnight and further vacuum dried for four hours at 60°C to get rid of any residual DMF solvent.

3.2.3 Nanofibre diameter measurement

The nanofibre diameter was measured using a scanning electron microscope (SEM) after vacuum drying the ENMs. A small section of ENM, around 10 x 10 mm, was mounted on a double-sided carbon tape which was attached to a metal stub. The sample was then coated with gold particles on sputter coater for 60 seconds. The samples were then imaged under the SEM at 10 K magnification, 10 kV accelerating voltage, and a working distance of around 10 mm. The SEM images were analysed using ImageJ software to determine the fibre diameter. For each sample, 100 fibres were measured from five different images having 10 K magnification. The fibre diameter distribution was plotted as a histogram using the Minitab17 software.

3.2.4 Air permeability, porosity and thickness

Air permeability was measured using MO21S instrument according to the IS EN ISO 9237:1996 standard at 20±2°C temperature and 65±2% relative humidity. The schematic of the air permeability measurement is displayed in Figure 3-2. A small area (4.91 cm²) of ENM was mounted on the sample holder. The air was blown through the sample until the pressure reaches up to 100 Pa. The reading on the rotometer was recorded in L/min. The air permeability was then converted into mm/s per unit area of the sample using Eqn. 3-1. Ten readings were averaged to determine the air permeability. The effect of collector speed and electrospinning time on the air permeability of ENM was established through the analysis of variance (ANOVA) between ENM groups.
Figure 3-2 (a) Air permeability measurement principle, (b) Instrument (model MO21S) for measuring air permeability.

\[ R = \frac{q_v}{A} \times 167 \]  

(3-14)

Where, \( R \) is air permeability (mm/s), \( q_v \) is flow rate (L/min), 167 is a conversion factor from L/min to mm/s, and \( A \) is an area of the sample (cm\(^2\)).

The porosity is the ratio of void volume to fibre volume. It is calculated theoretically taking into account the ideal basis weight and thickness values. Eqn. 3-2 was used to calculate the porosity [12, 194].

\[ \varepsilon = \frac{V_0}{V_0 + V_s} = [1 - \frac{\rho_{ENM}}{\rho_s}] = [1 - \frac{w}{A \cdot t \cdot \rho_s}] \]  

(3-2)

Where \( \varepsilon \) is porosity, \( V_0 \) is void volume, and \( V_s \) is the volume of nanofibres in the ENM, \( \rho_{ENM} \) is the density of ENM and \( \rho_s \) is the density of PAN polymer (1.184 gm/cm\(^3\)). \( w, A \) and \( t \) are weight, area and thickness of the ENM, respectively.

ENM thickness measurement using SEM cross-section is difficult [139]. It was attempted to freeze the cross-sectional view of ENM by using liquid wax. Subsequently, a top portion of the wax was ground and polished with silica several times to view the cross-section under a microscope. However, this method was time-consuming and did not get success due to the requirement of extremely fine polish. Hence, the thickness was measured using a conventional
micrometre commonly used to measure the thickness of textile fabrics. Five readings from different places of ENMs were averaged.

3.3 Results and discussion

3.3.1 Nanofibre diameter and distribution

Figure 3-3 shows the nanofibre images of ENMs obtained at various collector speeds and different electrospinning deposition times. The average nanofibre diameter ranges from 494–594 nm for all the variations made. This result indicates that fibre diameter is independent of collector speed (3–9 rpm) and electrospinning time. Figure 3-4 shows the fibre diameter distribution histograms of ENMs prepared from different collector speeds and electrospinning times. A relatively narrow fibre diameter distribution has been reported [117] at higher collector speed ranging from 30 to 100 rpm. In this case, the collector speed ranges from 3 to 9 rpm, which is too low to elongate nanofibres and change the fibre diameter distribution. Nanofibre diameter and its distribution have a strong influence on the air permeability of the ENM [195]. The small fibre diameter reduces pore size and porosity [196] whereas large fibre diameter has larger pore size obtained by reducing the number of pores in the ENM [195]. More permeable ENMs can be fabricated by increasing the fibre diameter, but this may reduce filtration performance. Thus the choice of fibre diameter should be based on the desired filtration efficiency at maximum air permeability. The air permeability of fabrics could be controlled by fibre diameter size and basis weight [140].
**Figure 3-3** SEM images of 8% (w/w) PAN ENMs at the collector drum speed of three rpm for (a) 20min (b) 40 min, (c) 60 min; at six rpm for (d) 20 min (e) 40 min, (f) 60 min; and at nine rpm for (g) 20min (h) 40 min, (i) 60 min.
Figure 3-4 Nanofibre diameter distribution in ENM at collector drum speeds of three rpm for (a) 20min (b) 40 min, (c) 60 min; at six rpm for (d) 20min (e) 40 min, (f) 60 min; and at nine rpm for (g) 20min (h) 40 min, (i) 60 min.

Although the electrospinning time did not alter the fibre diameter, it did affect the basis weight and the porosity of the ENM. In the case of longer electrospinning time, more fibres are deposited in the same unit area which reduces the inter fibre spaces. Hence, a small increment in the deposition time (at least 20 min) can affect the porosity and thus air permeability.

3.3.2 Effect of electrospinning parameters on air permeability

Table 3-1 shows the air permeability values of pristine wool/polyamide woven substrate and ENMs at various collector speeds and electrospinning times. The air permeability of the control fabric was 694 mm/s which is much higher than any of the ENMs produced in this study (243–554 mm/s). This comparison suggests that even a small layer of ENM on the substrate with
20 min of spinning time significantly reduces the air permeability. The smaller diameter of fibres can explain the reduction in air permeability despite a low coverage of ENM for 20 min compared to the micron-sized woven substrate. The smaller fibre diameter occupies more volume fraction than a larger fibre in a given area further reduces the pore size which restricts the airflow through the ENM. The small pore size formation is also due to overlapping of the fine fibres over each other. At constant deposition times, the air permeability of ENM was found comparable at different collection speeds. This result can be explained as the likewise fibre diameters of ENMs at equal spinning times. Thus, the collection speed (3 to 9 rpm) does not affect air permeability, unlike electrospinning time.

**Table 3-1** Air permeability, thickness and porosity of ENMs at different collector speed and deposition time.

<table>
<thead>
<tr>
<th>Collector speed (rpm)</th>
<th>Electrospinning time (min)</th>
<th>Air permeability, mean ± SD (mm/s) at 100 Pa</th>
<th>ENM Thickness (μm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control fabric</td>
<td>-</td>
<td>693.8 ± 18.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ENMs</td>
<td>3</td>
<td>554.4 ± 53.2</td>
<td>41.9 ± 1.9</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>346.9 ± 102.4</td>
<td>56.8 ± 5.5</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>243.1 ± 42.4</td>
<td>69.1 ± 4.2</td>
<td>97.7</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>549.3 ± 61.1</td>
<td>45.5 ± 4.7</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>306.1 ± 69.4</td>
<td>63.2 ± 7.1</td>
<td>97.1</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>278.9 ± 53.8</td>
<td>71.2 ± 1.8</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>520.3 ± 66.2</td>
<td>42.3 ± 3.8</td>
<td>97.4</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>314.6 ± 37.8</td>
<td>64.9 ± 5.2</td>
<td>97.6</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>236.3 ± 24.6</td>
<td>74.4 ± 4.1</td>
<td>96.1</td>
</tr>
</tbody>
</table>
Table 3-2 shows that there is no significant change (p > 0.01) in air permeability when the collector rpm varied from three to nine rpm. This finding indicates air permeability is independent of the collector rpm range which can be justified by comparing ENMs thickness at constant deposition times. The thickness values are comparable at the different collector speeds. For instance, after 20 min of electrospinning, the thickness range was in between 41–45 µm for the ENMs collected at three, six and nine rpm.

Table 3-2 Analysis of variance (ANOVA) for air permeability between ENM groups.

<table>
<thead>
<tr>
<th>Case</th>
<th>Degrees of freedom (df)</th>
<th>Probability ratio (F value)</th>
<th>Significance (p-value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use of ENM</td>
<td>99</td>
<td>47.25</td>
<td>0.00</td>
</tr>
<tr>
<td>Change in collector speed (3–9 rpm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>for 20 min</td>
<td>29</td>
<td>0.92</td>
<td>0.41</td>
</tr>
<tr>
<td>for 40 min</td>
<td>29</td>
<td>0.83</td>
<td>0.46</td>
</tr>
<tr>
<td>for 60 min</td>
<td>29</td>
<td>2.94</td>
<td>0.07</td>
</tr>
<tr>
<td>Change in deposition time (20–60 min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>for 3 rpm</td>
<td>29</td>
<td>49.78</td>
<td>0.00</td>
</tr>
<tr>
<td>for 6 rpm</td>
<td>29</td>
<td>58.05</td>
<td>0.00</td>
</tr>
<tr>
<td>for 9 rpm</td>
<td>29</td>
<td>100.50</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 3-2 shows that there is no significant change (p > 0.01) in air permeability when the collector rpm varied from three to nine rpm. This finding indicates air permeability is independent of the collector rpm range which can be justified by comparing ENMs thickness at constant deposition times. The thickness values are comparable at the different collector speeds. For instance, after 20 min of electrospinning, the thickness range was in between 41–45 µm for the ENMs collected at three, six and nine rpm.

Table 3-2 also indicates that the air permeability of ENM is significantly (p < 0.01) affected by the change in electrospinning time. When the time increased from 20 to 60 min at three rpm,
the air permeability reduced from 554 mm/s to 243 mm/s (Table 3-1). This drop could be due to the reduced inter-fibre spaces owing to thickness and basis weight increase with electrospinning time [141, 197] which eventually elevates the packing density of the ENM [198]. Therefore, reducing electrospinning time is desirable to increase airflow through the ENM. The optimisation of electrospinning time is an important factor to maintain a balance between filtration performance and air permeability.

3.3.3 Correlation between air permeability, porosity and thickness

There is a straightforward correlation between porosity (Figure 3-5a) and thickness (Figure 3-5b) with air permeability. A positive correlation (R² = 0.89) was observed between air permeability and porosity. This correlation indicates that a porous structure allows easy airflow through ENM. On the other hand, a negative correlation (R² = 0.84) found between air permeability and thickness. A thick ENM reduced the air permeability [140, 141] mainly due to the decreased pore size and increased packing density. The air permeability is inversely proportional to the thickness which would indicate that an ENM with a minimum thickness is desirable, provided the functional requirements such as the required filtration efficiency be met.

![Figure 3-5](image)

**Figure 3-5** Correlation between (a) air permeability and porosity; (b) air permeability and thickness of ENMs.

3.4 Concluding remarks

In this study, a laboratory scale collector assembly was fabricated to obtain ENMs in continuous form. PAN ENMs were collected at three, six and nine rpm of the collector drum for 20, 40 and 60 min, respectively. The effect of collector speed and the electrospinning time on
fibre diameter and air permeability of ENM was investigated. The SEM images showed that the fibre diameter ranged from 494 to 594 nm. The variation in the collector speed from three to six and nine rpm did not significantly alter the fibre diameter and the air permeability of ENMs. Likewise, the fibre diameter remains unchanged at different deposition times. However, when the deposition time increased from 20 min to 60 min, air permeability reduced from 554 to 243 mm/s. It is found that at constant electrospinning parameters, air permeability is a function of electrospinning time. A positive correlation was found between air permeability and porosity of ENM while thickness and air permeability were negatively correlated. The future experiments should quantify packing density and pore size along with optimisation of electrospinning time to achieve maximum air permeability while having excellent filtration performance.
Chapter 4

Beaded bilayer ENM for enhanced air filtration

4.1 Introduction

Electrospinning is a versatile technique for the fabrication of nanofibre membranes with tunable fibre morphologies. Electrospun nanofibre membranes have several advantages such as small pore size, interconnected pore structure and a large surface area to volume ratio [199], which makes them suitable for a broad range of applications, including filtration [110]. These characteristics of ENMs favour diffusion (mass transfer) and interception effects for 500–50 nm particles [73], resulting in high filtration efficiency compared to melt blown and microfiber filter media [82, 200]. Another advantage of ENMs which makes them commercially attractive is the small basis weight required as compared to traditional filtration media for the same level of filtration performance against 1–10 µm particles. [201]. A commercial glass fibre based medium requires a higher basis weight (80 g/m²) to attain a specific desired filtration performance, which limits its application in respirators and protective clothing [137].

Although an ENM provides high filtration efficiency, it suffers from a high pressure drop, which is a significant disadvantage in respiratory filtration. The challenge for respirators is to considerably reduce the pressure drop of ENMs while maintaining high filtration efficiency. The quality factor [86] is a useful performance measure that takes into account both, filtration efficiency and pressure drop. The quality factor has only a weak dependence on basis weight, which simplifies the analysis of test results but is intimately linked with packing density and pore structure [137].

There have been several attempts to improve the quality factor of ENMs. In a multilayer structure, ENMs having similar packing density stacked on each other [75, 139] on an individual nonwoven substrate. However, multiple nonwoven substrates increase the thickness of overall filter media. As the quality factor get affected with packing density and small pore size [137], multilayer ENMs reduce the quality factor because the multilayer structure results in smaller pore size and higher pressure drop. Multilayer scaffold-like structures improved the quality factor only after bimodal distribution of fibres and chemical modifications [112]. Composite
ENM structures using multi-jet spinning [137] and various spinning jet ratios [115, 137] required different polymers and solvent systems.

Beads, in electrospun fibres, are oval-like shaped protrusions on fibres generated through jet fragmentation of dilute polymer solutions via Rayleigh instability [202-205] due to the increased slippage between polymer chains [123, 206-208]. The beads have significantly larger diameters than the average fibre diameter. Beaded and bead-free nanofibres can be distinguished by differences in the standard deviation of the mean fibre diameter [120]. The lowest range of spinnable polymer concentration, high electrospinning voltages and high feed rates are the critical parameters for obtaining beaded nanofibres [120, 209, 210]. Beads help in optimising packing density and increasing the distance between nanofibres thereby reducing the pressure drop [211]. In a recent report [122], porous beads on string structures showed improvements in the specific surface area, however, the effect of the beaded string structure on the thickness and packing density is not reported, and its impact on air filtration is unknown.

This chapter focuses on a beaded structure approach to improve quality factor by reducing the pressure drop of ENM. It examines the effect of uniform beaded ENMs in single and bilayer structures on membrane characteristics, pressure drop and filtration efficiency. The arrangements are formed from a single polymer system, and structural changes are achieved exclusively by altering electrospinning parameters. The membrane characteristics such as thickness, packing density, and pore size due to the beaded nanofibres and their layered arrangements in the ENMs have been characterised in detail. The effect of basis weight on structural changes in the ENMs and on the resulting air filtration performance has been investigated.

4.2 Experimental

4.2.1 Materials and solution preparation

Polyacrylonitrile (PAN) (MW 150,000 g/mol, Sigma-Aldrich, USA) and N, N-dimethylformamide (DMF) (Merck, 99.7%) were used as received without further purification. 4% and 9% (w/w) PAN solutions were prepared by dissolving the PAN in DMF with constant stirring for 3 hours at 60°C to obtain homogeneous solutions. The viscosity of the solutions was measured by a viscometer (Brookfield DV-II+Pro, USA) with a spindle number SC4–21. The
electrical conductivity was measured using a conductivity meter (FE30, Mettler-Toledo Group, Switzerland). The surface tension was measured by the inverted vertical rod–pull method [212].

### 4.2.2 Electrospinning

The electrospinning set-up (Figure 4-1) utilised in this study comprised a rack mount DC voltage power supply (Spellman SL150, USA), a syringe pump (NE1000, New Era Pump Systems, Inc. USA) and a ground electrode (a metal surfaced drum collector, diameter 13 cm, and width 19 cm). A DC voltage attached to a metallic needle (18 gauge, ID=0.84 mm) with a 5 ml syringe (Terumo) containing the PAN solution. The distance from the needle tip to the collector drum was fixed at 20 cm. The drum was wrapped in a polyester–viscose nonwoven substrate (weight 45 g/m², thickness 0.16 mm and average pore size 12 µm). The PAN nanofibres were collected on the nonwoven wrapped collector drum (180 RPM, surface speed 30 mm/s) that was moving at constant speed laterally (left, right) over a distance of 25 cm. The border of the electrospun web of 3 cm width around the perimeter of the sample was discarded. After electrospinning, all ENMs were dried at room temperature for 48 hours followed by a further 6 hours at 50°C in a vacuum oven.

![Electrospinning experimental setup](image)

**Figure 4-1** Electrospinning experimental setup comprised of high voltage supply, syringe pump, rotary collector and software system.
4.2.3 Single and bilayer ENM with bead structure

PAN solutions were electrospun according to process parameters listed in Table 4-1 and optimised to obtain controllable beaded and bead-free ENMs. These solutions were used to form single layers (S4 and S9) or bilayer ENMs (B4 and B9) as depicted in Figure 4-2. The basis weight of ENM (m) was estimated by multiplying the polymer concentration ($c_p$) with feed rate ($r_f$) and electrospinning time ($t_s$) as polymer was applied across the collector area ($a_c$) of 19 x 34 cm size. ENMs were produced with three different basis weights of 0.6, 1.2 and 2.4 g/m$^2$ according to Eqn 4-1:

$$m = \frac{c_p r_f t_s}{a_c}$$

(4-1)

Table 4-1 Optimized electrospinning parameters used to obtain continuous beaded and bead-free ENMs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Beaded ENMs</th>
<th>Bead-free ENMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN polymer concentration (%) (w/w)</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Voltage (kV)</td>
<td>25</td>
<td>18</td>
</tr>
<tr>
<td>Flow rate (ml/h)</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The electrospinning time (nanofibre deposition time) was varied between 54–240 min to achieve a target basis weight that was the same for all structures combinations, including single layer and bilayer ENMs (Table 4-2). Bilayer ENMs were produced by changing the electrospinning solutions exactly after half of the basis weight was applied and without any time gap between layer depositions.
Figure 4-2 A schematic representations of single and bilayer ENM structures where S represents: Single layer, B represents: Bilayer, 4 represents: 4% PAN and 9 represents: 9% PAN.
Table 4-2 Electrospinning time to produce uniform basis weight of layered ENMs.

<table>
<thead>
<tr>
<th>ENM Structure</th>
<th>Scheme</th>
<th>Basis weight (g/m²)</th>
<th>Electrospinning time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single layer - Beads</td>
<td>S4</td>
<td>0.6</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.2</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>240</td>
</tr>
<tr>
<td>Single layer - Bead-free fibres</td>
<td>S9</td>
<td>0.6</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.2</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>192</td>
</tr>
<tr>
<td>Bilayer - Beads on top of fibres</td>
<td>B4</td>
<td>0.6</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.2</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>216</td>
</tr>
<tr>
<td>Bilayer – Fibres on top of beads</td>
<td>B9</td>
<td>0.6</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.2</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>216</td>
</tr>
</tbody>
</table>

4.2.4 ENM characterisation

The morphologies of the ENMs were examined using a Field Emission Scanning Electron Microscope (FE–SEM) (Zeiss Gemini 2 Merlin). The ENMs were iridium coated and imaged at an acceleration voltage of 3 kV. The nanofibre diameter was measured using Image-J software and the distribution histogram obtained using Minitab17.

The ENMs were very soft, easily deformed with applied force and therefore susceptible to compression. Considering the sample preparation difficulties of SEM cross-sectional measurement, the ENM thickness was measured using a non-contact 3D laser scanning digital microscope (Olympus LEXT OLS 4100). The method was non-invasive [213] and measured the ENM thickness based on step height (Figure 4-3). The step height was the difference between the ENM deposited on a microfibre nonwoven substrate against the pristine nonwoven. The step height was measured across an average area of 0.5 mm² at X5 magnification to determine the thickness of the ENM.
The packing density of the ENM was estimated from Eqn 4-2:

$$\alpha = \frac{m}{z \times \rho} \quad (4-2)$$

where $\alpha$ is the packing density (dimensionless) of the ENM, $m$ and $z$ are the estimated basis weight and thickness, respectively and $\rho$ is the density of the PAN polymer (1.184 g/cm$^3$).

The pore diameter and pore size distribution of each membrane (13 mm diameter) were determined using a capillary flow porometer (Porous Materials Inc, USA) with Galwick as the wetting agent (surface tension 15.9 mN/m). Pore diameter ($dp$) is related to the pressure gradient needed to displace the Galwick from a pore capillary in a pressure range of 0 to 30 psi and can be calculated using Eqn 4-3.

$$dp = \frac{4\sigma \cos \theta}{\Delta P} \quad (4-3)$$

where $\sigma$ is the surface tension of the wetting liquid (N/m), $\theta$ is the contact angle that the wetting liquid forms with the filter and $\Delta P$ is the differential pressure (Pa) applied across the filter.

### 4.2.5 Air filtration performance

The experimental design employed to investigate air filtration performance of ENMs is shown in Table 4-3. Figure 4-4 shows the experimental setup for the air filter test. The ENM
sample was held in the sample holder having a diameter of 109 mm and active filtration area of 93.26 cm². The measurements were performed at face velocities of 0.05 m/s, 0.08 m/s, and 0.15 m/s, corresponding to flow rates of 20 L/min, 32 L/min, and 55 L/min, respectively. An atomiser generated potassium chloride particles (aerosols) with a size range of 0.3–5 μm, which were detected by a pair of optical particle counters (TSI 9306–03) located upstream and downstream of the sample. Results were reported as the average of five successive replicates measured throughout 30 seconds.

**Table 4-3** Experimental design for the single and bilayer ENMs to measure air filtration performance.

<table>
<thead>
<tr>
<th>Single layer ENM structure</th>
<th>Basis weight (g/m²)</th>
<th>Face velocity (m/s) for air filtration test</th>
<th>Bilayer ENM structure</th>
<th>Basis weight (g/m²)</th>
<th>Face velocity (m/s) for air filtration test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beads on top</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>0.5</td>
<td>0.08</td>
<td>B4</td>
<td>0.5</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08</td>
<td></td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.05</td>
<td></td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08</td>
<td></td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.08</td>
<td></td>
<td>2</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>Fibres on top</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S9</td>
<td>0.5</td>
<td>0.08</td>
<td>B9</td>
<td>0.5</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08</td>
<td></td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.05</td>
<td></td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08</td>
<td></td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.08</td>
<td></td>
<td>2</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
</tbody>
</table>
Air filtration performance parameters, including filtration efficiency $\eta$, pressure drop $\Delta P$ and quality factor $Q$ were calculated according to Eqn 4-4, 4-5 and 4-6:

\[
\eta = \frac{n_1 - n_2}{n_1} \quad (4-4)
\]

\[
\Delta P = P_1 - P_2 \quad (4-5)
\]

\[
Q = \frac{-\ln \left( \frac{n_2}{n_1} \right)}{\Delta P} = \frac{-\ln (1-\eta)}{\Delta P} \quad (4-6)
\]

where $n_1$ is the upstream aerosol particle concentration; $n_2$ is the downstream aerosol particle concentration; $P_1$ is the upstream absolute air pressure, and $P_2$ is the downstream absolute air pressure.

The pressure drop characterises the resistance to air flow through the membrane and determines the breathability of the filter medium.
4.3 Results and discussion

4.3.1 Effect of solution properties on fibre morphology

Table 4-4 shows PAN solution properties at different concentrations used in the formation of the beaded and non-beaded ENM. The viscosity markedly increased from 27.4 to 445.8 cPs as the polymer concentration increased from 4 to 10%. The high viscosity is mainly attributed to large molecule chain entanglement at the higher concentration. Viscosity invariably increases with polymer concentration [83, 137, 214, 215]. Both conductivity and surface tension increased with the polymer concentration which is due to the higher concentration of current carrying molecules and strong cohesive intermolecular forces, respectively. However, in literature, conductivity and surface tension values do not show a consistent relationship to polymer concentration. Some solutions show increasing conductivity and surface tension properties [137, 214, 215] while some reported decreasing conductivity and surface tension properties [122, 126, 215] with increasing polymer concentration.

The balance between viscosity, conductivity and surface tension can control fibre morphology. A higher concentration enhances viscoelastic and electrostatic repulsion forces but suppresses the effects of surface tension [216]. At a lower concentration, these forces become unstable [122, 217] thus resulting nanofibres with different morphologies.

Table 4-4 PAN solution properties.

<table>
<thead>
<tr>
<th>PAN concentration (w/w) (%)</th>
<th>Viscosity (cPs)</th>
<th>Conductivity (µs/cm)</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>27.4</td>
<td>14.05</td>
<td>24.4</td>
</tr>
<tr>
<td>10</td>
<td>445.8</td>
<td>21.96</td>
<td>28.6</td>
</tr>
</tbody>
</table>

Electrospinning of the 4% PAN solution produced a consistent bead on string structure (Figure 4-5), even at the higher electrospinning voltage of 25 kV. The low solution viscosity and less stretching of polymer chains in the jet resulted in beads. This behaviour has been explained as the entanglement of individual polymer chains, which can prevent breakage in the charged jet,
but cannot suppress capillary instability [120, 210], hence promoting the formation of the beaded nanofibres. The individual beads of 200 nm diameters are held together by approximately 55 nm thick strings (Figure 4-5b). The beads and strings follow a normal frequency distribution (Figure 4-5c–d) ensuring uniformity in the structure.

![Image](image_url)

**Figure 4-5** Bead on a string structure (a) SEM image, (b) schematic presentation, (c) bead diameter distribution, and (d) string fibre diameter distribution.

The fibre morphology changed entirely when electrospinning at the 10% PAN solution (Figure 4-6). The beads disappeared, and fibre diameter increased to 400 nm. The fibre diameter increased at the higher concentration due to the higher solution viscosity [83, 126, 135, 138]. The rough texture on the surface is prominent when the PAN nanofibres were viewed at a low accelerating voltage (3kV).
Figure 4-6 Bead free uniform nanofibres from 10% PAN solution (a) SEM image; (b) fibre diameter distribution.

4.3.2 Single and bilayer ENM characteristics

Table 4-5 summarises the average nanofibre diameters of the single layer and the bilayer ENMs. S4 and B4 have similar diameters of beads (≈200 nm) and strings (≈55 nm). Also, the nanofibre diameters S9 and B9 are likewise similar (≈400 nm). This result is logical since the single layer and bilayer ENMs were spun from the same solutions using identical parameters, except their order in the stacking position is reversed. Representative SEM images of B4 and B9 are shown in Figure 4-7.

Table 4-5 Nanofibre and bead diameters of single and bilayer ENMs.

<table>
<thead>
<tr>
<th>ENM</th>
<th>Nanofibre diameter (nm)</th>
<th>Bead diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4</td>
<td>55 ± 12</td>
<td>204 ± 44</td>
</tr>
<tr>
<td>S9</td>
<td>416 ± 44</td>
<td>-</td>
</tr>
<tr>
<td>B4</td>
<td>49 ± 9</td>
<td>168 ± 65</td>
</tr>
<tr>
<td>B9</td>
<td>418 ± 48</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4-7 SEM images of bilayer ENM produced from PAN 4% and PAN 9% solution (a) B4 – beads on top of bead-free fibres and (b) B9 – fibres on top of beads.

ENM thickness linearly increased with basis weight (Figure 4-8a). The ascending order of thickness for the ENMs is S4 < B4 < B9 < S9 at all the three basis weight levels (0.5, 1 and 2 g/m²). Despite the presence of beads, S4 showed consistently lower membrane thickness compared to S9 for given basis weight. For example, at 0.6 g/m², S4 was 76 μm thick compared to 134 μm of S9. The increase in thickness of S9 ENM is probably due to the larger fibre diameter (400 nm) compared to the string dimensions in S4 (55 nm). A linear relationship between ENM thickness and fibre diameter at equivalent basis weight is reported in a simulation study [218]. Within the fibre/bead bilayer ENMs, B4 exhibited a smaller thickness than B9 at all basis weight levels. The thickness decrement for B4 was more prominent at 2 g/m² (165 μm) as against 220 μm for B9.

The packing density has a more pronounced effect on filtration than thickness [75]. The low packing density decreases air resistance [219] as it reduces the tortuous path that particles need to travel [115, 126, 135, 220] which results in a lower pressure drop. Figure 4-8b presents the packing density of the ENMs at the different basis weights. S4 showed the highest packing density (10.95 x 10⁻³) at 2 g/m² which is attributed to the lowest thickness (157 μm) amongst all the ENMs. In contrast, the packing density of S9 was reduced to 8.20 x 10⁻³ which correlates to the thickest ENM (247 μm) at 2 g/m². Amongst all the ENMs, S9 exhibited the lowest packing density (3.19 x 10⁻³) at 0.5 g/m².
The thickness and packing density of B4 and B9 are both between those of S9 and S4 ENMs (Figure 4-8b). The reason for this can be derived by comparing SEM images of the ENM cross-sections (Figure 4-9) especially to the thickness and packing density measurements. S4 ENM at 0.5 g/m² is still loose but denser than S9. As the basis weight is increased to 1 g/m², the packing density increases while the thickness does not change much. At 2 g/m² the packing density of ENMs increased as well as the thickness. The increase in packing density is most pronounced for S4, which can be attributed to the thin connecting strings of only 55 nm diameters. These thin strings go hand in hand with the smallest increase in thickness (of S4). The fibres in S9 have much higher bending stiffness therefore forming a very open nonwoven web at 0.5 g/m². This structure shows the largest increase in thickness with basis weight and the smallest increase in packing density due to high bending stiffness.

As already noted above, the structure of beads on top of bead-free fibres, as for B4, does not lead to the same result as reversing the sequence (B9). SEM images for B4 suggest that the fibrous web is compacted heavily by the strings and beads layer on top, which is supported by the thickness measurements (Figure 4-8). In the case of B9 where a dense layer of beads is laid down first, the fibrous layer on top retains the capacity to form a very lofty nonwoven. Hence the properties of B9 are more similar to S9.
Figure 4-9 Cross-sectional images of ENMs at different basis weights.

Figure 4-10 summarises the pore size distribution of the layered ENMs. Pore size refers to the mean size of capillaries formed by overlapping fibres. The average pore size of all the ENMs is reduced with the basis weight. The increment in the basis weight of nanofibres overlaps the capillaries resulting in small pore size. S4 shows a broad pore distribution compared to S9 which is due to the peculiar geometry of beads creating irregular intra-fibre voids [122]. The average pore size of S4 (0.48 µm) is smaller than the pore sizes of S9 (2.30 µm) at 1 g/m². This reduction in pore size could be due to the lower bending stiffness as the diameter of strings (55 nm) is smaller than bead-free fibres (400 nm) of S9, hence causing the beaded strings to move closer together.
The formation of bilayer ENMs did effectively narrow the pore distribution compared to the monolayer S4. This narrow distribution in the bilayers is a result of partly replacing the bead on string geometry by the uniform and thicker fibre structure. The pore characteristics at the top of bilayer B4 and B9 structures still resemble those of S4 and S9, respectively. However, the average pore size of B4 was consistently smaller than B9. This result implies that the change of stacking position alters the pore characteristics of the bilayer ENMs.

4.3.3 Comparison of air filtration performance

The filtration efficiencies for various particle sizes (0.3–5 µm), for the different flow rates and mass coverage, are shown in Figure 4-11a–f. The filtration efficiency of ENMs was found to be higher at 0.08 m/s face velocity in comparison to 0.15 m/s. At the low face velocity (low air flow rate) the inertia can transport a small aerosol (≤ 0.3 µm) which increases the probability of particle capture by the fibres.
S4 shows superior filtration efficiencies (81–83 %) over S9 (52–56 %) for 0.3 µm particles at 0.5 g/m$^2$(Figure 4-11a–b). However, with the increasing particle size the filtration efficiency of S9 increases which can be explained using the effective interception mechanism. Interception occurs when particles (greater than 0.1 µm) of small mass and low inertia come close to fibre and tend to attach themselves to the fibre surface [78]. The beads (200 nm) of S4 can intercept 0.3 µm particles much better than the 400 nm fibres of S9 for the small basis weight ENMs of 0.5 g/m$^2$. Thus S4 has shown high filtration efficiency.

S9 outperformed S4 at the higher basis weights for all particle sizes (Figure 4-11c–f). The filtration efficiency increased from 83% to 96% at 2 g/m$^2$. This improvement in filtration efficiency for a given combination of nanofibre diameter and basis weight can be explained by a significant difference in the thickness between S9 and S4 ENMs at the similar basis weights. For instance, S9 was 247 µm thick in contrast to 157 µm of S4 at 1 g/m$^2$. This result supports the finding [14, 19] that ENM thickness and filtration efficiency are strongly correlated. However, this correlation may not hold for thin ENMs (< 2 g/m$^2$). At equivalent small basis weight, for example, 0.5 g/m$^2$, small fibre diameter (200 nm) of S4 ENM showed better filtration efficiency than that of S9 (400 nm) ENM.

The superior filtration efficiency performance of B9 (99%) compared to B4 (88%) (Figure 4-11e) can be attributed to two reasons; firstly, the high thickness of B9 (220 µm) over B4 (165 µm) and secondly, the decreasing order of the pore size in the structure. For example, the large pores (2.93 µm) of B9 improve the diffusion through the top layer followed by an interception of the aerosols by the smaller pores (0.42 µm) below. This result implies that for a bilayer nanofibre filter media, both diffusion and interception mechanisms can be used to explain filtration behaviour, but only one of the other dominates depending on particle size, thickness and pore size of the ENM.

B9 showed better filtration than S9, which is likely due to the integrated combination of 55 nm strings, 200 nm beads and 400 nm bead-free nanofibres in the ENM compared to only 400 nm nanofibres in S9. A reduction in pore size may also have assisted in further improving the filtration efficiency [87]. Overall, the bilayer B9 ENM exhibited best filtration efficiency among all ENMs investigated.
Figure 4-11 Filtration efficiency of ENMs at 0.5, 1 and 2 g/m² basis weight at 0.08 m/s and 0.15 m/s face velocity.

Figure 4-12 presents pressure drop for the ENMs fabricated at the different basis weights. The hypothesis that a beaded structure would result in a lower pressure drop owing to the bulky nature of beads turns out to be incorrect. For example, S4 has a higher pressure drop (317 Pa) than S9 (122 Pa) at 1 g/m² (Figure 4-12a). This can be explained as the high packing density of S4 (8.53 x 10³) with the undulating pathway between beads (200 nm) and strings (55 nm)
compared to an unconstricted channel between bead-free nanofibres (400 nm) of S9 ENM. This finding is different from the Matulevicius et al. [120] where the pressure drop reduction is attributed to the beaded nanofibres (292 ± 101 nm). However, the frequency distribution of the beads is not reported, and hence a direct comparison cannot be made.

![Graph](image)

**Figure 4-12** (a) Pressure drop of ENMs at 0.08 m/s and 0.15 m/s face velocity (b) Pressure drop normalised with thickness.

Despite equivalent basis weights, the change in the stacking position for B4 to B9 revealed quite significant differences in corresponding pressure drop (Figure 4-12). A pertinent experiment was carried out to test the hypothesis that is just changing the whole structure upside down brings a dramatic shift in the pressure drop. As shown in Table 4-6 no drastic change was observed in the pressure drop between the face side and reverse side. However, in B4 and B9 where stacking order of nanofibres is opposite to each other, a significant difference in pressure drops is observed. Thus, changing the electrospinning sequence of fibres and beads is producing real structural differences with consequences on pressure drop, as was confirmed by the cross-sectional image of ENMs in Figure 4-9.
The reason B9 exhibits a lower pressure drop than B4 is probably related to due to the high porosity and less packing density of the fibrous part and possibly also to the deceased compactness of the strings and beads portion of the structure. Furthermore, when the pressure drop is normalised for thickness (Figure 4-12), B9 was observed to have a lower pressure drop at all three basis weights in comparison to B4. Thus the stacking position of nanofibres is an essential consideration in the design of bilayer ENMs.

The filtration performance of ENMs was compared with respiratory filter norms prescribed in the AS/NZS standard [88]. S4 with 0.5 g/m² basis weight at 0.08 m/s face velocity exhibited a filtration performance ($\eta = 81.5\%$; $\Delta P = 110$ Pa) which is on par with commercial P1 type respirator masks ($\eta = 80\%$; $\Delta P = 110$ Pa). The bilayer B4 structure with 0.5 g/m² basis weight ($\eta = 95\%$; $\Delta P = 112$ Pa) outperforms commercial P2 type respirator masks ($\eta = 94\%$; $\Delta P = 120$ Pa). These results indicate that beaded ENMs are effective particularly at small basis weights.

### Table 4-6 Pressure drop of ENMs at 0.08 m/s face velocity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basis weight (g/m²)</th>
<th>Face side (Nanofibres facing the air flow) pressure drop (Pa)</th>
<th>Reverse side (Microfiber nonwoven facing the air flow) pressure drop (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4</td>
<td>0.5</td>
<td>110 ± 1.0</td>
<td>115 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>317 ± 2.3</td>
<td>330 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>376 ± 3.0</td>
<td>396 ± 5.1</td>
</tr>
<tr>
<td>S9</td>
<td>0.5</td>
<td>51 ± 1.5</td>
<td>62 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>122 ± 3.5</td>
<td>114 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>376 ± 0.6</td>
<td>381 ± 1.2</td>
</tr>
<tr>
<td>B4</td>
<td>0.5</td>
<td>112 ± 0.6</td>
<td>119 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>300 ± 1.8</td>
<td>302 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>451 ± 2.8</td>
<td>467 ± 3.2</td>
</tr>
<tr>
<td>B9</td>
<td>0.5</td>
<td>63 ± 0.4</td>
<td>71 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>201 ± 1.7</td>
<td>214 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>254.6 ± 0.5</td>
<td>268 ± 2.8</td>
</tr>
</tbody>
</table>
The quality factor, which is the combination of filtration efficiency and pressure drop, is often used to evaluate air filtration performance of filter media. Figure 4-13 shows the quality factor values of the ENMs at different basis weights against 0.3 µm particles. All ENMs exhibit is increasing quality factors with decreasing basis weights, which is interesting since the quality factor is usually independent of basis weight. The change in basis weight from 0.5 g/m² to 2 g/m² has led to a reduction for the quality factor of B9 from 0.028/Pa to 0.020/Pa. Thus, a moderate change in basis weight of the ENM can strongly affect the quality factor [122, 139].

Figure 4-13 also indicates that B9 (bead-free top) consistently outperformed other structures by achieving the highest quality factor of 0.028/Pa for 0.5 g/m² at 0.08 m/s. Even at 2 g/m² basis weight, the quality factor of B9 (0.020/Pa) was found to be better than that of B4 (0.005/Pa). This result further strengthens the importance of the stacking order in bilayer ENMs. Bilayer ENMs with coarser, uniform fibres on top of fine nanofibres layer improved the filtration performance.

![Quality factor of ENMs at 0.08 m/s and 0.15 m/s face velocity.](image)

**Figure 4-13** Quality factor of ENMs at 0.08 m/s and 0.15 m/s face velocity.

Figure 4-14 shows the filtration performance of ENMs (1 g/m²) evaluated at 0.056 m/s face velocity which represents normal breathing. This filtration performance is compared with standards recommended by various authorities and some of the previously published reports. B9 showed an efficiency of 95.7% and a pressure drop of 137 Pa which meets the standard requirements of a respirator filter. The USA National Institute for Occupational Safety and
Health requires a minimum of 95% filtration efficiency for an N95 respirator mask [221]. The Chinese national standard for dust mask states that the pressure drop should be less than 147 Pa [82]. Also, the quality factor of B9 (0.023/Pa) is better than that of a carbon nanotube filter (0.010/Pa) or a quartz fibre filter (0.008/Pa) [222] and comparable to the PAN transparent filter (0.024/Pa) [114].

![Figure 4-14](image)

**Figure 4-14** Filtration efficiency, pressure drop and quality factor of ENMs at 0.05 m/s face velocity.

### 4.4 Conclusion

Beaded and bead-free PAN nanofibres were used to produce single and bilayer ENMs. Continuous and uniform beads of 200 nm connected to strings of 55 nm were obtained from a 4% PAN, while a 9% PAN produced uniform 400 nm fibres. Electrospinning parameters changed the geometry from beads to bead-free fibres, consequently resulting in different ENM thickness and packing density at equal basis weight. More than the geometry of the ENM, their stacking order in bilayer ENM influenced the air filtration performance the most. Bilayer ENM with 400 nm fibres on top and beads of 200 nm underneath greatly improved air filtration performance ($\eta = 95.7\%$; $\Delta P = 137$ Pa) in comparison to the reverse arrangement ($\eta = 94.7\%$; $\Delta P = 202$ Pa). The dynamic changes imposed by the airflow on the bilayer ENM consequently show the difference in the pressure drop which depends on the stacking order of beaded and bead-free ENM. The hierarchically stacked bilayer, beaded ENM was comparable to commercial respirator mask with 95.7% filtration efficiency with the improved quality factor. This simple approach of reproducible bilayer ENM fabrication can be useful for various air filtration applications in a quest for designing more efficient air filter media.
Chapter 5

Bilayer ENMs for an improved quality factor of an air filter media

5.1 Introduction

A high pressure drop is a drawback often associated with electrospun nanofibre membrane aiming at high filtration efficiency. Pressure drop is resistance to air flow through the filter material which is expressed as the pressure difference upstream (before) and downstream (after) of the filtration process. The pressure drop is inversely proportional to filtration efficiency. A high pressure drop causes higher breathing resistance in the case of respiratory filters. Hence, respiratory filter media with the lowest possible pressure drop is desirable to minimise the amount of work required to breathe [223, 224]. The quality factor takes into account both the pressure drop and the filtration efficiency allowing the reporting of filtration performance as a single number [86, 225].

Increasing the packing density or nanofibre basis weight increases the filtration efficiency, but this invariably results in lower quality factor due to an increase in pressure drop. Other methods that have been used to increase the quality factor include different nanofibre structures, such as a multilayer and multi-jet spinning [75, 115, 137, 139].

The previous chapter illustrated enhanced air filtration using bilayer beaded ENM. A subtle change in the sequence of nanofibre layering brought a dramatic change in the airflow across the ENM. The air filtration performance of the beaded ENM is comparable with commercial P2 type respiratory masks. However, the beaded ENM also showed a high variation in pore size distribution consequently affecting the pressure drop results.

This chapter aims not only to validate the effect of the nanofibre layer ordering detailed in the previous chapter but also to improve the filtration performance even further. Here, the hypothesis is that the hierarchical stacking of the order arrangement should work for the bead free nanofibres as well. Hence the bead structure is replaced by bead-free fibres of equivalent diameter (~ 200 nm). The electrospinning parameters were controlled to fabricate 200 nm bead-free fibres. The 400 nm bead-free fibres in the last experiment were reproduced as well. In this work, 200 nm fibres are called as fine whereas 400 nm are called coarse. The experimental
approach is similar to the previous chapter where two single layers and two bilayer ENMs were produced and their filtration properties measured.

This work is an excellent example of how manipulation does work on a small scale when the stacking of nanofibres is altered. A simple fabrication process of a bilayer ENM formation from a single polymer-solvent system is reported. The effect of small-scale manipulation, changing the sequence of coarse and fine nanofibres stacking during bilayer ENM formation, on fibre morphology and filtration performance is studied at a similar basis weight of ENMs.

5.2 Experimental

Polyacrylonitrile (PAN) (MW 150,000 g/mol) was obtained from Sigma-Aldrich, and N, N-dimethylformamide (DMF) (99.7%) from Merck. Both PAN and DMF were used as received without any further purification. PAN (7.5% and 9% w/w) was dissolved in DMF by stirring for twelve hours at room temperature. The viscosity of the solutions was determined using a viscometer (Brookfield DV-II+Pro, USA). The polyester-viscose nonwoven substrate (weight 45 g/m², thickness 0.16 mm and average pore size 12 μm) was used to support the PAN nanofibre prepared by electrospinning.

The electrospinning setup (Figure 5-1) was comprised of a DC voltage source (Spellman SL150, USA), a syringe pump (NE1000, New Era Pump Systems, Inc. USA) and collector assembly as the ground electrode. The DC voltage was applied to a metal needle containing the viscous PAN solution. The nanofibre formation due to electrospinning [3, 11, 15] is explained in the introduction chapter. In short, the high electrical voltage overcomes the surface tension of the solution droplet at the needle tip and travels towards the collector in jet form. When the jet moves, the solvent evaporated, and polymer nanofibres are deposited on the collector drum. The electrospinning parameters used to produce a single layer, and bilayer ENMs are mentioned in Table 5-1.
Figure 5-1 Electrospinning set up principle.

Table 5-1 Electrospinning parameters to produce nanofibre structures.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC voltage</td>
<td>18 kV</td>
</tr>
<tr>
<td>Flow rate</td>
<td>0.5 mL/h</td>
</tr>
<tr>
<td>Needle gauge</td>
<td>18</td>
</tr>
<tr>
<td>The distance between the needle tip and collector drum</td>
<td>20 cm</td>
</tr>
<tr>
<td>Collector surface speed</td>
<td>30 mm/s</td>
</tr>
</tbody>
</table>

5.2.1 Single layer and bilayer ENMs

Figure 5-2 shows a schematic of the single layer and bilayer ENMs to be electrospun using fine and coarse fibres. The single layer fine ENMs, made up from 200 nm diameter fibres, were produced using a 7.5% PAN solution while the 9% PAN solution was used to electrospin the coarse ENMs having 400 nm diameter fibres. The integrated bilayer structure was fabricated by stacking the two single layers together. Two possible combinations of bilayer were produced by manipulating the stacking order of the single layer nanofibres, as illustrated in Figure 5-2. The electrospinning time (nanofibre deposition time) varied from 96–120 minutes to achieve uniform basis weight of 1 g/m² for all the ENMs. Eqn 5-15 was used to estimate the basis weight:
where $c_p$ is polymer concentration (w/w), $\rho_s$ is solution density, $r_f$ is feed rate, $t_s$ is electrospinning time, and $A_c$ is collector area (19 x 34 cm).

\[
m = \frac{c_p \rho_s r_f t_s}{A_c} \tag{5-1}
\]

**Figure 5-2** Schematic representation of the single and bilayer ENM structures. S: Single layer; B: Bilayer; 7.5: PAN 7.5%; 9: PAN 9%.

### 5.2.2 ENM characterisation

The nanofibres were examined using a Field Emission Scanning Electron Microscope (FE-SEM) (Zeiss Gemini 2, Merlin) once the samples were coated with iridium for 40 seconds using a Cressington 208 HRD iridium sputter coater. The fibres were imaged at 3 kV at 10000X and analysed on Image–J software. The thickness of all the ENMs was measured using a non-contact 3D laser scanning digital microscope (Olympus LEXT OLS 4100) by determining the height difference between the ENM and the nonwoven substrate over an average area of 0.5 mm$^2$ at 5 x magnification. Eqn 5-2 estimated the packing density:
\[ \alpha = \frac{m}{z \times \rho} \quad (5-2) \]

where \( \alpha \) is the packing density, \( m \) is estimated basis weight per unit area, \( z \) is nanofibre structure thickness, and \( \rho \) is the density of PAN polymer (1.184 g/cm\(^3\)) [226].

A capillary flow porometer (Porous Materials Inc, USA) was used to determine the pore sizes and the pore distribution of the ENMs. In principle, capillary flow porometry is a measurement of the pressure gradient needed to displace a low surface tension liquid, Galwick (surface tension 15.9 mN·m\(^{-1}\)) through a pore capillary in a structure. The pore diameter is inversely proportional to the pressure gradient (Eqn 5-3). In this case, ENM samples of 13 mm diameter were used for pore size and distribution measurements. Three readings were averaged and a pressure range of 0–30 psi was employed to determine pore characteristics.

\[ dp = \frac{4 \sigma \cos \theta}{\Delta \rho} \quad (5-3) \]

where \( \sigma \) is the surface tension of the wetting liquid (N/m), \( \theta \) is the contact angle that the wetting liquid forms with the filter and \( \Delta \rho \) is the differential pressure (Pa) applied across the filter.

### 5.2.3 Air filtration performance

The air filtration performance of the ENMs was measured using the air filter set up (Figure 5-3) described in Chapter 4. In brief, potassium chloride particles were generated in an atomizer using compressed air to form aerosols of size 0.3 to 5 \( \mu \)m. The aerosols flowed in the duct system at an adjustable flow rate. Once the particle concentration reached to the specified range and the filtration system was calibrated, the test was conducted. The filtration properties of ENMs were measured at two different flow rates, 20 L/min, and 32 L/min corresponding to 0.06 m/s and 0.08 m/s face velocity. Optical counters measured the particle concentration before and after passing through the ENM to derive the filtration efficiency (Eqn 5-4). The difference in the air pressure, the pressure drop, before and after filtration was calculated using Eqn 5-5. The filtration efficiency and pressure drop were jointly expressed using a single number, quality factor (Eqn 5-6).
Figure 5-3 Experimental air filtration setup comprised of filter rig, particle counters, sample holder, sample adapter, HEPA filter and KCl solution to prepare aerosols

\[ \eta = \frac{n_1 - n_2}{n_1} \]  
\[ \Delta P = P_1 - P_2 \]  
\[ Q = \frac{-\ln (1-\eta)}{\Delta p} \]

Where \( \eta \) is filtration efficiency, \( n_1 \) is the upstream aerosol particle concentration, \( n_2 \) is the downstream aerosol particle concentration, \( \Delta P \) is the pressure drop, \( P_1 \) is the upstream air absolute pressure, \( P_2 \) is the downstream air absolute pressure and \( Q \) is a quality factor.

The air filtration performance of the ENMs was also simulated using the filtration modelling software package, FilterDict™. First of all, the 3D virtual fibre structures were generated using the bulk properties of ENM in the FiberGeo module. The voxel-based model was used to create a 3D structure of single layer ENM in a 200 \( \mu \)m\(^3\) volume at a voxel length of 50 nm. The pore size of the virtual single-layer ENMs was evaluated using Porodict simulation software. The filtration efficiency and pressure drop were simulated at 0.06 m/s face velocity.
using the Stokes equation in the FilterDict™ module. The simulation results then were compared with the experimental results.

5.3 Results and discussion

5.3.1 Solution viscosity

Solution viscosity is a measurement of resistance to flow or deformation when shear stress is applied. It is a critical rheological parameter which can be used to correlate the viscosity of the electrospinning solution to the morphology of the electrospun nanofibre. The rheology of the PAN solutions at concentrations of 7.5% and 9% (w/w) is shown in Figure 5-4. The viscosity of the PAN solution increased from 212 cPs to 424 cPs as the solution concentration increased from 7.5% to 9% w/w. The viscosity is found independent of shear rate (23/sec to 144/sec) in this concentration range of PAN solutions. The shear stress of both PAN solutions linearly increased with a shear rate which is in agreement with Qin et al. [227].

![Rheology study of PAN solutions at the shear rate range of 23/sec to 144/sec.](image)

**Figure 5-4** Rheology study of PAN solutions at the shear rate range of 23/sec to 144/sec.

5.3.2 Nanofibre diameter

**Figure 5-5** shows SEM images of the single and bilayer ENMs. The single layer (S) ENMs produced from the 7.5% (S7.5) and 9% (S9) w/w PAN solutions (Figure 5-5a-b) had an average diameter of 197 ± 26 nm and 397 ± 38 nm, respectively. The higher polymer concentration resulted in the larger diameter of nanofibres under similar electrospinning conditions. In two
different bilayer ENMs, fine fibres are placed on top of coarse fibres (B7.5) and vice versa (B9). **Figure 5-5c-d** presents the top surface of B7.5 and B9 of the bilayer ENMs, respectively. As expected, the fibre diameter from the upper layer of B7.5 (202 ± 22 nm) resembles with that of the S7.5 (197 ± 26 nm) ENM while the top layer of the B9 (399 ± 31) resembles that of the S9 (397 ± 38 nm) ENM. This resemblance is logical and expected since the upper surface layers of B7.5, and B9 bilayer ENMs were prepared using the same electrospinning parameters to those of S7.5 and S9 solutions, respectively. The rough texture of the PAN ENMs is visible at the smaller accelerating voltage (3kV) during FE-SEM examination. At higher voltages (5–15 kV) the surface details start to disappear, and the fibre showed a smooth appearance [120, 214].

**Figure 5-5** FE-SEM images of (a) S7.5, (b) S9, (c) B7.5 and (d) B9 ENMs at 1µm scale bar. All ENMs had an equal basis weight of 1 g/m² and produced using 18 kV applied voltage, 0.5 mL/h flow rate and 20 cm needle tip to collector distance.
5.3.3 Pore characteristics of ENM

Fibre diameter is known to influence pore size of ENMs [196]. The pore size, in this context, represents vacant space between the fibres, resulting in capillaries throughout the fibre structure. Pore size and its distribution in ENM determine the filtration performance as high filtration efficiency and high pressure drop are the consequence of a small pore size [115, 225].

**Figure 5-6** presents the pore size and pore distribution of the single and bilayer ENMs at 1 g/m² basis weight. The smallest average pore size is from S7.5 (1.6 µm) which is probably due to the lower fibre diameter (≈ 200 nm) compared to the larger fibre diameter (≈ 400 nm) of S9 which has a bigger pore size (2.6 µm). The pore size results of S7.5 (1.6 µm) and B7.5 (1.7 µm) are comparable. Similarly, the pore sizes for S9 (2.6 µm) and B9 (2.2 µm) likewise showed similar pore sizes. It is the nanofibres at the top surface that mainly influences the average pore size. This result indicates that the stacking order in the bilayer structure that determines the pore characteristics of the ENM. The pore size distribution of B9 was shifted towards a smaller pore size compared to S9. This shift was due to the presence of 200 nm fine fibres beneath 400 nm coarse fibres in the B9 bilayer ENM. On the other hand, when coarse fibres are present below the fine fibres, as in the B7.5 case, the pore size distribution moved towards higher number as compared to S7.5 ENM.
Figure 5-6 Pore size distribution of single and bilayer ENMs at the pressure range of 0-30 psi on capillary flow porometry.

5.3.4 Thickness and packing density

Figure 5-7 shows the thicknesses and packing density for the ENMs. The thicknesses of the ENMs differed despite the membranes being electrospun to equal basis weights (Figure 5-7). The single layer S7.5 ENM produced the smallest thickness membrane (129 µm) whereas S9 displayed the largest thickness (214 µm). This change in the thicknesses is due to the differences in the fibre diameters between the S7.5 and S9 ENMs. The coarser or larger fibres (≈ 400 nm) of S9 produce a thicker ENM than membranes produced from the smaller fibres (≈ 200 nm) of the S7.5 ENM.

The thickness of the bilayer ENMs can be estimated theoretically since the bilayer ENMs prepared from half the electrospinning time of two single layers. The half of the respective thickness of S9 and S7 would be 64.5 µm and 112 µm. Hence, the bilayer ENM should result into 176.5 µm thick ENM. The thickness of B7.5 (198 ± 25 µm) and B9 (165 ± 20 µm) is in good agreement with the theoretical estimation. This result suggests that B9 tends to press the finer beads. Because of this effect, B9 is thinner than B7.5.
The packing density of the ENMs has a more prominent effect on air filtration than the thickness [75]. The largest packing density ($6.64 \times 10^{-3}$) corresponds to the ENM S7.5, with the smallest fibre diameter and smallest thickness (129 µm) (Figure 5-7). ENM S9 has the smallest minimum packing density ($3.96 \times 10^{-3}$) because it is the thickest ENM (214 µm) due to the largest fibre diameter (397 nm). The packing densities of bilayer ENMs B7.5 ($4.31 \times 10^{-3}$) and B9 ($5.21 \times 10^{-3}$) are comparable as they represent membranes composed from a combination of the smallest and largest fibre diameters.

There is an inverse relationship between ENM thickness and packing density assuming the ENMs have the same weight basis. In respiratory filtration, a balance between thickness and packing density is desirable where an ENM will have least breathing resistance (less thickness, less packing density) and high filtration efficiency (high thickness and high packing density) at the same time. With B9 bilayer ENMs, the inverse relationship between thickness and packing density found to be narrowed down.

![Graph showing thickness and packing density of single and bilayer ENMs at 1 g/m² basis weight.](image)

**Figure 5-7** Thickness and packing density of single and bilayer ENMs at 1 g/m² basis weight. Thickness is measured using a laser microscope while packing density is estimated based on thickness, basis weight and density of the polymer.
5.3.5 Air filtration performance

Figure 5-8a shows the filtration efficiency of single and bilayer ENMs at 0.06 m/s face velocity. S7.5 ENM resulted in the highest filtration efficiency (98.2%) for 0.3 µm particles. The small fibre diameter (≈ 200 nm) and small pore size (1.6 µm) could trap the 0.3 µm particles in the S7.5 ENM with diffusion [73, 82] being the main capture mechanism at the low face velocity. The filtration efficiency of B7.5 (96.8%) follows S7.5 (98.2%) which is due to the presence of fine fibres at the top surface of the bilayer ENM. However, S9 and B9 showed relatively lower efficiency (around 91%) owing to the coarse fibre diameter (≈ 400 nm) on the top surface and big pore size (2.6 µm). All ENMs showed improved filtration efficiency with increase in particle size. However, the more considerable improvement is observed for S9 and B9 ENM where the filtration efficiency increased from 91% (against 0.3 µm) to 100% (against 5 µm).

At 0.08 m/s face velocity (Figure 5-8b), a similar trend is observed where filtration efficiency improved with particle size. S9 and B9 ENMs showed better efficiencies (94%) compared to that of 0.06 m/s face velocity for 0.3 µm particles. For larger particles (≥ 0.7 µm), S9 and B9 ENMs outperformed S7.5 and B7.5 despite having coarse fibre diameter. This result can be explained as an improvement in the interception mechanism. There is an excellent probability of particle interception at high face velocity when the particle size is bigger and fibre diameter is thicker.

The results suggest that S7.5 ENM cannot be disregarded for diffusion of particles less than 0.3 µm while interception of big particles is better with thick fibres at high face velocity. Thus, diffusion and interception mechanism seems work together in bilayer ENM where both coarse and fine nanofibres contributing to particle capture, resulting in highest filtration efficiency.
Figure 5-8 Filtration efficiency of single and bilayer ENMs against KCl aerosols (0.3–5 µm) at (a) 0.06 m/s and (b) 0.08 m/s face velocity.

Figure 5-9 shows that pressure drop among ENMs highly varied despite an equal basis weight. At 0.08 m/s face velocity, S7.5 has the highest pressure drop (208 Pa) which is due to smallest fibre diameter (≈ 200 nm) and smallest pore size (1.6 µm). ENM S9 shows smaller pressure drop (122 Pa) than S7.5 due to the largest fibres diameter (≈ 400 nm) and largest pore size (2.5 µm). ENM bilayer B7.5 shows a smaller pressure drop (150 Pa) compared to S7.5 (208 Pa). Among the samples studied, ENM bilayer B9 has the lowest pressure drop (87 Pa) at 0.08
m/s face velocity. The similar trend is observed at 0.06 m/s face velocity where B9 shows the lowest pressure drop (64 Pa). ENMs with thicker fibres and therefore larger pores on the upper surface of B9 provide high interspacing allowing better air flow. It highlights the advantage of hierarchical stacking in bilayer ENM.

![Graph showing pressure drop of single and bilayer ENMs at 0.06 m/s and 0.08 m/s face velocity.](image)

**Figure 5-9** Pressure drop of single and bilayer ENMs at 0.06 m/s and 0.08 m/s face velocity.

The quality factor is a comprehensive indicator of filtration performance as it is a function of both filtration efficiency and pressure drop. **Figure 5-10** shows the quality factors of ENMs at face velocities of 0.06 m/s and 0.08 m/s. The quality factor of ENMs was found to be better at the lower face velocity [75] which is a consequence of high filtration efficiency and decreased pressure drop as seen in **Figure 5-8** and **Figure 5-9**. At 0.06 m/s face velocity, the quality factor of S7.5 (0.029/Pa), S9 (0.028/Pa) and B7.5 (0.031/Pa) were comparable. However, B9 had the highest quality factor (0.036/Pa). At 0.08 m/s also, B9 recorded highest quality factor (0.033/Pa). This result implies that the stacking order of nanofibres in a bilayer ENM has a profound effect on the quality factor. Furthermore, the quality factor of the bilayer B9 ENM (0.036/Pa) was found to be better than the PAN transparent filter (produced from fibre diameter of 200 nm) recently reported in the literature (0.024/Pa) [114].
Figure 5-10 Quality factor of single and bilayer ENM at 0.06 m/s and 0.08 m/s face velocity. The graph is an average of five measurements.

5.3.6 Simulation of ENM structure and its filtration performance

Figure 5-11 shows a representation of a 3D ENM structure based on FE-SEM measurements of S7.5 and S9. ENM structure distinctly simulated into a grid having 200 µm³ volume with an edge length of 2 µm. The fibres in the grid are represented in a red colour. The empty spaces represent air pores whose dimensions are mainly dependent on the fibre diameter thickness. The pore size results of the simulation study are in good agreement with the experimental results (Table 5-2). The difference in structure due to fibre diameter thicknesses of S9 compared to S7.5 is easily seen in Figure 5-11. The calculated average pore size increased from 1.20 µm to 2.35 µm. The simulation study also showed that the thicker fibre with higher pore size reduces the pressure drop [228-230]. The filtration efficiency was simulated at 0.06 m/s face velocity for the default particle size of 0.67 µm. The simulation study showed higher filtration efficiency compared to the experimental results (Table 5-2). This difference is because the theoretical calculations only take into account one particle size (0.67 µm) instead of the relatively broad distribution (0.5–0.8 µm) of particle sizes in the actual air filtration measurement. Although the filtration efficiency results of empirical and simulation study slightly varied, the simulation results showed a good representation of fibre network and precisely predicted pore size and pressure drop.
Figure 5-11 Simulation of fibre structure based on FE-SEM measurements (a) S7.5 (≈200 nm), (b) S9 (≈400 nm) ENM.
**Table 5-2** Experimental and simulation results of pore size, pressure drop and filtration efficiency of ENMs S7.5 and S9.

<table>
<thead>
<tr>
<th></th>
<th><strong>S7.5</strong></th>
<th><strong>Simulation</strong></th>
<th><strong>S9</strong></th>
<th><strong>Simulation</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average pore size (µm)</td>
<td>1.6</td>
<td>1.20</td>
<td>2.5</td>
<td>2.35</td>
</tr>
<tr>
<td>Minimum pore size (µm)</td>
<td>1.5</td>
<td>0.81</td>
<td>2.54</td>
<td>1.59</td>
</tr>
<tr>
<td>Maximum pore size (µm)</td>
<td>2.6</td>
<td>1.63</td>
<td>3.7</td>
<td>3.25</td>
</tr>
<tr>
<td>Pressure drop (Pa) at 0.06 m/s face velocity</td>
<td>145.4</td>
<td>159.36</td>
<td>81</td>
<td>64.15</td>
</tr>
<tr>
<td>Filtration efficiency (%) for 0.67 µm particles</td>
<td>98.5</td>
<td>100</td>
<td>89.7</td>
<td>92</td>
</tr>
</tbody>
</table>

### 5.4 Conclusion

Air filtration performance of single layer and integrated bilayer ENMs is described in this chapter. The single layer ENMs prepared from fibre diameters of 200 nm (fine) and 400 nm (coarse). The integrated bilayer ENMs fabricated by altering coarse and fine nanofibre stacking order. The thickness and packing density of ENMs differed despite equivalent basis weight. This study is an excellent example to show how manipulation did work on a small scale when the stacking order of nanofibres was altered. The bilayer ENM with 400 nm fibres on top of 200 nm showed a significant reduction in pressure drop (from 208 to 87 Pa) but had comparable filtration efficiency (95%). The quality factor also improved (from 0.01 to 0.03/Pa) due to the specific stacking order which is primarily due to the difference in pressure drop. The bilayer ENM formation was secure to fabricate and scalable. Such an approach can be used in respiratory air filtration where less pressure drop is desirable. The simulation of single layer ENMs shows good agreement with the experimental result.
Chapter 6

PAN/β–CD composite ENM for simultaneous multifunctional air filtration

6.1 Introduction

Different air filtration methods are required for aerosols and VOCs owing to their diverse physical and chemical properties such as size and volatility [16]. Activated carbon is commonly used to adsorb VOCs owing to its very high surface area and porous structure as well as their low price [231]; however, it is not effective against solid/liquid aerosols. Activated carbon in powder or granular form also has practical limitations when it comes to handling and reusability [163]. On the other hand, electrospun nanofibres are an excellent filter medium for solid/liquid aerosols [16, 92, 120], but show very low adsorbing capacities for gases, without being modified.

For air filtration applications, a small fibre diameter (less than 400 nm) ENM is more efficient (as has been explained in chapter 2). Previously reported composite β–CD nanofibres using polymers such as polymethylmethacrylate [121, 232, 233], polystyrene [107, 178], polyester [106], polycaprolactone [234] and polyurethane [179] have a fibre diameter of more than 400 nm. Some studies prepared composite β–CD nanofibres with fibre diameters ranging from 150–400 nm using polyvinyl alcohol [180] and zein [235], which were intended only for gas adsorption but not for air filtration.

This chapter reports on the simultaneous air filtration and gas adsorption performance of composite PAN/β–CD electrospun nanofibre membranes (ENMs) incorporating β–CD (15%, 30% and 45% w/w in PAN). The influence of β–CD concentration on the solution properties and fibre morphology was measured. The composite nanofibres were characterised using X-ray photoelectron spectroscopy (XPS), field emission–scanning electron microscopy (FE–SEM), IR and water contact angles. The air filtration performance was measured against KCl aerosol ranging from 0.3–5 µm. The gas adsorption of composite ENMs was investigated using formaldehyde (HCHO), xylene and benzene. The toxicity of the PAN/β–CD composite ENMs was also studied against human lung cells.
6.2 Experimental

6.2.1 Materials

PAN (MW 150,000 g/mol, Sigma-Aldrich, USA), β–CD was purchased from Sigma Aldrich. The 1,2,3,4-butane tetracarboxylic acid (BTCA) and sodium hypophosphite monohydrate (SHP) were obtained from Fluka. The formaldehyde (formalin solution, 37%) was obtained from Chem-supply, Australia, and N-dimethylformamide (DMF), xylene, benzene, and ethanol were purchased from Merck. The CellTiter96® Aqueous One MTS Solution Reagent obtained from Promega. All chemicals were of laboratory grade and used as received without any further purification. Commercial P2 type mask (K208) obtained from At-Call Safety, Australia for comparison of VOC adsorption performance. Polyester viscose (50:50) (PV) nonwoven (gifted from Textor Technologies Ltd. Australia) having a basis weight of 45 g/m², thickness 0.16 mm and average pore size of 12 µm was used as a control fabric.

6.2.2 Solution preparation and properties

PAN powder (8 g) was dissolved in DMF (92 g) with constant stirring at room temperature over three hours to prepare 8 % (w/w) PAN stock solution which was then divided into four groups weighing 20 gm each. The first one was marked as control (P8) and remaining three to make P8C15, P8C30 and P8C45. β–CD powder (15% (0.24 g), 30% (0.48 g) and 45% (0.72 g) on the w/w of PAN polymer was added to make composite solutions of P8C15, P8C30 and P8C45. The composite mixture was stirred overnight at room temperature. The viscosity of the solutions was measured by a viscometer (Brookfield DV-II+Pro, USA) with a spindle number SC4–21. The electrical conductivity was determined using a conductivity meter (FE30, Mettler-Toledo Group, Switzerland).

6.2.3 Electrospinning

The electrospinning setup (Figure 6-1a) comprised of a rack-mounted DC voltage power supply (Spellman SL150, USA), a syringe pump (NE1000, New Era Pump Systems, Inc. USA) and a ground electrode (a metal surfaced drum collector, diameter 13 cm, and width 19 cm). The DC voltage was connected to a metallic needle (23 gauge) with a 5 ml syringe (Terumo) containing the polymer solution. The needle tip to the collector drum distance was fixed at 20 cm. The nanofibres were collected on a polyester–viscose nonwoven substrate (weight 45 g/m²,
thickness 0.16 mm and average pore size 12 µm). The nonwoven substrate (unmodified) was wrapped around the metal surfaced collector drum (surface speed 30 mm/s). After electrospinning, all ENMs were dried overnight at room temperature and then in a vacuum oven for 4 hours at 50°C.

Figure 6-1 (a) Electrospinning setup with PAN and β-CD solution, (b) image of a composite nanofibre.

6.2.4 ENM characterisation

The morphologies of the ENMs (Figure 6-1b) were examined using a Field Emission Scanning Electron Microscope (FE–SEM) (Zeiss Gemini 2 Merlin). The ENMs were first iridium coated before imaging at an acceleration voltage of 3kV. The diameter of 100 nanofibres was measured using Image-J software, and the distribution histogram was obtained using the Minitab17 software. The pore size and pore size distribution of the ENM (13 mm diameter samples) were determined using a capillary flow porometer (Porous Materials Inc, USA) using Galwick as the wetting agent (surface tension 15.9 mN.m\(^{-1}\)). The specific surface area was measured using the Brunauer–Emmett–Teller (BET) technique. The values were determined
from their adsorption and desorption isotherms of nitrogen at -196°C using a Quantachrome Autosorb-I volumetric adsorption system. The samples were degassed under vacuum at 40°C for 22 h before analysis.

The surface wettability (water contact angle) of the ENMs was measured using a pocket goniometer (PG-3, Fibro system). A deionised water drop (4 µL) was dropped on the ENM sample, and the water contact angle measured over 6 sec and expressed as an average of 10 readings using PG proprietary software.

X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Nova spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα source at a power of 180 W (15 kV x 12 mA). A hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (analysis area: 0.3 mm x 0.7 mm). The total pressure in the main vacuum chamber during analysis was typically between 10⁻⁹ and 10⁻⁸ mbar. Survey spectra were acquired at a pass energy of 160 eV. High-resolution spectra were recorded from individual peaks at 40 eV pass energy (yielding a typical peak width for polymers of < 1.0 eV) to obtain more detailed information about the chemical structure and oxidation states. Each specimen was analysed at an emission angle of 0° as measured from the surface normal. Assuming typical values for the electron attenuation length of the relevant photoelectrons the XPS analysis depth (from which 95% of the detected signal originates) ranges between 5 and 10 nm for a flat surface. The actual emission angle is ill-defined in the case of fibres (ranging from 0° to 90°); hence the sampling depth may range from 0 nm to approximately 10 nm.

CasaXPS processing software (Casa Software Ltd., Teignmouth, UK, version 2.3.15) was used to identify and quantify all elements from the survey spectra. The atomic concentrations of the detected elements were calculated using integral peak intensities using default sensitivity factors.

6.2.5 Air filtration

The air filtration setup employed was similar to the previous chapters 4 and 5. ENM samples with a diameter of 10.9 cm were placed into a filter holder which has an active test area of 93.26 cm². An atomiser generated KCl aerosols which were detected by a pair of optical particle counters (TSI 9306–03) located upstream and downstream of the sample. Results were reported as the average of five successive replicates measured over a period of 30 sec. All ENMs
were tested at the face velocity of 0.06 m/s (flow rate 20 L/min) and 0.09 m/s (flow rate 32 L/min) which simulates regular breathing (during the slow walk) and deep breath (during the fast step), respectively [223, 224]. The air filtration performance parameters, including filtration efficiency, pressure drop and quality factor were calculated according to the equations described in chapter 2, section 2.3 (Eqn 2-7, 2-10, 2-11).

6.2.6 VOC adsorption

6.2.7 VOC adsorption measurement

VOC adsorption performance of the fabric samples was evaluated for three model VOCs, xylene, benzene and formaldehyde (HCHO). The experimental set up for the VOC measurements is shown in Figure 6-2. The setup is comprised of a 4.5 L (0.0044 m³) capacity plastic jar with a modified lid. The lid had a steel wire and a mesh system to hold the ENM sample to be tested. The lid was wrapped with paraffin film during the measurement protocol to avoid loss of VOCs analytes. The target analyte (xylene or benzene) (80 μL) was injected into the jar using micropipette. The jar containing the sample and xylene or benzene analytes analyte was kept in a conditioned room at 20 ± 2°C. The sample was exposed to the xylene or benzene analytes for four hours. Afterwards, the fabric sample was immersed in 15 mL ethanol and kept overnight to extract the adsorbed xylene or benzene analytes. The ethanol solution was then analysed using UV-Vis spectroscopy. A standard calibration curve was obtained using different calibration standards (0, 40, 80, 120, 160 and 200 mg/L) of xylene and benzene in ethanol. VOC adsorption was expressed as µg/mg of fabric sample considering the fabric mass, UV-absorbance and the calibration standard. The detailed example of calculations is described in Appendix 1.
Figure 6-2 Experimental setup for VOC measurement. The lid of a plastic jar modified with a steel wire and metal mesh. The jars kept airtight after injecting the target VOC. Once the VOC exposed to the ENM sample for the required time, the ENM sample immersed into 15 mL ethanol, stored overnight and the solution is analysed with the help of UV spectroscopy.

The formaldehyde solution was diluted tenfold in demineralised water, and from this solution 20 μL was injected into the jar. The lid had a septum at the top (Figure 6-3) to keep the jar airtight, during residual HCHO measurement, after puncturing with a needle (Terumo, 18 gauge) at the end of the fourth hour. The needle was connected to a PPM formaldemeter (PPM Technology Ltd.) by an adaptor as shown in Figure 6-3. The formaldemeter works on the principle of the electrochemical sensor which consists of two metal electrodes and an electrolyte. When air is drawn into the meter, the sensor generates a voltage which is directly proportional to the HCHO concentration in the sample. The residual HCHO of a blank (without any sample) was also measured as a reference. The blank reading was subtracted from the sample readings to obtain a net residual HCHO. The net concentration reading of the HCHO was converted into a
mass considering the constant volume of the jar (0.0044 m³). The details of the calculations are described in Appendix 2. All VOC adsorption experiments were repeated three times.

![Formaldemeter (PPM Technology) and rubber septum used for HCHO measurement.](image)

**Figure 6-3** Formaldemeter (PPM Technology) and rubber septum used for HCHO measurement.

### 6.2.8 Cytotoxicity testing

The cytotoxicity of the ENMs was assessed using human adenocarcinomic lung cell line A549. Each ENM specimen (15 mm diameter) was placed in a 24 well tissue culture plate, which was UV sterilised and secured with a stainless steel ring to ensure complete contact of the specimens with the dish. A549 cells were grown in 75 cm² cell culture flasks using DMEM (Dulbecco’s modified Eagle’s medium) with 10% serum, and then the cells were detached by adding one mL of TrypLE cell dissociation enzyme (Thermo Scientific). The separated cells were centrifuged and counted via the trypan blue assay using a hemocytometer. The numbers of cells used to seed each specimen were 5000 cells. Plain coverslips without the ENMs served as a positive control whereas the ENM without cells was used for background correction. The cytotoxicity of the cells was measured after 2, 4 and 6 days using a colourimetric CellTiter96® Aqueous One MTS Solution Reagent (Promega, Madison, WI, USA). On the day of analysis, the
cells were washed with phosphate buffer solution. An MTS solution (10%) in the serum-free medium was added and incubated for three hours under growth conditions. A 100 μl of each sample was pipetted into a 96-well spectroscopy plate reader. The absorbance spectrum of the formazan (artificial chromogenic product) due to the reduction of MTS was recorded at 492 nm.

6.3 Results and discussion

Effect of β–CD on PAN solution properties

Table 6-1 shows the viscosity and the conductivity of PAN/DMF solutions with and without β–CD. The viscosity of the PAN solution gradually increased from 310 cPs to 344 cPs as the concentration of β–CD increases. This increase in viscosity could be due to the intermolecular interactions between the hydroxyl groups of the β–CD and highly polar nitrile groups of PAN. The shear thinning (0–125/sec) of the PAN-based solutions did not alter significantly with the addition of β–CD which suggests pseudoplastic behaviour of the solution prepared. The conductivity of the PAN solutions, however, reduced from 112 µS/cm to 92.8 µS/cm as the concentration of β–CD increased. This reduction is due to the lower ionic mobility of the solution which is a consequence of the improved solution viscosity containing β–CD.

Table 6-1 Effect of β–CD on solution viscosity and conductivity.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample</th>
<th>Viscosity (cPs) at 22°C and 55% RH</th>
<th>Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P8</td>
<td>PAN</td>
<td>310</td>
<td>112</td>
</tr>
<tr>
<td>P8C15</td>
<td>PAN + 15 wt% β–CD</td>
<td>331</td>
<td>106</td>
</tr>
<tr>
<td>P8C30</td>
<td>PAN + 30 wt% β–CD</td>
<td>332</td>
<td>98.5</td>
</tr>
<tr>
<td>P8C45</td>
<td>PAN + 45 wt% β–CD</td>
<td>344</td>
<td>92.8</td>
</tr>
</tbody>
</table>

6.3.1 Nanofibre morphology

PAN/β–CD nanofibre morphology was strongly influenced with polymer concentration, flow rate and applied voltage [110, 236] Hence, these parameters kept unchanged for all the ENMs to study the effect of β–CD on nanofibre morphology. Figure 6-4 shows the FE–SEM
images of the various PAN/β–CD ENMs. The average fibre diameter for pristine PAN (P8) was 305 ± 48 nm. Previous literature [105, 236] regarding PAN/β–CD nanofibres reported thicker fibre, increased solution viscosity and decreased solution conductivity due to the presence of β–CD. This indicates limited jet stretching during electrospinning compared to pristine PAN. For example, PAN nanofibre diameter increased from 576 nm to 647 nm with the addition of β–CD during electrospinning. In the present study, the fibres became thicker with increasing concentration of β–CD. The composite PAN ENMs with 15 wt% β–CD (P8C15) has a fibre diameter of 365 ± 53 nm which is slightly smaller than the PAN with 30 wt% β–CD (P8C30) with a fibre diameter of 392 ± 52 nm. The thickest fibres of 463 ± 79 nm resulted from PAN with 45 wt% β–CD (P8C45). The nanofibre diameter range also broadens especially at the higher β–CD concentrations (Figure 6-5).

![Figure 6-4](image_url)

**Figure 6-4** FE–SEM images of ENMs (a) P8 (305 ± 48 nm), (b) P8C15 (365 ± 53 nm), (c) P8C30 (392 ± 52 nm) and (d) P8C45 (463 ± 79 nm).
Figure 6-5 Fibre diameter distribution of PAN/β–CD composite ENMs.

Table 6-2 shows the BET surface areas of PAN and the PAN/β–CD ENMs. P8 showed the highest surface area (14.67 m²/g) which correlates to the smallest fibre diameter (305 nm). The surface area of P8C15 (8.13 m²/g) and P8C30 (9.29 m²/g) was comparable which also correlated to the fact that their average fibre diameters are similar (365–392 nm). P8C45 exhibited the lowest surface area (5.03 m²/g) which corresponds to the largest fibre diameter, 463 nm). The change in fibre diameter influenced the surface area to volume ratio, i.e. specific surface area decreases with increasing fibre diameter. This change can be validated by a simple calculation and assumption where fibres can be considered as uniformly heightened cylinders. The shift in cylinder diameter from 305 nm to 465 nm, would reduce the theoretical surface area from 15 m²/g to less than 10 m²/g.
Table 6-2 Specific surface area (BET) and pore sizes of PAN/β–CD nanofibre membranes.

<table>
<thead>
<tr>
<th></th>
<th>Surface area (m²/g)</th>
<th>Pore size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Smallest</td>
</tr>
<tr>
<td>P8</td>
<td>14.67</td>
<td>1.55</td>
</tr>
<tr>
<td>P8C15</td>
<td>8.13</td>
<td>1.83</td>
</tr>
<tr>
<td>P8C30</td>
<td>9.29</td>
<td>2.19</td>
</tr>
<tr>
<td>P8C45</td>
<td>5.03</td>
<td>2.31</td>
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</table>

6.3.2 XPS characterisation

XPS can be used to determine the elemental composition of a material based on the binding energy levels of the elements. Binding energies were referenced to the C 1s peak at 285.0 eV (aliphatic hydrocarbon) or the N 1s peak at 399.5 eV (nitrile). The peak at 540.0 eV was associated with oxygen. The accuracy associated with quantitative XPS is approximately 10-15%. Precision (i.e. reproducibility) depends on the signal/noise ratio but is usually much better than 5%. The latter is relevant when comparing similar samples.

For the β–CD to be available for VOC adsorption, it needs to be at the fibre surface or close to the fibre surface assuming diffusion through the polymer surface is possible. Any β–CD buried in the polymer bulk is not available for immediate adsorption [101, 106]. XPS was used as an indirect mean of qualitatively establishing whether there is any β–CD present on the fibre surface. The XPS elemental composition of the various ENM membranes is shown in Table 6-3. The P8 ENM was taken as a baseline containing 75.14% carbon (C), 20.96% nitrogen (N) and 2.44% oxygen (O) (the remainder are trace impurities). With the addition of the β-CD, the % N should be reduced whereas the % O should be increased as β-CD has oxygen but no nitrogen present in its structure whereas PAN has nitrogen but no oxygen. Figure 6-6 presents the individual spectra of the ENMs and the atomic ratios of the O and N normalised to C. The increase in O 1s from 0.032 to 0.213 and drop in N 1s from 0.28 to 0.19 were attributed to the increasing quantities of β-CD (0–45%w/w) on the fibre surface. These results indicate the growing presence of β–CD on the surface of the ENM.
Table 6-3 Elemental compositions (atomic %) of PAN/β-CD ENMs obtained using XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P8</th>
<th>PC15</th>
<th>PC30</th>
<th>PC45</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>C 1s</td>
<td>75.14</td>
<td>0.18</td>
<td>71.60</td>
<td>0.12</td>
</tr>
<tr>
<td>N 1s</td>
<td>20.96</td>
<td>0.33</td>
<td>17.46</td>
<td>0.12</td>
</tr>
<tr>
<td>O 1s</td>
<td>2.44</td>
<td>0.04</td>
<td>7.61</td>
<td>0.06</td>
</tr>
<tr>
<td>P 2p</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Si 2p</td>
<td>1.19</td>
<td>0.03</td>
<td>3.06</td>
<td>0.18</td>
</tr>
<tr>
<td>Na 1s</td>
<td>0.10</td>
<td>0.02</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>S 2p</td>
<td>0.19</td>
<td>0.06</td>
<td>0.19</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Figure 6-6 Individual spectra of PAN/β-CD ENMs and the atomic ratio of oxygen (O) and nitrogen (N) normalised against carbon (C).
6.3.3 Contact Angle

The contact angle decreases as the concentration of β–CD increased indicating increased hydrophilicity at the fibre surface, providing additional evidence of the presence of β–CD at or near the fibre surface. The increasing quantities of β–CD increases the hydrophilicity at the fibre surface to the extent that the water droplet spread out quickly and therefore only the first 6 sec instead of the average 10 sec was used in the measurement of the contact angle.

The water contact angle of P8 ENM (Figure 6-7) was measured at 123° indicative of a hydrophobic surface. The addition of 15% β–CD (P8C15) slightly reduced the contact angle to 112°, which is due to the presence of hydrophilic hydroxyl groups from the β–CD on the fibre surface. Increasing the amount of β–CD from 15% (P8C15) to 30% (P8C30) and 45% (P8C45) sharply decreased the water contact angle to around 36°. This substantial reduction is due to the presence of the polar hydroxyl groups from the β–CD on the surface of the nanofibres providing further evidence of surface modification.

In a heterogeneous blend system, a low molecular weight component tends to migrate towards the surface to minimise surface energy and entropy [106]. In the present case, β–CD has lower molecular weight (1153 g/mol) than PAN polymer (150 000 g/mol). Thus, β–CD migrates toward the surface of the PAN/β–CD composite nanofibres. This migration behaviour is well supported by the water contact angle results.
6.3.4 Infrared spectroscopy

Figure 6-8 shows the IR spectra of the composite ENMs as well as PAN and β–CD powder samples. PAN powder and P8 exhibits characteristics peaks at 2243 cm$^{-1}$ and 1450 cm$^{-1}$ due to the stretching of the nitrile (C≡N) group and bending of the saturated carbon (CH$_2$) respectively. These peaks stay unchanged during the addition of the β–CD. The characteristic peaks for β–CD at 1020 cm$^{-1}$, 1077 cm$^{-1}$ and 1152 cm$^{-1}$ correspond to C-O stretching of the acetal group in the glucopyranoside units of the β–CD. The peak at 3276 cm$^{-1}$ indicates intermolecular bonded O-H stretching within the β–CD. These peak frequencies also remain unchanged during the addition process. However, the magnitude of PAN peaks reduces while the peaks due to β–CD increases as the amount of β–CD in the ENM increase. No new peaks are observed indicative of no new bonds between β–CD and PAN.
Figure 6-8 FTIR spectra of PAN powder, β–CD powder, PAN nanofibre and PAN/β–CD composite ENMs. The spectra were normalised against 2243 cm$^{-1}$, which corresponds to nitrile group of PAN.

6.3.5 Air filtration performance

Figure 6-9 shows the filtration performance of the PAN/β–CD ENMs at 1.2 g/m² basis weight using KCl particles ranging from 0.3 to 5 µm at face velocities 0.06 and 0.08 m/s. For 0.3 µm particles, P8 showed the highest filtration efficiency (95.5%) which correlates with the smallest fibre diameters (305 nm) and the smallest pore size (1.62 µm) of ENM resulting in adequate diffusion of the challenge particles. For P8, filtration efficiencies increase from 95 to 98% as the particle sizes increase (larger particles are more accessible to filter as described in chapter 4, section 4.3.3). The results at both face velocities (Figure 6-9) show that ENM P8C15 follows the same trend as P8 but with relatively lower filtration efficiency over the entire particle size range.

ENMs P8C30 and P8C45 also showed a lower efficiency (90%) compared to P8 for 0.3 µm particles (95.5 %) which are attributed to coarse fibre diameter (392–463 nm) and large pore size. However, P8C30 and P8C45 performed better than P8 for the particle sizes ranging from 0.5 µm to 5 µm. This dramatic improvement may be explained if interception and straining
filtration capture mechanisms in addition to diffusion are used. Fibres of 305 nm diameter and 1.62 μm pore size can diffuse particles smaller than 0.3 μm while fibres of 463 nm diameter and 2.44 μm pore size can intercept and strain particles larger than 0.5 μm.

Straining is an essential mechanism in microfibre filtration where the filtration efficiency is improved with larger particle size [42]. The straining in microfibre filter media could be analogous to the straining in ENMs. However, the straining mechanism is not usually used to explain particle capture by nanofibres [16]. The larger pore size of P8C45 (2.44 μm) and randomly interconnected pore structure formed by the overlapping electrospun fibres allows smaller aerosols to enter into the arrangement like depth straining in microfibres [42] and constricts the larger particles at the surface.
Figure 6-9 Filtration efficiency of PAN/β–CD ENMs against KCl particles at (a) 0.06 m/s face velocity and (b) 0.08 m/s face velocity. KCl particle size varies from 0.3 to 12.5 µm.
Figure 6-10 shows FE-SEM images of ENMs after air filtration. It can be seen that smaller particles were trapped in P8 ENM. While in the composite ENMs (b, c and d) fewer but larger particles have been trapped. These images support the better filtration efficiency observed for P8 ENM. Therefore nanofibre morphology and the target particle size can be used to explain filtration efficiency in terms of particle capture mechanism (diffusion, interception and straining).

![Figure 6-10](image)

Figure 6-10 FE-SEM micrographs of ENMs after filtration (a) P8, (b) P8C15, (c) P8C30 and (d) P8C45 at the scale bar of 2 μm.

With increasing β–CD content, the pressure drop of the PAN/β–CD ENMs reduced significantly (Figure 6-11), from 257.2 Pa for P8 to 145.8 Pa for P8C45 at 0.08 m/s face velocity. At 0.06 m/s, the pressure drop was small for all the ENM samples; however, the trend observed was similar, with the pressure drop decreasing from 185.6 Pa for P8 to 92 Pa for P8C45. The decrease in pressure drop could be attributed to the increase in fibre diameter (Figure 6-4) and also pore size (Table 6-2) due to the presence of β–CD. Thus the fabrication of
Composite ENMs is another method that can be used to reduce the pressure drop compared to that of unmodified polymer in this case neat PAN.

**Figure 6-11** The pressure drop of PAN/β-CD ENMs at 0.06 m/s and 0.08 m/s face velocities.

The quality factor is a better overall indicator for the comparison of aerosol filtration performance of the different ENMs. **Figure 6-12** shows the quality factor results of the ENM samples for 0.3 μm particles at 0.06 m/s and 0.08 m/s face velocities. P8C30 and P8C45 showed better quality factors compared to P8C15 and P8 at both face velocities. The high-quality factors of P8C45 (0.027/Pa) and P8C30 (0.026/Pa) are probably due to the significant reduction in pressure drop as discussed earlier. Although the pressure drop reduction of P8C45 was higher than P8C30, filtration efficiency was inferior to P8C30. Thus the quality factors are comparable for the two samples.
6.3.6 VOC adsorption

VOC adsorption performance of PAN/β–CD ENMs is evaluated for three pollutants; namely, xylene, benzene and HCHO. The adsorption performance of powder samples (PAN and β–CD) and commercial P2 type face mask were also determined for comparison. UV-Vis was used to quantitate the amounts of xylene, benzene and HCHO adsorbed by the ENMs and other control materials.

Figure 6-13 shows a calibration curve of xylene for different calibration standards (0, 40, 80, 120, 160 and 200 mg L\(^{-1}\)) plotted against absorbance at 268 nm. A linear relationship is found between absorbance and xylene concentration up to 200 mg/L with a good correlation coefficient (R\(^2\)=0.9999). The regression equation (y=271.55x) was used to convert absorbance values of xylene into the concentration of xylene per unit mass of fabric sample (Appendix 1).
β–CD can form complexes with a wide variety of molecules including aromatics and heterocyclic [159]. Xylene is an aromatic hydrocarbon which is known for its strong smell. Xylene was chosen as a target VOC considering the hazardous nature of the pollutant and its ability to form complexes with β–CD. Figure 6-14 displays xylene adsorption by PAN/β–CD ENMs along with powder samples and P2 mask. The mask has adsorbed the least amount of xylene (1.49 μg/mg) as the cover is intended only for aerosol capture. The xylene adsorption by β–CD powder (10.84 μg/mg) and PAN powder (8.52 μg/mg) is very roughly comparable. The adsorption improved dramatically when β–CD is part of an ENM. This is due to the larger surface area of the PAN nanofibre (14 m²/g) compared to the PAN powder (0.77 m²/g). (PAN ENM (P8) showed more than ten times improvement (116 μg/mg) in xylene adsorption. The addition of 15% β–CD, further improved xylene adsorption (201 μg/mg) which can be attributed to the additional β–CD on the nanofibre surface. However, increasing the β–CD content (30% and 45%) does not improve xylene adsorption. P8C30 and P8C45 nanofibres were thicker with the decreased surface area (and therefore less CD on the fibre surface) which could be the reason that the xylene adsorption did not improve.

This result infers that nanofibre morphology becomes the dominant factor in determining xylene adsorption instead of the quantity of β–CD added above 15%. However, it is noteworthy that β–CD containing ENMs invariably showed better xylene adsorption compared to pristine
PAN ENM. It indicates the importance of β-CD as an effective additive for VOC adsorption. Additionally, xylene adsorption of PAN/β–CD composite ENMs (13.16 µg mg\(^{-1}\)) is found much better than previously reported composite polyurethane/fly ash ENMs (0.04 µg mg\(^{-1}\)) [103].

Figure 6-14 Xylene adsorption performance of PAN powder, β–CD powder, P2 type mask and PAN/β–CD composite ENMs. The values were obtained using UV spectroscopy at the characteristic wavelength of 268 nm.

Figure 6-15 shows the calibration curve of benzene for the different standards (0, 40, 80, 120, 160 and 200 mg L\(^{-1}\)) against the absorbance at 255 nm. A linear relationship is found between absorbance and benzene concentration with a good correlation coefficient (\(R^2=0.9949\)). The regression equation (\(y=494.03x\)) was used to convert absorbance values of benzene into ppm which were then expressed as benzene adsorption per unit mass of fabric sample (Appendix 1).
Figure 6-15 Calibration curve of benzene in ethanol at different concentrations. A good correlation has been found at an absorbance of 255 nm using UV-Vis spectroscopy.

Figure 6-16 presents benzene adsorption performance. Between powder samples, β–CD powder shows higher benzene adsorption (8.32 μg/mg) than PAN powder (5.25 μg/mg). The P2 mask which is made up of polypropylene microfibres has the very little capacity to absorb benzene (5.27 μg/mg). The production of nanofibres (P8 ENM) from PAN powder significantly improved benzene adsorption (113.85 μg/mg) which is due to the higher surface area of the nanofibres compared to powder. The benzene adsorption was further enhanced with the addition of β–CD. P8C15 showed the highest benzene adsorption capacity (176.85 μg/mg), while the adsorption performance of P8C30 and P8C45 ENM were found to be comparable. These results suggest that addition of β–CD during PAN electrospinning also assists in benzene adsorption. However, beyond 15% addition of CD results in an increase in fibre diameter and reduction of surface area which limits the benzene adsorption. The profiles between benzene and xylene are similar which is not surprising given their similar chemical structure.
Figure 6-16 Benzene adsorption performance of powder samples of PAN and β–CD, P2 mask and PAN/β–CD ENMs. The values were obtained using UV spectroscopy at the characteristic wavelength of 255 nm.

Figure 6-17 displays HCHO adsorption for the different samples. It is clear that a P2 mask has least capacity to adsorb HCHO (0.002 μg/mg). Among powder samples, it can be seen that β–CD adsorbs larger quantities of HCHO (0.056 μg/mg) compared to PAN powder (0.031 μg/mg). ENM P8 also adsorbs larger amounts of HCHO (0.049 μg/mg) than PAN powder which is due to the larger surface area of ENM. The HCHO adsorption improved when the concentration of β–CD in composite ENMs increased. P8C15 ENM only had slightly increased (0.054 μg/mg) HCHO adsorption compared to P8. However, P8C30 and P8C45 showed some increase in HCHO adsorption (0.08 μg/mg) which is due to the increasing concentration of β–CD in the composite ENMs.
β–CD triggers the HCHO adsorption in two ways. The cavity of β–CD can be a host for an HCHO guest molecule. While the cavity of solid phase β–CD is hydrophobic, it possesses some water molecules [159, 169] which act as a driving force in molecular complex formation. The second way is due to the exterior hydrophilic nature of β–CD powder with plenty of OH groups on the surface. The high affinity between aldehydes functionality of the HCHO and the OH groups of the β–CD do assists in the adsorption of the HCHO. A recent report [105] showed improvement in HCHO adsorption using β–CD as an additive during electrospinning. However, the basis weight of the samples in the reported study is unknown hence a direct comparison cannot be made.

HCHO adsorption by β–CD is also supported by the characterisation data of composite ENMs. XPS and water contact angle results indicate that β–CD is present on the surface of composite ENMs. The surface functionality brought by β–CD with increasing concentration levels assisted in HCHO adsorption and masked the loss in the specific surface area compared to pure PAN ENM.
6.3.7 Cytotoxicity test

Although PAN and β–CD are reported as biocompatible materials [237, 238], the ENM fabrication uses DMF as a solvent which is classified as an irritant. For a safe respiratory filter, it is desirable that there are no toxic components that would adversely affect human health. As a result, the cytotoxic effect of the composite PAN/β–CD ENMs on a human lung cell line A549 was assessed. Toxicity analysis (Figure 6-18) shows a steady growth of A549 cells from day 2 to day 6 for all samples. At day 2, the cell growth on the composite ENMs was comparable to cells grown on tissue culture plate which served as a positive control. There were no significant differences in the growth of A549 cells for the P8, P8C15, P8C30 and P8C45 ENMs at day 4 and 6. Importantly, there was no significant decrease in cell proliferation on the ENMs, indicating that the ENMs have no cytotoxic effect on the human lung cell line and that the PAN/β–CD composite ENMs could be used in air filtration application without having a negative impact.

![Figure 6-18](image)

**Figure 6-18** Toxicity analysis of nanofibres on human lung cell line A549 measured at day 2, 4 and 6. The absorbance of formazan product at 492 nm compared between samples. The tissue culture plate without the nanofibre sample was considered a positive control.

6.4 Conclusion

PAN/β–CD composite nanofibres were electrospun using β–CD concentrations of 15, 30 and 45% by the weight of PAN polymer. The average diameter of the composite nanofibres ranged from 305–463 nm. The addition of β–CD made the composite nanofibres thicker with
larger pores. XPS analysis and water contact angle results confirmed the surface modification of composite ENMs caused by the presence of β–CD. The composite ENMs outperformed pristine PAN in filtration efficiency for aerosol particles at 0.5 µm and above, despite having a larger fibre diameter and therefore a smaller surface area. These results could be explained using the interaction and straining capture filtration mechanism models. The pressure drop and quality factor of the composite ENMs with 30 and 45% β–CD were better than pure PAN P8 and P8C15.

Along with excellent air filtration performance, composite ENMs adsorbed xylene, benzene and HCHO vapour. Thus, multifunctional air filtration in one step was achieved using PAN/β–CD composite ENMs. Overall, among the different combinations of composite ENMs, PAN with 30 wt% β–CD was found to be better with greater than 95% particle aerosol filtration efficiency, low pressure drop (112 Pa) and high quality factor (0.026 Pa⁻¹). This result is at par with the commercial respiratory standard recommended for NIOSH standard (95% efficiency) [89]. Composite ENMs fabricated by incorporating β–CD significantly improved xylene, benzene and formaldehyde adsorption capacity compared to PAN ENM and a commercial mask. Cytotoxicity studies confirmed the nontoxic nature of the composite ENMs. Such nontoxic ENMs along with lower air resistance, excellent aerosol filtration efficiency and VOC adsorption capacity are the promising candidates for designing multifunctional respiratory filter media.
Chapter 8

Bio-nanomembrane for multifunctional air filtration

7.1 Introduction

Air filter manufacturing, irrespective of end use, is dominated by synthetic fibres like glass and polypropylene [239]. Low cost, high performance and excellent mechanical/chemical resistance are the reasons behind the choice of synthetic polymers. However, their manufacturing and disposal is a major environmental concern [240]. Use of renewable biopolymers over synthetics is a promising alternative towards a sustainable society [241]. Moreover, synthetic fibres do not have inherent functionality which is essential for multifunctional air filtration. Biopolymers with multiple functional groups can be employed for this purpose.

Gelatin is a biopolymer obtained from partial hydrolysis of collagen which is a structural protein abundantly found in bones, skin, cartilage and tendons [242]. Gelatin has attractive qualities such as biodegradability, biocompatibility, film-forming ability, gas barrier ability (oxygen and carbon dioxide), ease of electrospinning and importantly commercial availability at low cost [243, 244]. Not surprising, gelatin nanofibres has predominant use in biomedical applications such as tissue engineering, drug delivery and wound dressings [242, 245-247]. Food packaging is another area where gelatin is commonly being used [248, 249]. However, the use of gelatin for air filtration and VOC adsorption remain relatively unknown. This could be due to the considerable success in other applications and inherent susceptibility of gelatin to the ambient environment. However, cross-linking treatment for gelatin improves water resistance, thermal stability and mechanical properties [244].

Gelatin is fairly soluble in warm water. However, it can lead to gelation which makes the solution difficult to electrospun. Gelatin electrospun nanofibres, were first reported in 2004 and used 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the solvent [250]. The other solvent employed for gelatin electrospinning is 2,2,2-trifluoroethanol (TFE)[247]. However, HFIP and TFE are both corrosive and may degrade the protein [245]. Solvents such as formic acid and acetic acid can also be used which are less toxic.
Gelatin, being a protein, has high reactivity towards aldehydes. Thus it can be suitable for formaldehyde adsorption. Additives can be added while preparing gelatin solution for electrospinning to enhance the VOC adsorption of gelatin synergistically. Two different biomaterials, namely β-cyclodextrin (β-CD) and saponin have been selected for this purpose. β-CD is found as a beneficial additive during PAN electrospinning which enhances toxic gas adsorption. Saponin is a plant-derived surfactant and foaming agent and has a good medicinal value [251, 252]. Saponins are extracted from seeds and barks of many vegetables, commercially from Quillaja Bark [253].

This chapter looked at the electrospinning of gelatin-based blends with β-CD and saponin none of which is reported so far. The use of gelatin nanofibres and its blend for air filtration and VOC adsorption is also being studied for the first time. The aim is to design multifunctional ENMs, constructed from biomaterials, which can efficiently trap aerosols and VOCs. All composite ENMs were characterised with regards to fibre morphology and surface chemistry. The air filtration and VOC adsorption performance of these ENMs were measured.

7.2 Experimental

7.2.1 Materials

Gelatin (from porcine skin, Type A), β-cyclodextrin and saponin powder were obtained from Sigma Aldrich. Casein powder was obtained from Cabiochem (USA). The solvents used were formic acid (Merck), ethanol (Merck) and demineralised water. Xylene (Merck), benzene (Merck) and formaldehyde (37% formalin) (Chem-supply, Australia) solutions were used to generate respective VOC vapours under controlled conditions. All the chemicals were employed as received without any further purification. The polyester viscose (50:50) nonwoven fabric was the control substrate, like in previous chapters, on which nanofibres were deposited.

7.2.2 Electrospinning of gelatin-based composite nanofibres

A series of electrospinning experiments were conducted to fabricate pure gelatin and gelatin-based composite nanofibres. Table 7-1 shows the details of materials and solvent combination employed to make different ENMs. Gelatin powder (16% w/w) was dissolved in the formic acid solvent at room temperature and stirred overnight. β-CD and saponin powder were added separately to the gelatin solution in various proportions. The composite mixture was
centrifuged using a rotor (JA 25.50) at 9000 rpm (9798 g) for 15 minutes at 17°C before electrospinning to remove any undissolved particles. The solution was electrospun at the applied voltage of 22 kV with a flow rate of 0.15 ml/h. The needle (23 gauge) to drum distance was fixed to 20 cm. The ENM was deposited on the control substrate.

**Table 7-1** Nomenclature of electrospinning solutions to prepare gelatin, gelatin/β–CD and gelatin/saponin composite ENMs.

<table>
<thead>
<tr>
<th>ENM label</th>
<th>Spinning solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>16% (w/w) Gelatin</td>
</tr>
<tr>
<td>GC1</td>
<td>16% (w/w) Gelatin + 10 % β–CD</td>
</tr>
<tr>
<td>GC2</td>
<td>16% (w/w) Gelatin + 20 % β–CD</td>
</tr>
<tr>
<td>GC3</td>
<td>16% (w/w) Gelatin + 30 % β–CD</td>
</tr>
<tr>
<td>GSL</td>
<td>16% (w/w) Gelatin + 25% saponin</td>
</tr>
<tr>
<td>GSM</td>
<td>16% (w/w) Gelatin + 50% saponin</td>
</tr>
<tr>
<td>GSH</td>
<td>16% (w/w) Gelatin + 75% saponin</td>
</tr>
</tbody>
</table>

### 7.2.3 ENM characterisation

ENMs were characterised using similar characterisation techniques as explained in previous chapters. In brief, viscometer determined viscosity, field emission scanning electron microscopy (FE-SEM) and transverse electron microscopy (TEM) analysed morphology, capillary flow porometer measured the pore size, Fourier transforms infrared (FTIR) spectroscopy identified chemical groups and energy dispersive X-ray (EDX) spectroscopy investigated elemental composition.

### 7.2.4 Air filtration and VOC adsorption measurement

The air filtration of ENMs was measured using the similar set up as explained in Chapter 4. In short, KCl aerosols of average sizes 0.3–5 μm were generated in the atomiser. The aerosols, which were guided through the rig at a flow rate of 20 L/min (face velocity 0.06 m/s), eventually hit the ENM. The filtration efficiency, pressure drop and quality factor were evaluated as per the equations mentioned in Chapter 2 (section 2.3.2, Eqn 2-7, 2-10 and 2-11).
VOC adsorption performance of fabric samples was evaluated for xylene, benzene and HCHO, as explained in Chapter 7 section 7.2.4. In brief, a known quantity of VOC was injected into a plastic jar with a specifically designed lid. The lid had rubber septa at the top, steel wire with a hook, and a mesh to hold the sample. VOC was exposed to the sample for four hours in the conditioned room at 20 ± 2°C. For xylene and benzene, exposed sample immersed in ethanol and kept overnight. Xylene and benzene extracted in ethanol were determined using UV-Vis spectroscopy at the characteristic absorbance of 268 nm and 255 nm, respectively. Three readings of VOC adsorption were averaged. The residual HCHO was determined using a formaldehydmeter™ (PPM Technology) and subtracted from the plain reading (without any sample, empty jar) to evaluate adsorption performance.

7.3 Results and discussion

7.3.1 Solution properties

Solution viscosity affects the spinnability and morphology of the electrospun nanofibres [3]. Table 7-2 shows the viscosity of the solutions prepared from gelatin and after blending or mixing with β–CD and saponin at the different concentration. Two things can be observed the solution viscosity increases firstly as the amount of CD (502 to 638cPs) and saponin (204 to 402 cPs) is increased, and secondly, the initial solution viscosity of the gelatin (16 %w/w) solutions are not similar. Even though this was repeated sometimes the same result i. e. different initial starting viscosity, was obtained. There can be some possible explanations for this observation. However the most likely reason is the acid hydrolysis of the formic acid which is used to solubilise the gelatin resulting in smaller molecular weight protein fragments resulting in decreased viscosity [254].
Table 7-2 Viscosity of the gelatin and gelatin blended solutions.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample code</th>
<th>Viscosity (cPs) at room temperature</th>
</tr>
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<tbody>
<tr>
<td>Group 1</td>
<td>G (16%)</td>
<td>502.4</td>
</tr>
<tr>
<td></td>
<td>GC1</td>
<td>518.4</td>
</tr>
<tr>
<td></td>
<td>GC2</td>
<td>566</td>
</tr>
<tr>
<td></td>
<td>GC3</td>
<td>637.6</td>
</tr>
<tr>
<td>Group 2</td>
<td>G (16%)</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td>GSL</td>
<td>319</td>
</tr>
<tr>
<td></td>
<td>GSM</td>
<td>377</td>
</tr>
<tr>
<td></td>
<td>GSH</td>
<td>402</td>
</tr>
</tbody>
</table>
7.3.2 Gelatin-β–CD composite nanofibres

Electrospinning of gelatin without any modification resulted in an average fibre diameter of 130 nm. FE-SEM images in Figure 7-1 show an increasing sequence of gelatin nanofibre diameters (130–247 nm) upon the addition of β–CD. This change in mean fibre diameter was attributed to the increase in the solution viscosity (502–637 Cps) owing to the increasing concentration of β-CD. This result is in line with the PAN/β–CD ENMs results from Chapter 7 where the fibre diameter gradually increases with increasing β–CD concentration.

Figure 7-1 FE-SEM images of gelatin-β–CD composite nanofibres (a) G (130 ± 13 nm); (b) GC1 (158 ± 18 nm); (c) GC2 (198 ± 24 nm); (d) GC3 (247 ± 24 nm).
Another interesting observation is the occurrence of “nanoweb” structures (16% w/w gelatin in Figure 7-2 composed of nanofibres much finer than the normal nanofibres. Such nanowebs are frequently observed in the membrane and could be useful for air filtration applications. Thus, gelatin is a potential candidate in the preparation of biomaterial based ENMs for air filtration.

Figure 7-2 Nanowebs embedded in gelatin 16% (w/w) ENM.
Gelatin/β–CD ENM morphology was further inspected using TEM. Figure 7-3 shows TEM images of gelatin/β–CD ENMs. The TEM micrograph of pure gelatin ENM shows smooth fibres. However, in gelatin/β–CD composite ENMs, β–CD can be seen aggregated in spots on the fibre surface. This finding implies the presence of β–CD in the composite ENMs. However, the distribution of the β–CD is not uniform occasionally resulting in local concentrations of β–CD.

**Figure 7-3** TEM images of gelatin/β–CD ENMs (a) G; (b) GC1; (c) GC2; (d) GC3.

IR spectra of gelatin powder, CD powder, gelatin ENM as well as the gelatin CD ENM are shown in Figure 7-4. The gelatin powder shows characteristic peaks at 1646 cm⁻¹ and 1537 cm⁻¹ corresponding to amide-I and amide II, respectively. Amide-I is associated with C=O stretching in conjunction with C–N stretch. Amide II is related to in-plane N–H deformation. The characteristic peaks for β–CD at 1023 cm⁻¹, 1077 cm⁻¹ and 1179 cm⁻¹ correspond to C-O
stretching of the acetal group in the glucopyranoside units of the β–CD. The peak at 3186 cm\(^{-1}\) indicates intermolecular bonded O-H stretching within the β–CD. These peak frequencies also remain unchanged during the addition process. However, no shifting of peaks has been observed in the composite gelatin/β–CD ENM. This analysis infers that although the presence of gelatin and β–CD is confirmed, no chemical interaction was found between the two.

![FTIR spectra of gelatin powder, β–CD powder and gelatin β–CD composite ENMs.](image)

**Figure 7-4** FTIR spectra of gelatin powder, β–CD powder and gelatin β–CD composite ENMs.

### 7.3.3 Gelatin-Saponin composite nanofibres

The presence of saponin tends to increase the fibre diameter (Figure 7-5). The fibre diameter of G (222 nm) doubled (449 nm) with the addition of 25% saponin (GSL). Further addition of saponins by 50% (GSM) and 75% (GSH) formed a flat ribbon-like fibres of 846 and 1162 nm, respectively. The flattening of nanofibres affected the pore size. The average pore size of gelatin ENM (0.86 µm) rose to 1.2 µm, 1.7 µm, and 2.2 µm with an increase in saponin content to 25%, 50% and 75%, respectively.
Figure 7-5 FE-SEM images of gelatin-saponin composite nanofibres (a) gelatin (222 ± 26 nm); (b) GSL (449 ± 157 nm); (c) GSM (846 ± 243 nm); (d) GSH (1162 ± 447 nm).

Table 7-3 shows EDX elemental analysis of gelatin/saponin composite ENMs. Gelatin is composed of 58% carbon (C), 22% nitrogen (N) and 19% oxygen (O). When saponin was introduced, the %O tends to increase while the %N drops. At maximum saponin content (GSH), O rose by 4%, and N dropped by 5% compared to gelatin (G ENM). The N/C ratio is decreased while the O/C ratio increased in the gelatin/saponin composites.

Table 7-3 EDX elemental quantification of gelatin/β–CD ENMs. Each measurement point is the average of five data points.

<table>
<thead>
<tr>
<th>ENM</th>
<th>C %</th>
<th>N %</th>
<th>O %</th>
<th>N/C</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>58</td>
<td>22</td>
<td>19</td>
<td>0.37</td>
<td>0.32</td>
</tr>
<tr>
<td>GSL</td>
<td>58</td>
<td>21</td>
<td>21</td>
<td>0.36</td>
<td>0.36</td>
</tr>
<tr>
<td>GSM</td>
<td>56</td>
<td>20</td>
<td>22</td>
<td>0.35</td>
<td>0.39</td>
</tr>
<tr>
<td>GSH</td>
<td>57</td>
<td>17</td>
<td>23</td>
<td>0.29</td>
<td>0.40</td>
</tr>
</tbody>
</table>
Figure 7-6 shows the FTIR spectra of gelatin/saponin composite ENMs. The gelatin powder shows characteristic peaks at 1646 cm⁻¹ and 1537 cm⁻¹ corresponding to amide-I and amide II, respectively. Amide-I is associated with C=O stretching in conjunction with C–N stretch. Amide II is related to in-plane N–H deformation [245]. GSL, GSH and GSM ENMs showed a broad OH peak around 3291 cm⁻¹. It confirms the presence of saponin in the ENMs. However, no chemical interaction occurred between gelatin and saponin [248], as the peaks unchanged in the composite ENMs. The weak interaction between gelatin and saponin has also been proved using dielectric permittivity [253]. The dielectric permittivity refers to the degree of electrical polarisation of a material subjected to an external electric field.

Figure 7-6 FTIR spectra of gelatin/saponin composite ENMs.

It is possible to electrospin gelatin/saponin ENMs with reproducible fibre diameter and pore size. However, some cracks have been found in all ENMs approximately a week after preparation. ENMs may dry out and become brittle resulting in cracks. The small basis weight (1 g/m²) of ENMs makes it more prone to damage. Such delicate and cracked ENMs would not be suitable for use in air filtration. Hence air filtration and VOC adsorption of gelatin/saponin were not evaluated.
Figure 7-7 Delicate nature of gelatin/saponin composite ENMs. From left, G, GSL, GSM and GSH ENM. Cracks formed in ENM within two weeks of preparation.

7.3.4 Air filtration performance

Gelatin/β–CD ENMs were found to be stable and resulting in no cracks. As a result, these ENM were evaluated for air filtration and VOC adsorption analysis. The air filtration performance of gelatin/β–CD ENMs is shown in Figure 7-8 for particle sizes ranging from 0.3 µm to 5 µm at 0.06 m/s face velocity. The filtration efficiency of G, GC1 and GC2 was found to be comparable for 0.3 µm particles (around 97%) and larger particle sizes (about 99%). GC3 showed lower filtration efficiency (88%) which is probably due to the increase in fibre diameter (247 nm) as compared to that of gelatin only ENM (130 nm).

Figure 7-8 Filtration efficiency of gelatin/β–CD ENMs at 0.06 m/s face velocity.
Figure 7-9 shows the pressure drop of the gelatin and gelatin/β–CD ENMs of 1 g/m² at 0.06 m/s face velocity. Gelatin ENM exhibited the highest pressure drop (163 Pa) resulting from the smallest fibre diameter (130 nm). The pressure drop of GC1 and GC2 ENMs is comparable (151 and 148 Pa) since the average fibre diameters of both ENMs ranged between 160 to 200 nm. GC3 ENM with the largest average fibre diameter (247 nm) showed the lowest pressure drop (125 Pa).

![Figure 7-9](image)

**Figure 7-9** Pressure drop of gelatin/β–CD ENMs of 1 g/m² at 0.06 m/s face velocity.

It can be seen from Figure 7-10 that the quality factor of gelatin ENMs improved (from 0.021/Pa to 0.029/Pa) due to the addition of 10% and 20% β–CD. The reduction in pressure drop (from 163 Pa to 148 Pa) at comparable filtration efficiency (97%) caused this improvement. Further addition of β–CD (30%), however, deteriorated the quality factor (0.017/Pa) despite a reduction in pressure drop (125 Pa). This deterioration of quality factor is attributed to the loss in filtration efficiency (88%) compared to other ENMs (97%). It is noteworthy that the quality factors of gelatin-based ENMs are being reported for the first time.
Figure 7-10 Quality factor of gelatin/β–CD composite ENMs for 0.3 μm particles at 0.06 face velocity.
7.3.5 VOC adsorption

Figure 7-11 shows the xylene adsorption performance of gelatin/β–CD composite ENMs, individual powder samples and commercial mask for comparison. Xylene adsorption of gelatin powder (23.19 μg/mg) is only marginally higher than β–CD powder (13.67 μg/mg). As expected, P2 mask showed least xylene adsorption (1.49 μg/mg).

Gelatin ENM exhibited the highest xylene adsorption (311 μg/mg) compared to all other ENMs in this thesis. For instance, PAN/β–CD composite ENM showed maximum xylene adsorption of 201 μg/mg. All other things being equal one explanation for the higher adsorption is that the gelatin nanofibre has smaller fibre diameter (130 nm) compared to PAN (305 nm), thereby providing a larger surface area exposing more β–CD to the fibre surface resulting in higher xylene binding. It infers that VOC adsorption is in this case and influenced by the fibre diameter. The smaller the fibre diameter, the higher would be the adsorption. With increasing levels of β–CD addition, xylene adsorption reduced (287-250 μg/mg). This finding can be linked with an increase in fibre diameter from 130 nm to 247 nm.

![Figure 7-11 Xylene adsorption performance of commercial mask, gelatin and β–CD powder, and gelatin/β–CD ENMs. The values were obtained using UV spectroscopy at the characteristic wavelength of 268 nm.](image)
Benzene adsorption performance of gelatin/β–CD ENMs, individual powder samples and the P2 mask is shown in Figure 7-12. The adsorption performance of β–CD powder (12.49 μg/mg) and gelatin powder (11.58 μg/mg) is comparable whereas P2 type mask has least benzene adsorption (5.27 μg/mg). Gelatin ENM showed the highest benzene adsorption (279 μg/mg) which again can be explained by the smallest fibre diameter (130 nm) of gelatin ENM. The benzene adsorption of GC1 and GC2 is comparable (242 μg/mg) since their fibre diameter range is also comparable. GC3 displayed the lowest benzene adsorption (176 μg/mg) explained by the larger fibre diameter (247 nm).

![Figure 7-12](image_url)

**Figure 7-12** Benzene adsorption performance of gelatin/β–CD ENMs, individual powder samples and P2 mask. The adsorbed benzene was extracted using ethanol and analysed by UV spectroscopy.

**Figure 7-13** shows HCHO adsorption performance. β–CD powder (0.07 μg/mg) and gelatin powder (0.04 μg/mg) both have low adsorption capacities. It is clear that a P2 mask has least capacity to adsorb HCHO (0.002 μg/mg). Overall gelatin based ENM showed higher HCHO adsorption values (0.38 μg/mg) compared to all other material combinations in this thesis. The adsorption is partly attributed to the affinity and reaction of the protein towards
HCHO as well as the EMNs possessing the smallest fibre diameters (130 nm) compared to PAN ENM (305 nm). With the addition of β–CD, HCHO adsorption was increased (maximum 0.75 μg/mg) for GC1. This result suggests that β–CD is more selective towards HCHO than xylene and benzene. Thus, the combination of gelatin and β–CD in a nanofibre form works synergistically and efficiently to capture HCHO.

**Figure 7.13** HCHO adsorption performance of gelatin/β–CD ENMs, their powder samples and commercial mask.

### 7.4 Conclusion

Gelatin/β–CD and gelatin/saponin composite solutions have been successfully electrospun to produce ENMs with fibre diameter ranging 130–247 nm and 222–1162 nm respectively. Gelatin/saponin ENMs were susceptible to cracking after a few days of drying while no cracks were observed for gelatin/β–CD ENMs. The air filtration efficiency of gelatin and gelatin/β–CD (10% and 20%) ENM is comparable (97%). However, gelatin/β–CD ENMs has less pressure drop (148 Pa). The filtration performance (filtration efficiency 97%; pressure drop of 148 Pa) of gelatin/β–CD ENM at 1 g/m² basis weight is suitable for respiratory filtration as per the NIOSH standards. Xylene (311 μg/mg) and benzene (279 μg/mg) adsorption performance of gelatin only
ENM was found superior over gelatin/β–CD composite ENMs which could be explained by the smaller fibre diameter (130 nm) and therefore the high surface area of the gelatin only ENMs. β–CD increases HCHO adsorption of the gelatin-based ENMs. Gelatin/β–CD composite ENMs adsorbed higher amounts of HCHO (0.75 μg/mg) compared to PAN CD ENM (0.08 μg/mg). Gelatin ENM showed excellent air filtration performance (97% efficiency, 148 Pa pressure drop) and good VOC adsorption making them promising prospects in respiratory air filtration.
Chapter 9

Concluding remarks and future work

8.1 Conclusions

This thesis has described the fabrication of ENMs which can simultaneously capture 0.3 μm aerosols and VOCs while offering minimum air resistance. Different experimental approaches such as bead-on-string ENMs, bilayer coarse/fine ENMs, composite ENMs with additives, functionalisation of textile substrates and use of biomaterial (protein) based ENMs were characterised and designed to attain multifunctional air filtration with least air resistance. The air filtration performance was measured regarding filtration efficiency, pressure drop and quality factor. Aerosol filtration and VOC adsorption were evaluated using specifically designed experimental methodology. ENMs comprised of PAN and gelatin polymers while β–CD was used as an additive for functionalisation.

Aerosol filtration performance strongly depends on membrane basis weight, thickness, morphology and structure of ENM. Electrospinning time was used to control basis weight and thickness of ENMs. When electrospinning time varied from 20 min to 60 min, the air permeability of the ENMs dropped dramatically from 554 to 243 mm/s. This result implies that shorter electrospinning time is desirable to achieve maximum breathability while keeping other electrospinning parameters constant.

PAN nanofibre morphology can be tuned by polymer concentration, solution properties and electrospinning parameters. Morphologies like bead-on-string ENMs were studied to reduce the pressure drop. Consistent and reproducible strings of 55 nm holding beads of 200 nm were fabricated. Filtration performance of such ENMs at 0.5 g/m² is comparable with commercial P1 type respiratory masks. The performance was further improved by covering bead-on-string under bead-free ENMs comprised of relatively larger fibre diameters of 400 nm. Sequentially stacked bilayer beaded ENM showed > 95% efficiency at a pressure drop of 137 Pa. Although the bead size was uniform and reproducible, the higher jet instability and uneven stretching of the polymer jet resulted in the relatively more extensive deposition of fibres in the beaded ENM compared to bead-free ENM. This broad deposition is due to the bead preparation process which
almost resembles electrospaying. The beaded ENM also showed a high variation in pore size distribution also affecting pressure drop results.

The pressure drop was further reduced to 87 Pa while the filtration efficiency remained unchanged with a bilayer ENM fabricated using a combination of coarse (400 nm) and fine (200 nm) nanofibres. Hierarchically prepared bilayer ENMs are a balance between thickness and packing density. This kind of bilayer ENM formation is easy to prepare as well as scalable, suggesting its practical use in designing respiratory filter media. The modelling of a single layer ENM exhibited moderate agreement with the empirical data. The experiment validates the importance of fibre diameter and pore size in achieving the desired filtration efficiency and pressure drop combination. It also highlights the significance of layering order. Thus, the bilayer ENMs can be engineered as per the filtration requirements with minimum pressure drop.

PAN nanofibres with β–CD, as an additive, can be electrospun to form multifunctional air filter media. The addition of β–CD made the composite nanofibres thicker and the ENM with larger pores. β–CD migrated towards the surface of composite nanofibres due to the significant difference in the molecular weight, surface energy and entropy. The presence of β–CD at the surface of composite ENMs was confirmed by XPS and water contact angle results. The surface modification of the composite ENM made it more functional as the cavities of β–CD becomes available for VOC adsorption. PAN/β–CD ENMs showed improved adsorption for HCHO, xylene and benzene compared to only PAN ENM. 30 wt% β–CD addition in 8% (w/w) PAN was found the best in achieving the highest quality factor (0.026/Pa). Cytotoxic testing using human lung cell line confirmed the nontoxic nature of the PAN/β–CD composite ENMs which implies their suitability for human use.

Biopolymer-based ENMs were produced for simultaneous air filtration and VOC adsorption. ENMs made from gelatin only and gelatin mixed with β–CD and saponins were prepared. However, gelatin/saponin ENMs were found to be susceptible to cracking. Gelatin and gelatin/β–CD ENM showed excellent air filtration performance (on par with commercial P2 type respirators) and also exhibited good adsorption of xylene, benzene and HCHO. The VOC adsorption of ENMs was fifty times higher than the commercial P2 type masks. Thus, gelatin ENM is a promising candidate for multifunctional respiratory air filtration.
8.2 Future scope

Ambient air quality is decreasing as industrialisation and urbanisation are increasing throughout the globe adversely affecting human health. Until more environmentally friendly processes are adopted worldwide, the challenge of designing protective respiratory air filter media will continue to evolve. Respiratory filters with lower pressure drop would encourage people to wear the filters decreasing the possibility of ill-health. The experiments in this thesis were focused on reducing pressure drop and improving the quality factor without compromising filtration efficiency. The argument also aimed at investigating VOC adsorption while maintaining filtration efficiency. Based on the experiments conducted and the results obtained the areas have been identified as worthy of further research:

Unlike conventional microfibres, the improvement of filtration efficiency of nanofibres is marginal for large particles beyond 0.5 µm. Nanofibres have been found efficient for removal of 0.3 µm and finer particles. The particle capture mechanism used to describe filtration changes with fibre diameter, pore geometry and target aerosol size. Thus, models for particle capture mechanism involving nanofibres require further investigations. Currently, the capture mechanism is described by the diffusion and interception models. The diffusion and interception mechanisms dominate each other based on the nanofibre morphology and target particle size. There are possibilities of straining and electrostatic attraction mechanisms which can be used to more accurately describe the particle capture mechanism. A more practical mechanism need to be build and then should be validated using experimental data.

The simulation of bilayer ENM requires an in-depth understanding of appropriate modelling software for use on a supercomputing platform would speed up the design of better air filtration systems. The modelling work can be extended to composite ENMs which are enabled with different additives not only regarding filtration efficiency but also calculating VOC adsorption.

Gelatin dissolved in an acid is prone to acid hydrolysis over the time. Thus, the solution preparation time, storage time and storage conditions have an enormous influence on gelatin viscosity. Gelatin (16% w/w) solutions prepared at different times showed considerable variation in viscosity (204 cPs and 502 cPs). A detailed rheology study of gelation solution would be helpful to understand the change in the viscosity and other fluid characteristics such as surface
tension and conductivity. This data can be used to find an association between fluid characteristics and nanofibre morphology.

Poor environment susceptibility of gelatin/saponin could be improved with appropriate cross-linking treatments. The effect of cross-linking on the properties of composite ENM, air filtration performance and VOC adsorption could then be investigated. Also, other bio-based material or industrial proteins such as keratin can be used as additives during gelatin electrospinning to improve VOC adsorption capacity for respiratory air filtration.

Bilayer ENM proved advantageous in reducing the pressure drop. In future studies, functional or composite ENM could be used as one of the layers in bilayer ENM. For instance, gelatin ENM can be a fine layer covered by coarse PAN ENM. In addition, the bilayer ENM should be produced from composite ENMs using additives such as β–CD. Thus, the advancement in respiratory filter media preparation continues to evolve.

References

24. Langrish, J.P., et al., Beneficial cardiovascular effects of reducing exposure to particulate air pollution with a simple facemask. Particle and Fibre Toxicology, 2009. 6(8).


62. Yoo, K.S., Gas sensors for monitoring air pollution, in Monitoring, Control and Effects of Air Pollution. 2011, InTech.


Appendices

Appendix 1

Xylene and Benzene adsorption measurement

1. Weigh the ENM accurately (2–20 mg) and place it in the metal mesh attached to the modified lid of the jar, as shown below:

2. Inject 80 μL of xylene into the jar using micropipette and close the jar immediately with the modified lid. The lid is wrapped with paraffin film to keep airtight. The jars, containing xylene and ENM inside, are held in a conditioned room (temp: 20±2°C) for four hours to obtain equilibrium.

3. After four hours, remove ENMs from the jar and place into bottles having 15 mL ethanol for extraction of xylene. Seal the bottles and store for 24 h.

4. After 24 hours, obtain spectra of solutions using UV-microscopy.
5 Before taking the spectra of the ENM samples, prepare different calibration standards for xylene/ethanol solution.

![Graph showing xylene adsorption per unit mass of ENM](image)

6 After receiving the calibration standards and characteristic UV spectrum of ENMs, calculate xylene adsorption per unit mass of ENM as per calculations are given in the following example:

<table>
<thead>
<tr>
<th>Sample</th>
<th>The wavelength at 268 nm</th>
<th>After subtraction from ethanol</th>
<th>Multiplying with a y value of calibration (271.55)</th>
<th>ppm is mg/L which is µg/mL</th>
<th>In 15 ml ethanol (x 15)</th>
<th>Sample weight (mg)</th>
<th>Xylene adsorption (µg/mg of the sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.005199</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P8</td>
<td>0.337654</td>
<td>0.332455</td>
<td>90.28</td>
<td>90.28</td>
<td>1354.17</td>
<td>12</td>
<td>112.85</td>
</tr>
</tbody>
</table>

7 For benzene, follow similar steps. The only difference is the characteristic wavelength (255 nm) and calibration value (494.03).
Appendix 2

**HCHO adsorption measurement**

1. Weigh the ENM accurately (2–20 mg) and place it in the metal mesh attached to the modified lid of the jar.
2. Add one mL of HCHO (37%) solution to demineralised water to make a volume of 10 mL.
3. From the above solution, inject 20 μL into the jar using micropipette.
4. Close the jar immediately with the modified lid holding the ENM sample. Make the jar airtight using paraffin film.
5. Keep the jar in the conditioned room (temp: 20±2°C) for four hours to obtain equilibrium.
6. After four hours, insert the needle (attached to the digital formaldehydemeter) into the lid to obtain residual formaldehyde concentration.
7. Repeat step 1 to 6 for three times without any sample to get the average blank reading.
8 Once the residual HCHO concentration with and without samples is obtained, convert the values in HCHO adsorption per unit mass of the sample as per the calculations are given in the below example:

<table>
<thead>
<tr>
<th>Code</th>
<th>Residual ppm</th>
<th>Net ppm (Subtract blank)</th>
<th>Convert ppm in mg/m³ (X 1.25)</th>
<th>The volume of the jar (m³)</th>
<th>HCHO weight (mg) (mg/m³ x m³)</th>
<th>HCHO wt (μg) (X 1000)</th>
<th>Sample mass (mg)</th>
<th>HCHO adsorption (μg/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>11.2</td>
<td>0</td>
<td>14</td>
<td>0.0044</td>
<td>0.0616</td>
<td>61.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>11.04</td>
<td>0.16</td>
<td>0.2</td>
<td>0.0044</td>
<td>0.00088</td>
<td>0.88</td>
<td>2.3</td>
<td>0.3826</td>
</tr>
<tr>
<td>ENM</td>
<td>11.04</td>
<td>0.16</td>
<td>0.2</td>
<td>0.0044</td>
<td>0.00088</td>
<td>0.88</td>
<td>2.3</td>
<td>0.3826</td>
</tr>
</tbody>
</table>