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Conference Paper

Electrospun Nanomaterials: Biotechnology, Food, Water, Environment, and Energy

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Over the past decade, electrospinning and electrospraying techniques have become affordable platform techniques for growing numbers of students, researchers, academics, and businesses around the world, producing organic and inorganic nanofibres and nanoparticles for a range of purposes. This review illustrates various advances in the science and engineering of electrospun nanomaterials and their applicability in meeting the growing needs within five crucial sectors: clean water, environment, energy, healthcare, and food. Although most of these sectors are principally dominated by synthetic polymer systems, the emergence of natural polymer and hybrid natural-synthetic electrospun polymer systems offers particular advantages. Current scientific and materials engineering advancements have resulted in highly competitive nanofibre, electrospun products, offering credible solutions to real-world applications.

1. Introduction

Electrospinning has attracted increased attention as a versatile technique, applicable to numerous organic and inorganic systems which can result in a tightly controlled size distribution of nanomaterials [1]. The resulting nanosystem can be described as highly porous network structure, with a large *surface area to volume* ratio, the dimensions of which can be easily tailored and optimised during production. It is commonly accepted that a material, which is termed *nano* in size, must possess at least one dimension of the order of 100 nm or less [2]. *Nanomaterials* can be produced in tube, wire, or particulate form and from both natural or synthetic material precursors [2, 3]. Numerous methods are employed to prepare higher volumes of nanomaterials, including chemical synthesis [4, 5], electrodeposition [6], templating [7], catalytic growth [8], chemical vapour deposition [9], and, more recently, electrospinning [10] techniques.

The electrospinning method allows for the high volume production of light weight, highly functional, nanoscale, mesh-like structures. Electrospraying is a similar technique to electrospinning, which electrostatically accelerates solution droplets onto a target, forming uniformly sized particulates or thin film coatings. The accelerated droplets can also be charged, leading to self-dispersion upon collection at the target. These *electrohydrodynamic* techniques result in a porous structure, which can be in film form as a coating or multidimensional network structure. The highly versatile technique of electrospinning allows for the selective formation of micron to nanoscale fibrous systems by optimisation of electrostatic forces on a jet of polymer solution. In its most basic form, the electrospinning process involves placing a polymer solution in a pipette, between two electrodes, which can create potential difference in the kV regime. This large voltage then electrostatically draws the polymer solution towards a grounded target in a thin, continuous jet, leading to a deposition of a fibrous web. The resulting pore size and distribution within the web can be controlled by varying such parameters as the jet height, voltage, target type (static or rotated dynamically), and jet spindle speed. In addition to the optimisation of system parameters, advances in higher throughput electrospinning system designs continue to be developed [11–14].

Though acknowledging that the topic of electrospinning has its basis in early studies [15–17], the first filed patent based on an electrostatically controlled deposition system for plastics was in 1934 [18]. Since then in excess of 700 associated patents have been filed [19], citing Formals' core patent [18]. Overall nearly 2,500 patents associated with electrospinning have been filed for patenting [19]. Aligned with this patent trend has been an explosive increase in the number of journal publications related to electrospinning over the last 20 years [20], presented in Figure 1 with the number of citations inset. This increase has been attributed to both market and industry demands and also to the progress made in the field of nanotechnology. It is unsurprising that the number of patents granted in the same term mimics the same exponential increase over recent years. Figure 2(a) presents a graphical illustration of the number of patents granted over recent years, together with a global distribution analysis of those patents in Figure 2(b), displaying the emergence of electrospinning as a real solution to current commercial and industrial needs.

This review aims to provide a review of current electrospun nanomaterials research, processing, applications, technological limitations, and remaining challenges specific to the fields of biotechnology, food, water, environment, and energy.

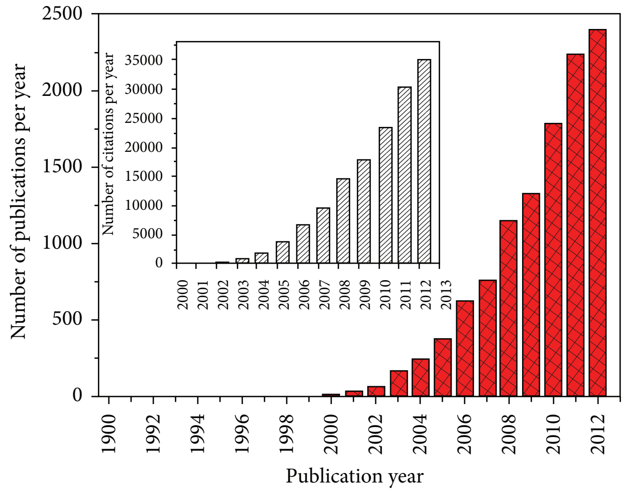


Figure 1: Graph displaying the yearly number of journal publications which include electrospinning in the concept (1990–2012). Inset: yearly number of citations for the same period.

2. Materials and Production

As described previously, electrospinning and electrospraying both involve simple *electrohydrodynamic* processing to form fibre sheets, particulates, or thin films from host solutions. The morphology of the final nanomaterial depends both on the type of polymer and solvent, under varying experimental conditions. This process can be adapted to any soluble polymers with sufficient molecular weight to electrospun. Electrospinning nanofibres will result in systems with high surface area to volume ratio, low weight, high density of pores, and high permeability with controlled, small fibre diameters. Numerous materials have been employed to produce electrospun fibres, tailored to meet the demands of specific functional requirements, including both natural and synthetic polymers, polymer blends, hybrid polymer systems, and ceramics and metals compounds [1, 21–23]. The diverse *real-world* applications have continued to steadily grow over recent years and include such areas as high performance air filters, sensors, textiles, medical wound dressing, photovoltaic cells, fuel cells, batteries, capacitors, and scaffolds for tissue engineering [1]. Figure 3 highlights some of the diverse and wide ranging potential applications and the potential applications in which natural polymers may provide a plausible solution.

In conjunction with the wide diversification of potential commercial applications, Figure 4 presents the electrospinning focussed patents granted between 1994 and 2012 in five main areas of interest to this review, highlighting the amazing versatility of electrospun polymer products. Currently there continues to be a keen focus on the biotechnology sector not only at research and development stage but also from a commercialisation viewpoint.

In conjunction with the growth in journal publications and patent filings, there are many well established companies who currently supply electrospun nanofibres to the market. A selection of current commercial suppliers of nanofibre-based commercial products is presented in Table 1.

3. Applications

Recently there has been a shift in focus from pure material fabrication towards end-use applications and appropriate functionality. Numerous overview papers have been published over recent years in the area of electrospinning [24–30]. This paper will focus on recent trends in electrospinning using various polymeric materials, emphasizing use of natural polymers specific to five main areas of interest—biotechnology, food, water, environment, and energy. Through continual progress in electrospinning techniques, we note the proliferation of coaxial, composite, and core-shell nanofibre systems with advanced functionality and the emergence of natural polymer systems as a solution to meet industrial needs.

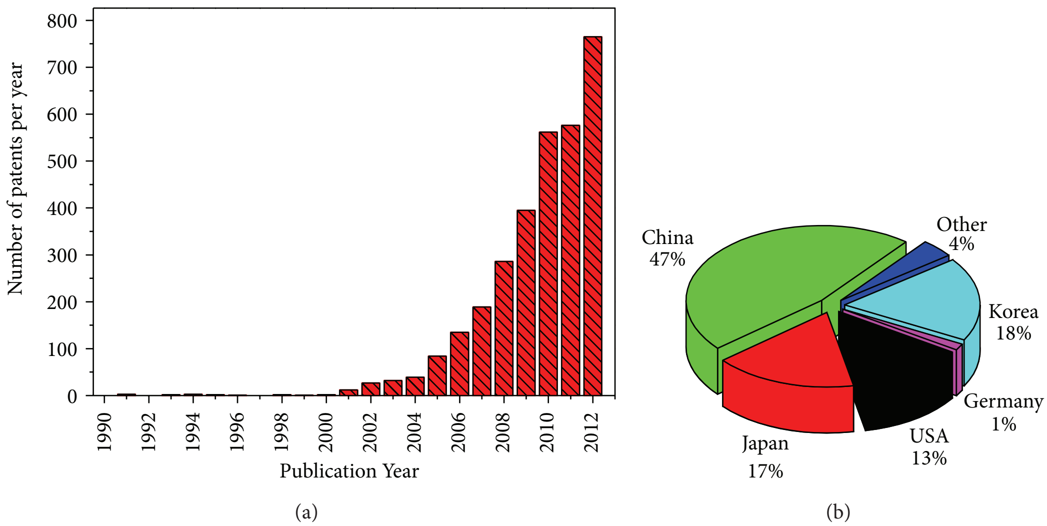


Figure 2: (a) Graph displaying the yearly number of patent filings which include electrospinning in the concept of 1990–2012. (b) Graph displaying the main geographical spread of the patent filings from (a) (1990–2012).

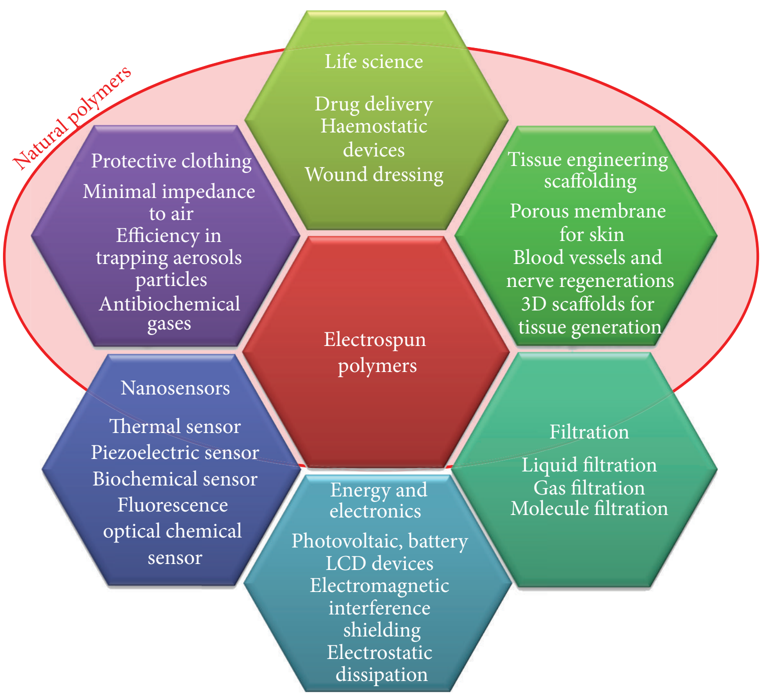


Figure 3: A selection of potential applications for electrospun polymer systems, highlighting the current areas of most interest for natural polymers.

However challenging the fabrication process may be for *real-world* applications, natural polymer could hold key advantages over the synthetic counterparts, such as biocompatibility, low toxicity, renewable source materials, controlled biodegradation, and, with increasing output, the possibility of lower production costs. Specific to the biotechnology sector, the ability to fabricate electrospun, naturally occurring proteins can provide cells with a physiologically relevant platform and promote a natural state of differentiation of the cellular components. Various natural proteins have been successfully electrospun to date, including silk, collagen, gelatin, and fibrinogen. Complex carbohydrate biopolymers such as polysaccharides have also been electrospun [30]. However, many natural polymers suffer from poor mechanical and thermal properties, which limit their applications. To overcome this limitation, several plausible routes have

Table 1: Selection of commercial suppliers of electrospun nanofibre-based products.

	Company Name	Country of origin	Website
1	Donaldson Company Inc.	USA	http://www.donaldson.com/
2	Espin Technologies Inc.	USA	http://www.espintechnologies.com/
3	US Global Nanospace	USA	http://www.usgn.com/
4	Finetex Technology	Republic of Korea	http://www.finetextech.com/
5	Nanoval GmbH and Co. KG	Germany	http://www.nanoval.de/
6	Japan Vilene Company Ltd.	Japan	http://www.vilene.co.jp/
7	Toray	Japan	http://www.toray.com/
8	Elamarco	Czech Republic	http://www.elmarco.cz/
9	Hills Inc.	USA	http://www.hillsinc.net/
10	Esfil Tehno	Republic of Estonia	http://www.esfiltehno.ee/

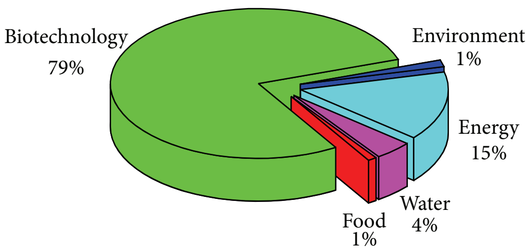


Figure 4: Chart displaying five of the main commercial applications for electrospun nanofibres, a function of overall patent filing percentage, of 1994–2012.

Table 2: Table of some recently electrospun synthetic and natural polymers and the main function in the biotechnology sector.

Common Polymer	Function	Reference
Polyurethane, PU	Tissue engineering, functional biomaterial	[32]
	Biosensor	[33]
Poly(lactic acid), PLA	Tissue engineering, functional biomaterial	[34]
Poly(ε-caprolactone), *PCL*	Tissue engineering, functional biomaterial	[35]
Chitosan	Tissue engineering, functional biomaterial	[36]
Collagen	Tissue engineering, functional biomaterial	[37]
Cellulose Acetate	Biomolecule immobilization, tissue engineering, and biosensor	[38]

been proposed and hybrid synthetic-natural, electrospun copolymer systems have emerged as possible contenders to solve current commercial demands [31].

3.1. Biotechnology. Applications and products which employ polymers in the biomedical field require tight tolerance of the resulting chemical and physical properties. In the mid-1990's, research began to focus on merging nanotechnology with tissue engineering. Today the primary, practical applications include tissue and cell regeneration, surgical implants, drug delivery, and wound healing. Some common materials that have been electrospun are biodegradable synthetic polymers, such as polylactic acid, polycaprolactone, and polyglycolic acid, nonbiodegradable synthetics such as polyurethane, and natural polymers such as cellulose, collagen, and chitosan. Table 2 presents some common electrospun synthetic and natural polymers which are currently under study in this sector.

The mimicking of the extracellular matrix is the core focus of nanofibre scaffold for tissue engineering and cell growth. The use of such scaffolds has been shown to yield a cellular response that differs positively from that of traditional smooth-surfaced substrates.

In a recent review Ramakrishna et al. [27] highlighted one such publication where, in most cases, electrospun scaffolds constructed from natural occurring proteins in the extracellular matrix such as collagen allowed much better infiltration of cells into the scaffold [39]. They also referenced the work on stromal cells [40, 41] (including haemopoietic stem cells [42], embryonic stem cells [43], and neural progenitor cells) which have been successfully cultured onto nanofibre meshes. Recently Jin et al. [44] reported a high proliferation of human dermal fibroblast growth on *Memecylonedule* polycaprolactone nanofibres when compared to that of other plant extracts with wound healing properties such as *Indigofera aspalathoides*, *Azadirachta indica,* and *Myristica andamanica*. With an average nanofibre diameter of 487 nm, the newly formed hydrophilic, *memecylonedule* polycaprolactone nanofibre scaffolds resulted in a 394% increase in the rate of cell proliferation between days 3 and 9 of the study.

Alternative materials and biotechnology applications which have recently been studied include nylon-6/lactic acid core-shell nanofibres [45], prepared using a two-step electrospinning and surface neutralization technique. The calcium lactate coated nanofibre scaffold displayed noted osteoblast cell growth. Sheng et al. [46] investigated the electrospinning of a novel vitamin E loaded silk fibroin nanofibrous mats from an aqueous solution for cosmetic tissue regeneration applications. Additionally a review of the emerging research into novel electrospun nanofibre/hydrogel composite systems has recently been published [47], comparing five unique approaches for creating composite scaffolds.

Collagen has several material properties that make it attractive for application in biotechnology such as biocompatibility, low antigenicity, biodegradability, low inflammatory and cytotoxic responses, high water affinity, and availability from a variety of sources. What has become evidently clear is that successful nanofibre scaffolds cannot just mimic the mechanical structure of the extracellular matrix; they must also promote a natural state of differentiation of the cellular components. A tailored, composite, nanofibre scaffold system, with the addition of proteins may be necessary to regulate and enhance cell proliferation. However the intrinsic instability of electrospun collagen needs to be addressed [48].

Composite materials have been widely investigated as potential for bone tissue engineering applications, such as alginate, chitosan, collagen, and hydroxyapatite composite systems fabricated by electrospinning [49]. This composite system was reported to lower the scaffold disintegration in 300–800 nm diameter nanofibres by 35% for 10 days in collagenase solution when compared to a collagen film. An alternative approach to fabricating collagen-based microfibre constructs was proposed via a layer-by-layer coating process onto preformed polyacrylonitrile and poly (DL-lactide-co-glycolide) microfibre bases [48]. This study looked for avoiding the use of volatile solvents during preparation and the resulting intrinsic instability of collagen. Other recent composite systems include collagen-chitosan-thermoplastic polyurethane blends, McClure et al. presented work on electrospun silk fibroin, collagen, elastin, and polycaprolactone prepared via a 3-1 input-output nozzle [50, 51], creating a trilayered structure. They investigated the effects on changing the composition of the medial and/or adventitial layers within the electrospun system, presented as architecturally mimicking the vascular wall and providing a mechanically positive match for vessel replacement.

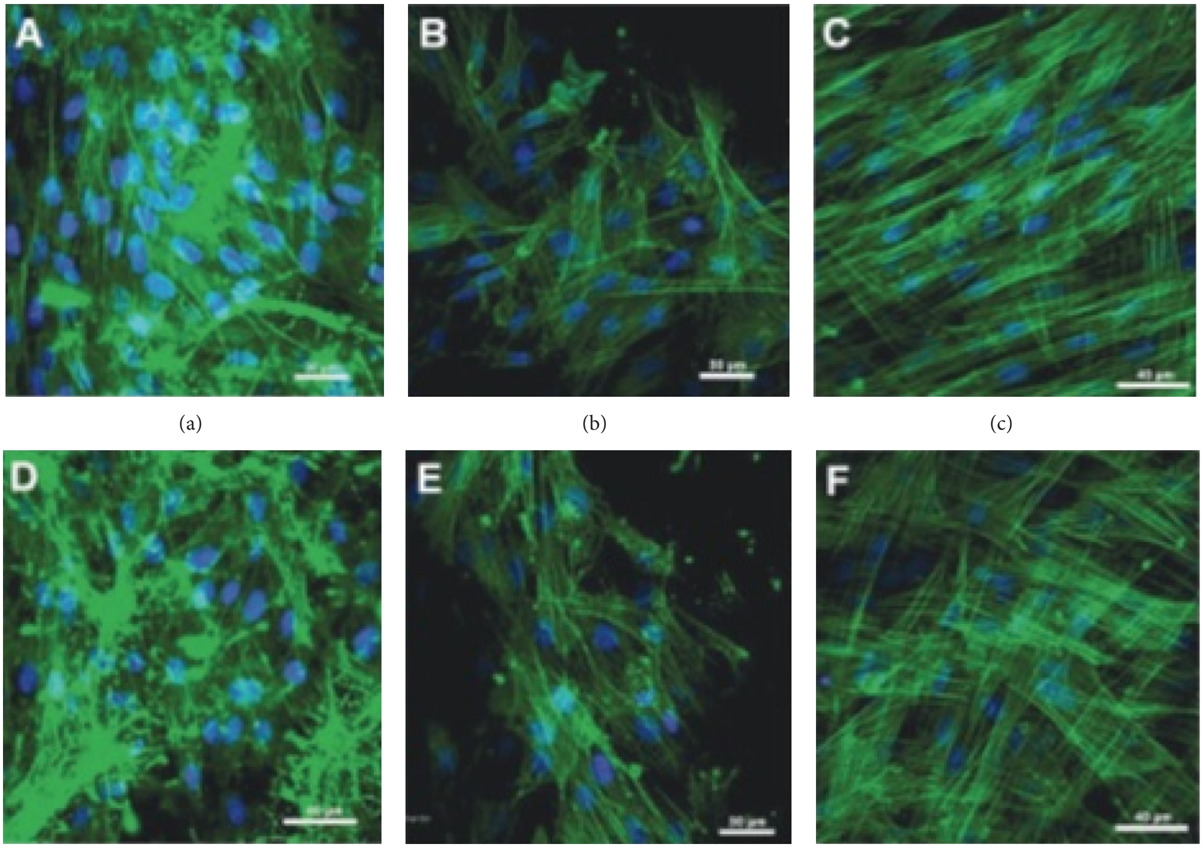
An emerging, cost effective alternative to collagen is gelatin—a biocompatible, biodegradable, nonimmunogenic protein, and it displays many integrin binding sites for cell adhesion and differentiation [52]. Recently a series of silk fibroin/gelatin nanofibre composites (diameters varying from 99 to 244 nm) were prepared for use as vascular scaffold systems [53]. A homogeneous bead-free nanofibre system was obtained for a 70 : 30 ratio (silk : gelatin). The subsequent high biocompatibility resulted in high cell proliferation and growth and was concluded to support long-term cell adhesion. Francis et al. [54] simultaneously employed electrospinning (of gelatin) and electrospraying (of nanohydroxyapatite) to successfully form biocomposite, nanofibrous scaffold on a rotating cylinder, which were crosslinked to increase stability.

Through the simultaneous electrospinning of two different polymer solutions, the coaxial electrospinning [55] technique can produce core-shell structured nanofibres, leading to advanced material functionality. Jiang et al. [56] successfully demonstrated the ability to coaxially prepare water-soluble bioactive agents into biodegradable core-shell nanofibres with polycaprolactone (PCL) as shell and protein containing polyethylene glycol (PEG) as the core. PCL has been well studied for is flexibility, biodegradability, and relatively hydrophobic nature. Ladd et al. [57] fabricated a dual scaffold system from both poly(ε-caprolactone)/collagen and poly(l-lactide)/collagen. They reported a noncytotoxic, 452–549 nm nanofibre system with three distinctly varying mechanical properties within different regions of a continuous structure for potential in muscle-tendon junction tissue engineering. Similarly Gluck et al. [58] prepared core-polyurethane nanofibre scaffolds with a shell composite mixture of poly(ε-caprolactone) and gelatin, where the surface functionality encouraged cellular migration to the interior of the scaffold. Functional photosensitive poly(3-hexylthiophene) (P3HT) containing PCL nanofibrous scaffolds were fabricated by electrospinning, on which the rapid growth of human fibroblasts cells occurs under light simulation [59]. It was concluded that blending photosensitive polymer P3HT with PCL would aid proliferation and morphology of fibroblast under light simulation by converting the optical energy from the light into electrical energy. Figure 5 illustrates the cell density and proliferated human dermal fibroblasts with various combinations of polymer blends.

3.2. Food. The nanofibres and novel structures are produced by electrospinning process from synthetic and natural polymers enabling their use in wide area of applications such as new food ingredients, food additives, novel packaging, food sensors, and additive encapsulations [60]. The use of electrospun nanofibres in the food sector is relatively low, since most of the nanofibres produced are usually composed of nonfood grade polymers. On the other hand nanofibres produced from natural polymers have potential applications in development of high performance packaging for food, food coatings, flavour enhancement, additive encapsulation, and nutraceutical applications due to their biocompatibility and biodegradability.

Food packaging is the largest growing sector and it is an integral part of food processing and supply operations. The main objective is to maintain the quality and protection from various hazards during the transportation and until it reaches to the customer. The food industry can use electrospun nanofibres in many ways. Food packaging materials constructed from biobased and natural polymers can be used to improve the shelf time and retain the flavours in the food. Furthermore intelligent active packaging materials can be produced by this process by incorporating the biosensors into the fibres for indication of the expiration date of the food products [61]. Biobased polyester multilayer structure packaging films produced with a high barrier interlayer of electrospun zein nanofibres were recently reported [62] for food packaging applications. By incorporating the zein electrospun nanofibre in the multilayer structure by compression moulding, the oxygen barrier properties were significantly improved.

Nanoparticles produced by electrospraying have potential cost saving in confectionery industry [63]. Electrospinning process uses lesser amount of chocolate sauces and the fibres/particles produced by this process would have different texture and mouth feeling compared to bulk chocolates. This could potentially help developing new food products and help saturated confectionery markets to grow.



(a) (b) (c)

(d) (e) (f)

Figure 5: Laser scanning confocal microscopic (LSCM) micrographs of HDFs grown on (a) PCL/P3HT (10) (S), (b) PCL (S), (c) TCP (S), (d) PCL/P3HT (10) (NS), (e) PCL (NS), and (f) TCP (NS), expressing F-actin [59].

Fast responding biosensors are probably the most popular nanofibre application allowing fast response, higher sensitivity, and selectivity compared to current solutions. Immobilisation of tyrosinase enzyme on a glassy carbon electrode covered by a polyamidic nanofibrous membrane showed rapid detection of phenolic compounds due to nanofibre coating on the electrode [64]. Similarly electrospun nanofibres made of nylon-6 are used to detect the migration of phenolic compounds from food such as cooking oils and mineral water [65]. By incorporating electrospun nanofibres in the active packaging material, it will greatly assist regulators and enhance health and safety controls.

Electrospun nanofibres produced from natural polymers such as cellulose and proteins will find applications in food packaging applications [66]. Due to their biodegradability and biocompatibility these nanofibres have potential applications in controlled release of drugs in gastrointestinal tract. Smart electrospun nanofibres are produced from poly(N-isopropylacrylamide) (PNIPAAm) which are capable of responding to external stimuli such as temperature changes. These materials may find use in many applications, such as smart packaging of food, controlled drug delivery, and tissue engineering. Figure 6 illustrates the smart electrospun fibres which are sensitive to temperature changes.

Nanofibres are deemed part of the "nano" family, which is currently a hot topic for many food regulatory bodies, due to potential health risks related to nanoparticles which may deposit in soft tissues. Until recently there was no clear definition of what kind of nanomaterials imposes risk in the food sector. Directorate for Science, Technology, and Industry Committee for Scientific and Technological Policy recently published regulatory frame works for nano technology in food and medical products [68]. This could significantly change how nanofibres can be used for various applications in food sector.

3.3. Water. The world is facing formidable challenges in meeting rising demands of clean water resources due to extended droughts, growing industrialization, and rising population. Ninety seven percent of surface waters are oceans which are hard to make suitable for drinking because of high salt content [69].

Advances in nanotechnology could greatly help overcome the current issues of meeting the demand of clean water supplies using novel, nanostructured membranes produced by electrospinning process. Currently electrospun nanofibrous membranes (ENMs) are a very attractive and plausible

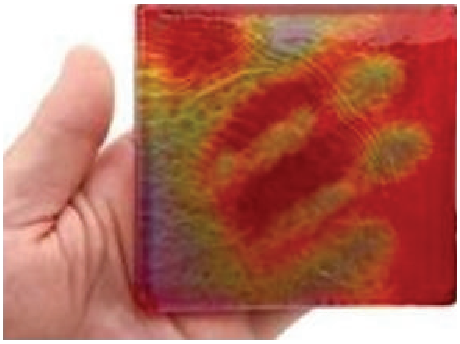


Figure 6: Smart electrospun nanofibre membranes produced PNIPAM [67].

solution in filtration technology due to their unique properties such as high porosity, micro- to nanoscaled pore sizes, interconnected open pore structure, and a large surface area per unit volume. Due to the flexibility of the electrospinning process, it is anticipated that membranes can be produced with various novel functionalities which could effectively remove salts and various toxic compounds to produce clean water for human consumption and various other day-to-day uses.

The primary function of a filtration membrane is to separate two distinct phases, preferentially regulating one phase through the membrane while simultaneously acting as a barrier to the other phase, such as suspended solids. Safe removal of waterborne pollutants is critical to clean water recovery and is an area of critical importance as the global population continues to rise to over 7 billion [70], applying severe pressure on diminishing global resources. Polymer filtration membranes are commonly prepared via the *phase inversion* method, various casting techniques, and electrospinning. Electrospun filtration membranes offer a plausible, alternative, and advantageous route for providing clean water via ease of scalability, low power consumption, and the nonusage of chemicals. Table 3 presents some common electrospun synthetic and natural polymers which are under current investigation for use in water filtration. The dimensionality of nanofibres allows for the high volume production of light weight, highly functional, nanoscale, mesh-like structures. Membrane filtration can be broadly divided into two types.

(a) The first type is micro- and ultrafiltration for the removal of larger particles, operating at low pressures with high productivity. The degree of separation process relies heavily on membrane pore dimension. Traditional polymer surfaces are hydrophobic which can lead to *membrane fouling* (issue where particulates deposit onto the membrane surface and clog the pores, leading to a degradation of the membrane performance).

(b) The second type is nanofiltration and reverse osmosis which remove dissolved salts from the aqueous system. In contract to category (a), the separation mainly occurs via diffusion through the membrane.

Table 3: Table of some recently electrospun synthetic and natural polymers and the main function in the water treatment sector.

Polymer	Function	Reference
Polyvinylidene fluoride, PVDF	Filtration membrane	[71]
Polyacrylonitrile, PAN	Filtration membrane	[72]
Poly(lactic acid), PLA	Filtration membrane, antifouling	[73]
Polyurethane	Affinity membranes	[74]
Chitosan	Filtration membrane	[75, 76]
Cellulose Acetate	Filtration membrane	[77]
Silk	Heavy metal ion recovery	[78]

In the review by Balamurugan et al. [24] reviewing the trends in air and water filtration, they highlighted reports which demonstrated that, by introducing expanded polystyrene nanofibres to conventional nanofibres, it increases the separation efficiency of the filter media by 20% [79]. They also reviewed the work by Gopal et al. [25] investigating electrospun polyvinylidene difluoride (PVDF) nanofibrous membranes for the microfiltration of varying micrometre size of polystyrene particles. The study proved the efficiency of electrospun nanofibres compared to the conventional microfiltration membranes reporting a high rejection rate of ~90% of polystyrene microparticles. Currently microglass fibres are commonly employed in the petrochemical industry for water/oil emulsion separation processing.

Together with increasing separation efficiency by nanofibre dimensionality, membranes fouling must be addressed. Recently Kaur et al. [80] blended a series of PVDF polymers with hydrophilic, surface modifying macromolecule prior to electrospinning to minimise the issue of membrane fouling. The surface modifying macromolecules were prepared from a urethane prepolymer with poly(ethylene glycol) (PEG) and poly(propylene glycol) of various average molecular weights. They also compared electrospinning to the phase inversion technique, noting that the contact angle varied significantly with technique, —0° for electrospun compared to 54° for asymmetric membrane (phase inversion technique), after blending with a PEG-based surface modifying macromolecule.

Other filtration application areas for hybrid or composite polymer systems included modified and crosslinked chitosan coupled with electrospun polyvinylidene fluoride (PVDF) [71]. This surface modified, electrospun membrane exhibited a wider operating environment range, maintaining a good flux rate and rejection efficiency of >98% in bovine serum albumin filtration tests at 0.2 MPa. This is higher than that of commercial ultrafiltration membranes (*Sepro UF, PES10*), while displaying low membrane fouling levels. Tian et al. [77] fabricated electrospun cellulose acetate nonwoven membranes, which were subsequently surface modified with poly(methacrylic acid) (PMAA) for heavy metal ion adsorption (Cu^{2+}, Hg^{2+}, Cd^{2+}). Adsorption experimental results reported that the higher initial pH value

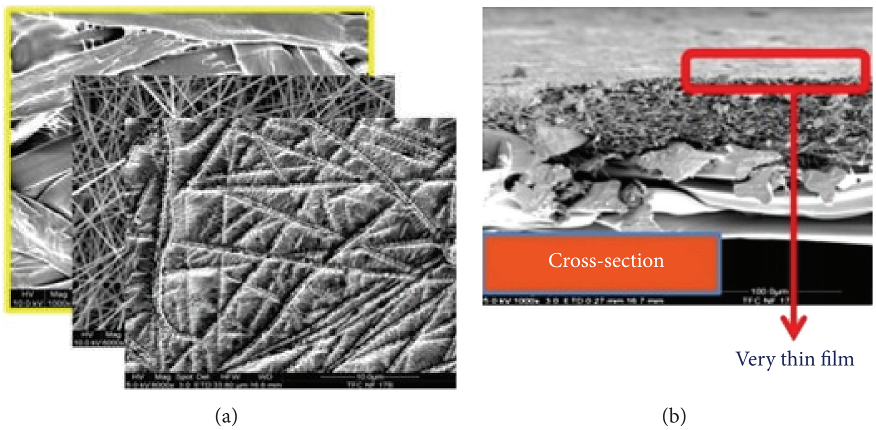


Figure 7: A three-tier architecture of TFNC membrane (a) and its cross-sectional view (b) [84].

corresponded to higher adsorption capacity. Back in 2007, Ki et al. [78] fabricated silk fibroin and wool keratose/silk fibroin blended nanofibrous membranes (diameter ~200–400 nm) which reportedly exhibited an excellent performance for the adsorption of metal ions, when compared to common filter (wool sliver, filter paper). Metal ion tests were performed with Cu^{2+} as a model heavy metal ion in a stock solution. Haider et al. [81] examined the metal adsorbability of high mechanical strength, chitosan electrospun nanofibre (diameter ~235 nm) mats. They noted Cu (II) adsorption rates of roughly six times higher than reported values from chitosan microspheres, underlining the critical role played by exposure of chitosan nanofibre's functional groups to the metal ions. Pantet al. [82] prepared nylon-6 nanofibre mats containing TiO_2 nanoparticles resulting in improved mechanical strength and UV blocking ability along with antimicrobial and hydrophilic properties, for use as both protective clothing and water filtration applications.

Much research attention has been placed on multilayered electrospun composite mats for water filtration, for higher water flux and filtration efficiency. However the intrinsic properties of chitosan as a hydrophilic, water-resistant, but water-permeable coating can play a significant role in enhancing the filtration properties. Back in 2006, Yoon et al. [83] presented a paper on demonstrating a new type of high flux ultra-/nanofiltration system based on a polyacrylonitrile (PAN) electrospun nanofibrous scaffold (diameter 124–720 nm, porosity ~70%), with a thin top layer of natural chitosan—a hydrophilic, water-resistant, but water-permeable coating. They fabricated a three-tire composite membrane, coarse nanofibre PAN/fine nanofibre PAN/chitosan, observing flux rates over an order of magnitude higher than commercial nanofiltration filter (*NF 270, Dow*) after 24 h operation, while maintaining good filtration efficiency.

This work led to the fabrication of high flux thin film nanofibrous composite membranes. A three-layer composite structure of *thin film nanocomposite* (TFNC) membranes was constructed for the desalination via nanofiltration of water [84]. Figure 7 illustrates the construction and three dimensional structure of TNFC membranes prepared by electrospinning processes. Nanofiltration membranes made by this process and employed in desalination of water have shown higher permeated fluxes and less fouling than conventional membranes.

One such paper presents an interfacially polymerized polyamide barrier layer composed of varying ratios of piperazine and bipiperidine, fabricated on both PAN electrospun nanofibre scaffolds and PAN ultrafiltration membrane [85]. They conclude that the piperazine concentration played a major role in the interfacial polymerization to optimize the flux and rejection performance. Even more recently, a double-layer mat was fabricated by electrospinning a thin poly(vinyl alcohol), PVA/surface oxidized multiwalled carbon nanotube (MWNT) layer on the electrospun PAN nanofibrous substrate for use as high flux thin film nanofibrous composite membranes to separate an oil/water emulsion [86]. The incorporation of MWNTs into the PVA barrier layer could improve the water flux significantly. This mechanically robust, double-layer membrane reported a high water flux (270.1 L/m^2 h) with high rejection rate (99.5%) in oil/water emulsion separation, even at low pressures (0.1 MPa).

3.4. Environmental Applications. As mentioned in Section 3.3, a recent publication [24] reviewed trends in water and air filtrations and concluded that polymer based-nanofibres embedded with nanoparticles can replace high-efficiency particulate air filters and overcome the current limitations in the filtration of chemical contaminants. These nanoparticle impregnated nanofibre filters offer a range of advantages from filtration efficiency, protection duration, and nonselective decontamination efficiency, to final product weight reduction. However many of these novel nanofibre/nanoparticle systems require simultaneous electrospinning/electrospraying methods to fabricate a useful filter [28]. Some common electrospun synthetic and natural polymers which are employed as plausible, alternative systems in this sector are presented in Table 4.

Previously Ahn et al. [92] studied the filtration efficiency of nylon-6-based nanofibre membranes, which outperformed already commercialized, high-efficiency particulate air filter. The key properties for high performance electrospun air filters are high filtration efficiency with low pressure drop and slow clogging of the filter during use. Amsoil [93] has introduced nanofibre technology in the form of air filtration membranes used in the auto/light truck market. The image in Figure 8 indicates the construction of air filtration membrane using electrospun nanofibres.

These air filtration membranes are highly efficient in removing the dust and have higher life time compared to cellulose-based, conventional air filtration membranes which are used currently in automotive industry.

Alternative synthetic polymers have also been well fabricated including a multi-layered nanofibre mat from polyacrylonitrile (PAN) by Zhang et al. [89]. They reported that a thin, multi-layered nanofibrous structure outperformed HEPA and military standard filters due to volume/layer compensation effects. As a gaseous filter, poly(methyl methacrylate) (PMMA) nanofibres containing the inclusion complex forming beta-cyclodextrin (β-CD) were fabricated for the removal of organic waste vapours from the environment [90]. They concluded that this nanofibre system can entrap organic vapours such as aniline, styrene, and toluene as a result of fibre surface, inclusion complexation with β-CD. Patanaik et al. [88] examined the effects of composite polyethylene oxide (PEO) nanofibrous membranes sandwiched between another nonwoven mat. They concluded that the increase in diameter of PEO nanofibres with the increased concentration has a positive impact on the filtration efficiency and pressure drop. Interestingly the composite filter media was reported to be more stable against cyclic compression when compared to membranes deposited over nonwoven mats. Wang et al. [94] electrospun polyvinyl chloride, (PVC)/polyurethane (PU) fibrous membranes composite air filters and reported filtration efficiency of the order of 99.5%, with a low pressure drop (144 Pa) performance for 300–500 nm sodium chloride aerosol particles. An optimal PVC/PU weight ratio of 8 : 2 was reported with enhanced mechanical and air permeability properties.

Even with the numerous potential advantages that nanofibres possess when compared to commercial filters, there must remain a consideration for the environmental effect via some current manufacturing routes. These often require a relatively large carbon footprint for low yield of filter material produced. Exploiting the intrinsic benefits of natural polymers, Cao et al. [91] recently reported the fabrication of jute cellulose nanowhiskers on PAN, PVA, and silica nanofibrous membrane supports. These new biobased and environmental friendly porous network materials offer an alternative route to manufacture, avoiding such issues as higher costs, lower productivity, and time efficiency and the potential need for harmful solvents.

3.5. Energy. The ever growing global demands for high-energy density electrochemical power sources have prompted a huge interest in such products as lithium- (Li-) ion batteries to exploit the high-energy density, long cycle lives, and

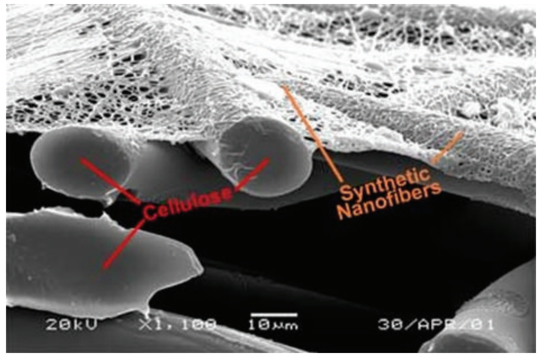


Figure 8: AMSOIL Ea air filters used for automotive industry [93].

Table 4: Table of some recently electrospun synthetic and natural polymers and the main function in the environmental sector.

Polymer	Function	Reference
Polyvinylalcohol, PVA	Air filtration	[87]
Polyethylene oxide, PEO	Air filtration	[88]
Polyacrylonitrile, PAN	Air filtration	[89]
Poly(methyl methacrylate), PMMA	Organic vapour waste, air filtration	[90]
Cellulose	Air filtration	[91]

flexible design as an effective solution [95]. This in turn has focussed huge efforts on fabricating low-cost, high capacity electrodes for such devices with long life cycles. Such work included carbon nanofibres prepared through electrospinning a blend solution of polyacrylonitrile and polypyrrole and subsequent carbonisation [96]. Without the addition of polymer binder or conductive material, these anode materials displayed high reversible capacity, improved cycle performance, relatively good rate capability and clear fibrous morphology even after 50 charge/discharge cycles. Table 5 presents some common electrospun synthetic and natural polymers which are currently under study in the energy sector. Aravindan et al. [97] recently examined NiO nanofibres to evaluate its potential as a high performance anode in Li-ion batteries. In evaluating the performance of a test cell, they reported good cycleability, exhibiting capacity retention of over 75% of reversible capacity after 100 cycles.

Specific to battery cathode systems, recent work includes the preparation of $LiFePO_4$/C submicrofibre composite by a facile electrospinning method in a host poly(4-vinyl) pyridine solution. These $LiFePO_4$/C submicrofibre composites reportedly delivered discharge capacities of 132 and 138 mAh g^{-1}, with excellent cycle performance at 25 and 55°C. Electrospun fibre systems are also employed in preparing the separator layer in Li-ion batteries. Polyimide nanofibre-based membranes have been fabricated for the separators, with higher capacity, lower resistance, and higher rate of capability, compared to the Celgard membrane separator [104].

In conjunction with the electrode and separator materials, low self-discharge composite electrolytes based on porous polymer membranes are another route of increasing

Table 5: Table of some recently electrospun synthetic and natural polymers and the main function in the energy sector.

Polymer	Function	Reference
Polyacrylonitrile, PAN	Battery, fuel cell	[98]
Polyvinylidene fluoride, PVDF	Battery	[99]
	Solar cell	[100]
Polyaniline, PANI	Solar cell	[101]
Cellulose	Battery	[102, 103]

the efficiency of high-energy density electrochemical power systems. These systems also offer a positive safety aspect with good compatibility and no leakage. Raghavan et al. [105] examined polymer gel electrolytes by activating nonwoven polyacrylonitrile electrospun membranes with different liquid electrolytes. The fabricated system showed good interfacial stability, oxidation stability, good cycle performance with high initial discharge properties, and low capacity fade under continuous cycling. Other work has focussed on composite electrospun systems such as TPU/PVDF with and without in situ ceramic fillers (SiO_2 and TiO_2), resulting in superior electrochemical and mechanical performances [106, 107]. Specific to the field of supercapacitor energy storage devices, recently tubular nanofibres of vanadium pentoxide were electrospun from a phase-separated vanadium oxytrihydroxide, poly(vinylpyrrolidone) (PVP) polymer solution.

Focusing on the emerging role of natural polymers, cellulose-based battery devices have previously been fabricated and are already being used for clinic diagnosis. Lee et al. [108] prepared human urine activated paper batteries as a power source to drive the on-board biosensors for healthcare screening of urine. Baptista et al. [109] fabricated a *biobattery*, composed of an ultrathin monolithic structure of an electrospun cellulose acetate membrane. Recently blended synthetic/natural solid state electrolytes were prepared from electrospun PEO, with a novel cellulosic reinforcement material, GELPEO [102]. Good thermal stability and high tensile strength show this as a promising material for use in various electrochemical devices such as lithium ion batteries and dye sensitized solar cells. Comparable ionic conductivities were achieved for both electrospun PEO and PEO + 5 wt% GELPEO nanocomposite systems.

As a viable, green technology energy supply, fuel cells have recently attracted enormous attention. In the simplest form, fuel cells efficiently convert stored energy into electrical energy via a catalytic reaction, resulting in a high power density supply. The main types of fuel cells are proton exchange membrane fuel cells (PEMFC), direct methanol fuel cell (DMFC), solid oxide fuel cell (SOFC), phosphoric acid fuel cell (PAFC), and alkaline fuel cells (AFC). Research in these areas is growing rapidly and is discovering noted advantages when incorporating electrospun component systems. In 2010, Tamura et al. [110] fabricated electrospun aligned sulfonated polyimide nanofibres for use as proton exchange membrane. They noted significant improvement in the membrane stability along with an increase in proton conductivity of the membrane.

Investigating and optimising the electrocatalytic performance of fuel cells have led to the fabrication of such systems as platinum (Pt) nanowires, prepared by the high temperature treatment (450°C) of electrospun PVP-Pt composite fibres. The researchers noted increased electrochemical specific and mass activities. Even more recently, Guo et al. [111] fabricated an electrospun palladium nanoparticle loaded carbon nanofibre composite which exhibited enhanced electrocatalytic performance toward methanol electrooxidation. In 2011 sulfonated poly(ether sulfone) (SPES) nanofibres were prepared via electrospinning techniques and a new class of triple-layer polyelectrolyte membranes based on Nafion-filled nanofibrous webs was fabricated [112]. These systems were deemed suitable for high-performance direct methanol fuel cells. Additional published research included the electrospraying of platinum-carbon catalyst nanoparticle suspensions in Nafion-alcohol solutions over carbon paper to prepare cathodes for proton exchange membrane fuel cells [113]. This work found that the relative power density was substantially higher for any of the electrosprayed electrodes (comparing platinum loading). Chen et al. [114] prepared carbon fibre mats via a layer-by-layer electrospinning of polyacrylonitrile onto thin natural cellulose paper as a low cost and highly efficient electrode for the anode in microbial fuel cells. They concluded that much larger current densities would be obtained if you further increased the gap between the layers within the layered-carbon fibre mat. This would lead to thicker layered biofilm growth in every layer of the entire layered system.

Over recent years huge interest has been focussed on nanosized TiO_2 powders for use in photocatalysis, photocatalytic water splitting, solar energy conversions and catalytic devices. The ability to synthesize TiO_2 in different shapes and morphologies such as nanoporous structures, nanoparticles, nanotubes, nanowires, and nanofibres by various methods makes it a very interesting and versatile material. In a series of work, Veluru et al. [115] fabricated and subsequently annealed and functionalized multiwalled carbon nanotube MWNT-TiO_2 nanostructures via electrospinning and noted a dramatically enhanced hydrogen generation, primarily due to the increase in surface area of the hybrid nanostructures. Peining [116] also reported an optimum concentration of MWNTs in the TiO_2 matrix for best performance in dye-sensitized solar cells to be 0.2 wt%, with a 32% enhancement in the energy conversion efficiency.

To overcome some of the limitations of such photocatalysts as TiO_2 applied under visible light, many researchers are looking for alternative, visible light-induced photocatalysts with the appropriate band gap energy. Wu et al. [117] fabricated CdS/ZnO core-shell nanofibres via the electrospinning technique. They noted that the power conversion efficiencies of these hybrid solar cells were improved by more than 100% after the modification of CdS. Afeesh et al. [118] presented work highlighting the photocatalytic effects of a reusable, novel nematic shaped CdS-doped poly(vinyl acetate) electrospun mat. They noted no secondary pollution problem from the CdS nanoparticles. Shengyuan et al. [119] combined the two photocatalysts to form an electrospun

TiO_2-/CdS-based photoelectrode with a CoS counter electrode. They conclude that these CoS counter electrodes could be a good substitute for the expensive Pt counter electrode in CdS-sensitized nanocrystalline solar cells.

4. Conclusions

The high surface to volume ratio of the electrospun fibres makes them attractive for various applications such as high performance filters, energy generation, water filtration, and scaffolds in tissue engineering. Considering the versatility of electrospinning process the number of applications using various synthetic and natural polymers is increasing at an exponential rate in various fields. However, the use of natural polymers in various applications is relatively low compared to synthetic polymers due to incompatibility of the choice of the polymer for particular application and in some cases due to poor chemical and mechanical properties. Further developments are required to find new hybrid polymer systems based on synthetic and natural polymers that are suitable for electrospinning with improved functionalities suitable for across spectrum of applications especially food and biotechnology areas. They aim to exploit the key material advantages from both systems, whilst overcoming some of the individual limitations which have hindered the true exploitation of electrospun systems to date. As fabrication costs continue to reduce and higher volume electrospinning systems are brought on-stream, the resulting nanofibre-based products will become highly competitive alternatives to current, often out-dated, market solutions. Based on current studies it is not a surprise that electrospun nanofibres are expected to play a critically important role in many important application areas, such as water purification, renewable energy, and environmental protection in the coming years.

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