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Electrospun Polyurethane Nanofibers

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Abstract

The electrospinning process is highlighted with the ability of fabricating fibers with diameters on the nanometer scale, small inter-fibrous pore size and high porosity, vast possibilities for functionalization with high surface area to volume or mass ratio, ease of use and instrument setup, and adaptability. It attracted a great deal of attention due to its unique properties. More than 100 different polymers have been successfully electrospun into ultrafine fibers using this technique including synthetic polymers such as polyurethane (PU). Electrospun PU nanofiber mats exhibiting good mechanical properties may have a wide variety of potential applications in high-performance air filters, protective textiles, wound dressing materials, sensors, drug delivery, etc. This chapter deals with the electrospinning of polyurethane nanofibers and their potential applications.

Keywords: electrospinning, polyurethane, nanofibers, applications

1. Introduction

Electrospinning is a fiber spinning technique that is able to produce continuous ultrafine fibers from sub-micrometer to nanometer diameters, which uses electrostatic forces. The original ideas of using electrical potentials on the surfaces of droplets, amount of charge required for the deformation of droplets, and also apparatus for spraying of liquids by use of electrical charges can be traced back more than 100 years [1–3]. However, Formhals was recognized as the father of the electrospinning and he was the first to describe the operation of electrospinning in 1934 for producing polymer filaments by electrostatic repulsions between surface charges [4].

Despite these early studies, researches in nanofibers and electrospinning have received a great deal of attention, after 1990s, especially after Doshi and Reneker [5], Srinivasan and

Reneker [6], and Reneker and Chun [7], spun various kinds of polymers including polyethylene oxide, nylon, polyimide, DNA, polyaramid, and polyaniline, and were able to characterize their properties. Afterward this old technology rediscovered, refined, and expanded into non-textile applications. Electrospinning process is unique among other nanofiber fabrication techniques in terms of ease of use, vast possibilities of material selection and combination, and it has a potential for scale-up. This has led to electrospinning being considered as a key platform technology that will be studied to develop products for a wide range including drug delivery, tissue scaffolding, wound dressing, electronics, chemical sensors, filtration, and so on [8]. This rediscovery and attention are partly the results of leading-edge technology, especially, scanning probe microscopy and high-resolution electron microscopy, which enable the exploration of the “nanodimension.”

2. Electrospinning

The electrospinning process simply constituted of a high voltage power supply, a spinneret and a deposition area named as collector generally covered with an aluminum foil. The potential difference between the spinneret and the collector leads to the stretch of the polymeric solution and creates a thin nanofiber jet from solution toward to the deposition area. During this electrospinning process, the solvent evaporates and ultrafine fibers are collected [9, 10]. Main process equipments and setup are presented in **Figure 1**.

The electrospinning process has attracted a great deal of attention due to the ability to fabricate fibers with diameters on the nanometer scale [11, 12], vast possibilities for surface functionalization [13, 14] with high surface area to volume or mass ratio, small inter-fibrous pore size and high porosity [11, 15, 16]. Technically, almost any soluble polymer with a sufficiently high molecular weight can be electrospun, and [17] various polymers have been successfully electrospun into nanofibers cost-effectively compared to the other methods.

The method can be applied to synthetic and natural polymers, polymer blends, and polymers loaded with chromophores, nanoparticles, or active agents, as well as to metals and ceramics [18]. A large number of inorganic salts, inorganic and organic particles, and carbon nanotubes (CNTs), can also be immobilized in polymer fibers [19]. More than 100 different polymers have been successfully electrospun into ultrafine fibers using this technique [10] including synthetic polymers such as PU [20–29].

3. Polyurethanes

PU contains urethane group ($-\text{NH}-(\text{C}=\text{O})-\text{O}-$) in common (**Figure 2a**) [30, 31], while most PUs are thermosetting polymers, in contrast to thermosetting polymers, thermoplastic polyurethanes (TPUs) melt when they are heated (**Figure 2b**) and are easy to use in manufacturing processes. Varying the structure of PUs, their properties can be varied in a wide range [32]. PUs are formed by reaction of polyisocyanates with hydroxyl-containing compounds.

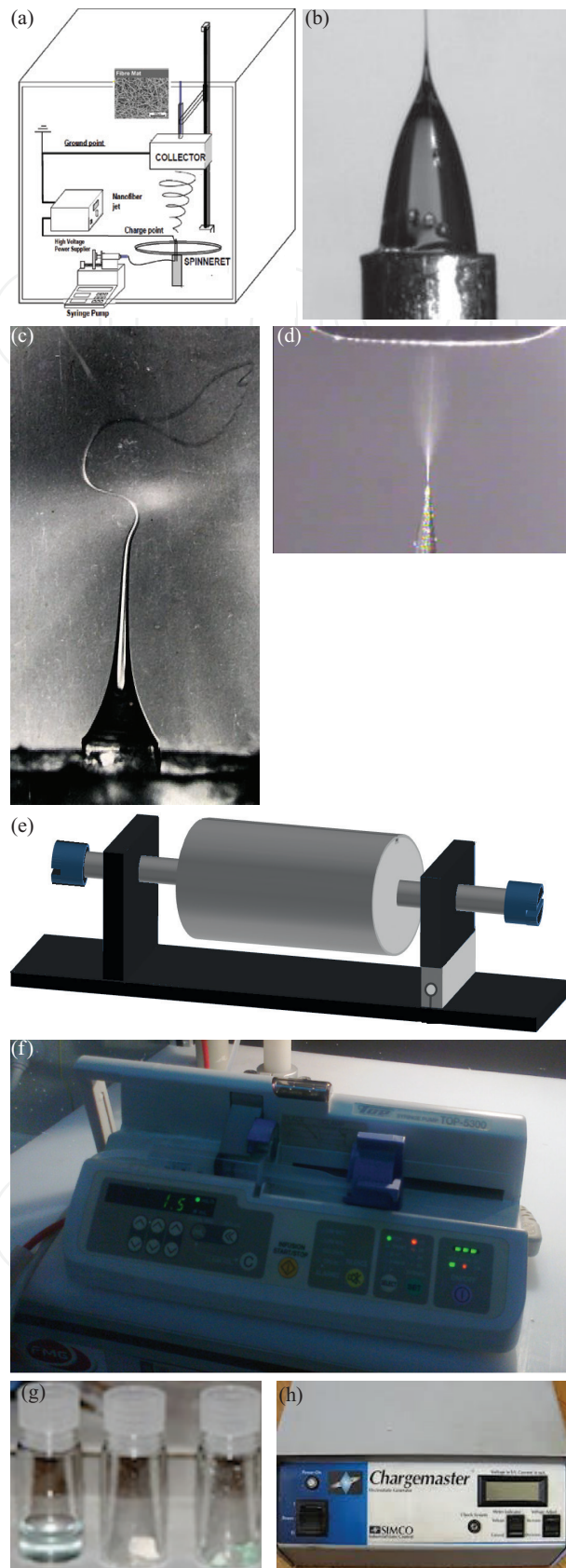


Figure 1. Electrospinning setup (a), Taylor cone (b), whipping (c), electrospinning jet (d), collectors (e), single syringe pump (f), polymer solutions (g), and high voltage supply (h).

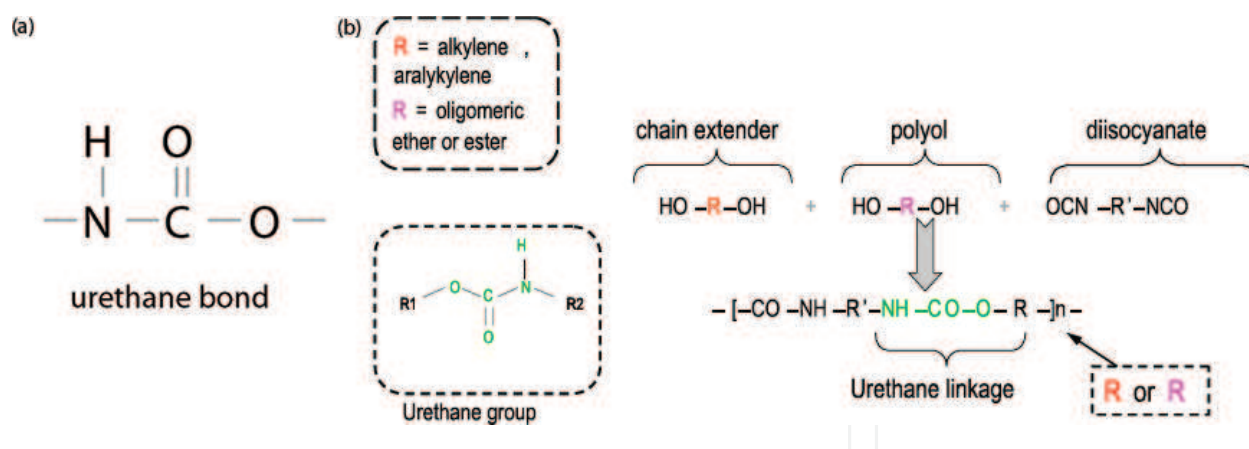


Figure 2. (a) Urethane group, (b) thermoplastic polyurethane general formula [35].

Desired properties can be tailored by selecting the type of isocyanate and polyols, or combination of isocyanates and combination of polyols [32, 33]. Strong intermolecular bonds make polyurethanes useful for diverse applications in adhesives and coatings, also in elastomers, foams, and medical applications because of their good biocompatibility [34].

The factors determining properties of a polyurethane elastomer are: structure of the polyol, type of diisocyanate, type of the chain extender, molar ratio NCO/OH, soft-segment concentration, molecular weight of the polyol and filler. In polyurethane elastomers, chains are linear, and cross-linking was achieved by physical bonds and hard domain formation. They flow when they are melted and harden by cooling (thermoplastic behavior). Displaying reversible cross-linking, domains are destroyed above the melting point of the hard phase, but are reformed when they get cooled. These materials are called “thermoplastic urethanes” (TPUs) [32]. In addition to the linear TPUs, obtained from difunctional monomers, branched or cross-linked thermoset polymers are made with higher functional monomers. Linear polymers have good impact strength, good physical properties, and excellent processibility, but limited thermal stability. On the other hand, thermoset polymers have higher thermal stability, but sometimes lower impact strength [33].

The vast selection of polyols, isocyanates, and chain extenders allows PUs to be varied from soft thermoplastic elastomers to adhesives, coatings, flexible foams, and rigid thermosets [25]. TPU elastomers are segmented block copolymers, comprising of hard- and soft-segment blocks. The soft-segment blocks are formed from long-chain polyester or polyether polyols and 4,4'-methylenebis(phenyl isocyanate) (MDI); the hard segments are formed from short-chain diols, mainly 1,4-butanediol and MDI [33]. The unique properties of linear TPUs are attributed to their long-chain structure. TPUs are resilient elastomers of significant industrial importance, which possess a range of desirable properties such as elastomeric, resistant to abrasion, and excellent hydrolytic stability [36, 37].

PU is often chosen as a material for composing a nanoweb due to its chemical stability, mass transport, good mechanical properties, and also excellent nanofiber forming characteristic [24, 38]. Electrospun PU nanofiber mats exhibiting good mechanical properties may have a wide variety of potential applications in high-performance air filters, protective textiles,

wound dressing materials, sensors, in biomedical applications, drug delivery, etc. [21, 37–44]. It is also frequently used in wound dressing studies because of its good barrier properties and oxygen permeability. It has reported that semipermeable dressings, many of which are PU, enhance wound healing [21, 39]. Degradable and biocompatible aliphatic PU could also be formed into scaffolds via melt electrospinning [42]. Beside these biomedical applications, the PU nanofiber filters were prepared by electrospinning process based on 3D particle filtration modeling and some theoretical predictions were obtained for the filtration efficiency [45]. In another study, PU cationomers (PUCs) containing different amounts of quaternary ammonium groups were synthesized and electrospun into non-woven nanofiber mats for use in antimicrobial nanofilter applications [46].

Varying the structure of PUs, the properties of PUs can vary in a wide range [32]. The flexibility to tailor the structure during processing is one of the main advantages of PUs over other types of polymers. A lot of different types of PU used in electrospinning process, some of them were synthesized before electrospinning according to the researchers intended use and some of them were used as they received.

This chapter deals with the electrospinning of PU nanofibers including TPUs and their potential applications. The nanofiber morphology and influence of experimental parameters including the solution concentration, flow rate, collection distance, and electric voltage are discussed in terms of electrospinning of PU nanofibers and potential applications of PU nanofibers are reviewed.

4. Electrospinning of PU nanofibers

There are many parameters that affect the electrospinning process and the resultant fiber morphology. Several authors investigated the effects of solution and process parameters such as material composition, concentration, rheological properties, applied voltage, tip-to collector distance, collector types on the resultant PU nanofibers [26, 27, 47–49]. Among these parameters, polymer solution properties have the most significant influences on the process and the resultant fiber morphology [9], since viscoelastic and gravitational forces play a major role. Viscoelastic force depends on polymer solution concentration, average molecular weight of the polymer, final viscosity, and surface tension of the solution [47].

4.1. Solvents for electrospun PU nanofibers

Electrospinning solution properties are also directly related to the solvent type. The type of solvent and their concentration influenced the morphology of electrospun nanofiber mat significantly. Process involves the stretching of the solution caused by repulsion of the charges at its surface. Thus, if the conductivity of the solution is increased, more charges can be carried by the electrospinning jet [13], which increases the stretching of the polymer solution. As much as solution conductivity, the dielectric constant of a solvent has also a significant influence in electrospinning process. Higher dielectric property reduced the bead formation and the diameter of the resultant electrospun fibers [47].

Most commonly used solvents that dissolve PUs are highly polar organic solvents such as N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-Methylpyrrolidone and tetrahydrofuran (THF) [50, 51]. Ketones such as acetone, methyl ethyl ketone, cyclohexanone are partial solvents for TPUs. Aliphatic alcohols such as ethanol and isopropanol cause a slight swelling; aliphatic esters such as ethyl acetate and butyl acetate strongly cause severe swelling of TPUs [50]. Investigation of the effects of solvents in electrospinning of TPU appeared in the study of Mondal [29] and Cay et al. [52]. Mondal used four different solvents (THF, DMF, N,N-dimethylacetamide, and DMSO) and reported that the morphology of the resultant nanofibers changed significantly with the solvent selection. Solvent conductivity and vapor pressure of the solvents were found to be the important factors (**Table 1**). In the study of Cay et al., the effects of the incorporation of ethyl acetate or tetrahydrofuran into TPU/DMF solvent system were investigated. The solutions of TPU in pure DMF and DMF/EA were found to be easily electrospinnable. DMF seemed to be the best solvent to dissolve TPU pellets but diluting TPU solutions with 10 or 20% of EA ensured positive effect on fiber diameter by means of achieving thinner fibers. Incorporation of THF to DMF led to thicker fibers compared to TPU/DMF solutions. With the increasing THF volume fraction, electrospinning is restricted due to high viscosity and low conductivity.

A mixed-solvent system of THF and N,N-dimethylacrylamide (DMAA) in the study of Kidoki et al. to investigate the relationships between the structural features and mechanical properties of electrospun segmented PU (SPU) meshes. They studied the polymer concentration and solvent mixing ratio to achieve different formulations and investigated the operation parameters such as applied voltage, tip to collector distance, and feeding rate. SPU was electrospun from the mixed solvent of THF and DMAA with different mixing ratios [DMF content: 5, 10, and 30% (v/v)]. An increase in DMAA ratio significantly affects the degree of bonding between SPU fibers at contact sites and leads to thinner fibers formation. The porosity of the electrospun SPU meshes decreased with increasing DMF ratio according to the porosimetric characterization. The pore size distribution exhibited three representative peaks of approximately 5, 20, and 70 μm void sizes. Increasing DMAA ratio markedly decreased the proportion of the 20 μm void. In addition to these, an increase in DMAA ratio induced an increase in elasticity of the mesh. The authors pointed that electrospun SPU meshes using a mixed-solvent system with low- and high-boiling point solvents may be useful in the engineering of SPU-fiber-based matrices or scaffolds [57].

4.2. Solution and processing conditions for electrospun PU nanofibers

The diameter of the nanofibers produced by electrospinning is a key parameter for most of the applications. The diameter of the nanofibers defines the structural features such as pore sizes and specific surface areas. These features affect the selectivity of filters, the permeability of filters, catalytic activities in systems using nanofibers to immobilize catalysts, or the cell proliferation in tissue engineering relying on nanofiber-based scaffolds [1]. Solution parameters, especially polymer concentration and the spinning parameters including feeding rate, applied voltage, tip to collector distance, have the strongest impact on the fiber diameter. The properties of PUs can vary in a wide range according to the structure of PU, thus below investigated parameters were particular for the selected PUs.

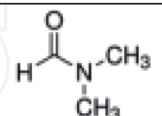

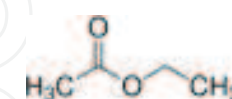
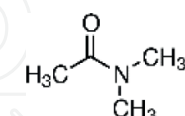
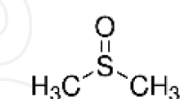
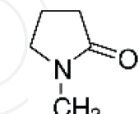
Solvent	Chemical formula		Molecular weight (g/mol)	Boiling point (°C)	Density (g/mL)	Dipole moment (Debye)	Solubility parameter (δ) (cal/cm ³) ^{1/2}	Dielectric constant (ϵ)
N,N-dimethylformamide (DMF)	C ₃ H ₇ NO		73.09	153	0.944	3.86	12.14	37
Tetrahydrofuran (THF)	C ₄ H ₈ O		72.1	65–67	0.889	1.75	9.52	7.5
Ethylacetate (EA)	CH ₃ COOCH ₂ CH ₃		88.11	76.5–77.5	0.902	1.78	9.10	6
N,N-dimethylacetamide	CH ₃ CON(CH ₃) ₂		87.12	164.5–166	0.937	3.72	11	37.78
Dimethylsulfoxide (DMSO)	(CH ₃) ₂ SO		78.13	189	1.10	3.960	12.93	47
Methylpyrrolidone	C ₅ H ₉ NO		99.13	202	1.028	4.09	10.95	32.2

Table 1. Properties of selected solvents [52–56].

A 3^2 factorial experimental design was used to investigate the tip to collector distance and applied voltage effect for PU nanofibers by Yanilmaz et al. [27]. They used TPU (PU, 270,000 g/mol) supplied from Coim Co. and chose THF for 10% (w/w) TPU solution, 5, 7.5, and 10 cm for tip-to collector distances and 10, 15, and 20 for applied voltages. From their design, it was seen that the distance and applied voltage had significant effects on the fiber diameter and it depends on the applied voltage and distance; furthermore, the interaction of these factors affects fiber diameter significantly.

Akçakoca Kumbasar et al., used DMF for TPU (Pellethane 2103-80AE) solutions and investigated the effect of TPU concentration (6, 8, 10, 12, and 14% (w/w) represented in **Figure 3**), tip to collector distance (8, 10, 12, and 15 represented in **Figure 4**), feeding rate (0.3, 1.5, 2.5, and 3.5 ml/h), and applied voltage (7, 10, 13 kV) on nanofiber diameters. Their results showed that 6% of TPU concentration is too low and 14% is too high for smooth nanofibers and as expected nanofiber diameter increased with increasing TPU concentration. With the increasing tip to collector distance, they were able to achieve better nanofiber morphologies and thinner nanofibers. They showed that decreasing the tip to collector distance caused insufficient solvent evaporation, which makes membrane-like surface instead of nanofibrous surface. Their results also revealed that increase in the feeding rate caused too much polymer deposition on the collector in a short time and that caused conjunction of nanofibers. They concluded that in case of thinner and smoother nanofiber production, 10% of TPU concentration, 20 cm tip to collector distance, 0.3 ml/h feeding rate, and 13 kV applied voltage are suitable [58].

Zhuo et al., also investigated the process parameters, including the applied voltage, feeding rate, and solution concentration. They synthesized PU from PU resin (number-average molecular weight = 180,000 g/mol), based on Poly(ϵ -caprolactone) diol containing a 75% soft-segment content, and 4000 soft-segment length by the bulk polymerization method. They found that 12.0 kV was a critical value for their synthesized PU. For preparing uniform PU nanofibers, diameters ranging from about 700 to 50 nm used 5.0 wt% PU/DMF solutions. However, when the applied voltages were increased to a high value, such as 20.0 or 25.0 kV, the diameters of nanofibers were not uniform and many loops were formed. Higher feeding rate (e.g., 0.1 mm/min) caused larger fibers compared to lower feeding rate (e.g., 0.06 mm/min), and smaller and uniform nanofibers were observed with lower feedings. The fiber diameters increased with the increasing solution concentration. They used five PU/DMF solutions (3.0, 5.0, 7.0, 10.0, and 12.0 wt%), did not observe jet formation in the PU/DMF solutions above 12.0 wt% because of the higher viscosity, whereas in a too diluted solution (e.g., <3.0 wt%), the jet broke into droplets and they observed electrospinning instead of electrospinning. Finally, they concluded that uniform PU nanofibers could be produced by using 5.0–7.0 wt% of PU/DMF solutions, applied voltages of 10–15 kV, and feeding rates of 0.06–0.08 mm/min [38]. They also observed that increasing the applied voltage caused stickier fibers [38].

Andrews et al. investigated some other spinning parameters for Poly(ether urethane), Tecoflex[®] SG-80A (Thermedics Polymer Products, Wilmington, MA), including flow rate,

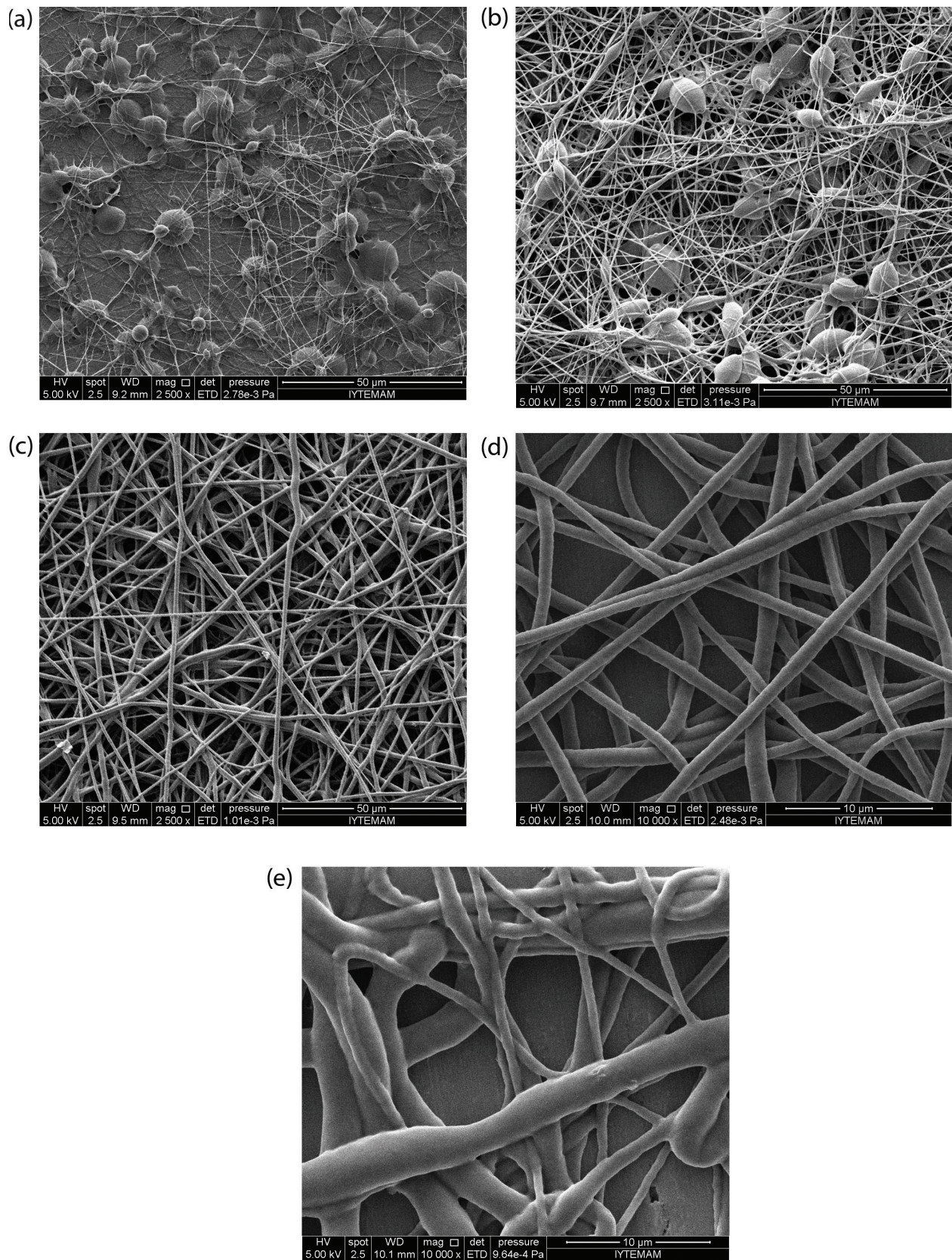


Figure 3. (a) 6%, (b) 8%, (c) 10%, (d) 12%, and (e) 14% w/w electrospun TPU nanofibers [58].

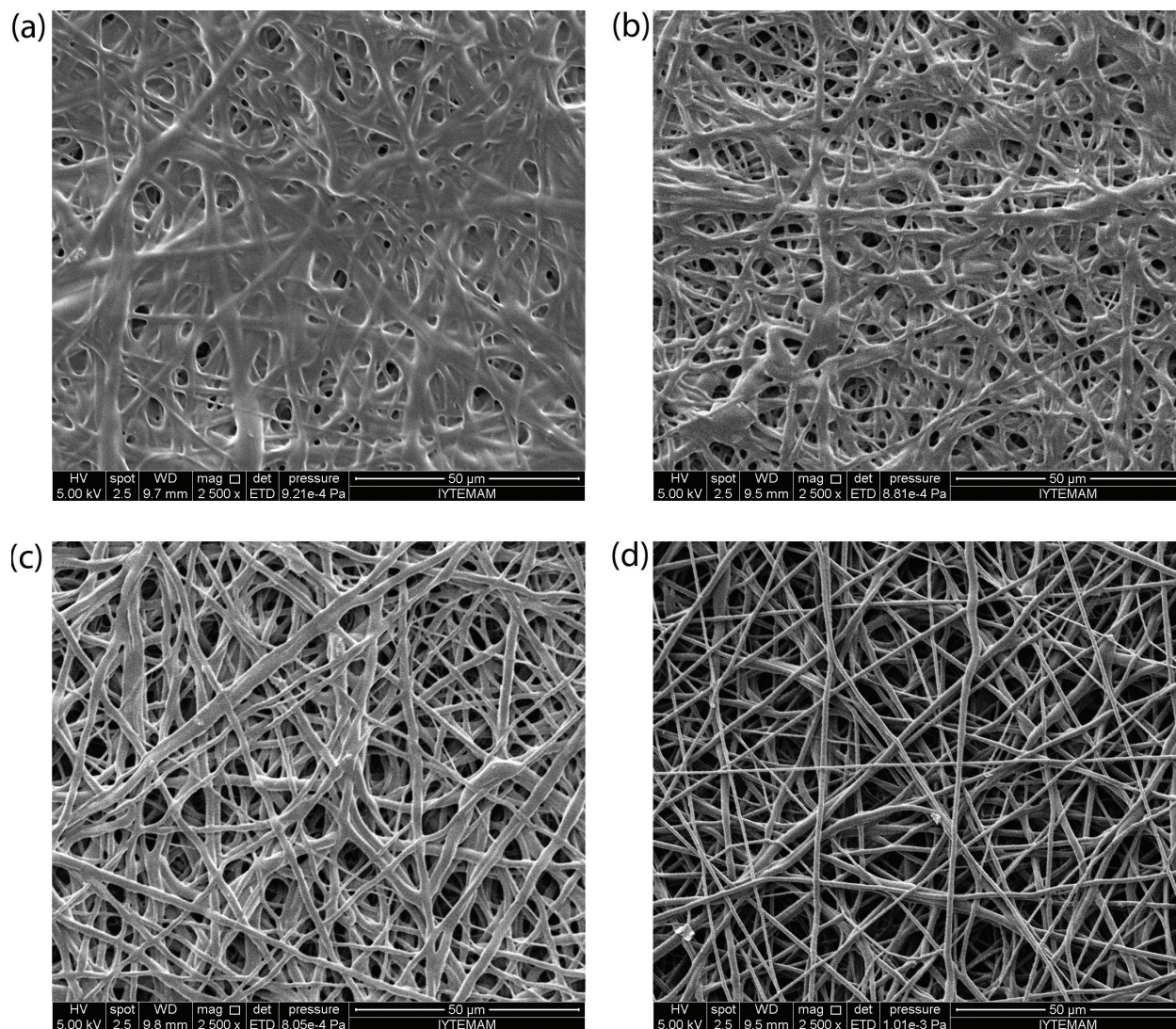


Figure 4. SEM images of the TPU nanofibers at tip-to collector distance: (a) 8, (b) 10, (c) 12, and (d) 15 cm [58].

relative spray height, spray distance, traverse speed, mandrel speed, grid voltage, and mandrel voltage. Dimethylacetamide (DMAc):2-butanone [methyl ethyl ketone (MEK)] were used in the ratio of 1:1.68 to obtain 12.5% w/v PU solution. Their results indicated that inter-fiber separation was significantly affected by flow rate, spray distance, grid voltage, and mandrel voltage, but not by relative spray height, traverse speed, and mandrel speed whereas fiber diameter was significantly affected by flow rate and mandrel voltage, there was no significant difference brought about by changes in relative spray height, spray distance, traverse speed, mandrel speed, and grid voltage. Void fraction was significantly affected by flow rate but not by relative spray height, spray distance, traverse speed, mandrel speed, grid voltage, and mandrel voltage. Fiber orientation on the external surfaces was significantly affected by traverse speed and mandrel speed, but not by flow rate, relative spray height, spray distance, grid voltage, and mandrel voltage. They indicated that the volumetric flow rate was the sole spinning parameter that affects the scaffold thickness [59].

Demir et al. prepared a segmented polyurethaneurea based on poly(tetramethylene oxide)glycol cycoaliphatic diisocyanate, and unsymmetrical diamine. They used 2-methyl-1,5 diaminopentane (DAP), dibutylamine (DBA), DMF as solvents and studied electrospinning behavior of produced elastomeric polyurethaneurea copolymer in solution. They observed fiber diameters increased with the increasing solution concentration and lower concentration favored beads, and increased concentrations favored curly fibers. Salt addition increased the solution conductivity, which led to increase in mass flow. They found viscosity and solution temperatures were dominant factors and improving the fiber morphology was possible with increasing solution temperature, and it was quicker to electrospun these solutions compared to the solutions that were at room temperature [20].

The effect of tetraethylammonium bromide (TEAB) salt on the spinnability of polyurethane (PUR, Larithane LS 1086, aliphatic elastomer based on 2000 g/mol, linear polycarbonated diol, isophorone diisocyanate, and extended isophorone diamine) was investigated in the study of Cengiz et al. They used a roller electrospinning method. They found that the conductivity, viscosity, spinning performance increased with salt concentration. Also, solution viscosity decreased with shear rate. PU including 1.82 wt% TEAB gives the best spinning performance although 0.87 wt% TEAB is the optimum value related to fiber properties such as diameter, uniformity, and morphology given the ideal PU nanoweb structure [60]. In another study of Cengiz et al., they discussed the effects of 1,1,2,2 tetrachlorethylen (TCE), a non-solvent addition on the independent (electrical conductivity, dielectric constant, surface tension, and the rheological properties of the solution etc.) and dependent parameters (number of Taylor cones per square meter (NTC/m²), spinning performance for one Taylor cone (SP/TC), total spinning performance (SP), fiber properties such as diameter, diameter uniformity, non-fibrous area). The effect of non-solvent concentration on the dielectric constant, surface tension, rheological properties of the solution, and also spinning performance were statistically important. Beside, non-solvent concentration affects the quality of fiber and nanoweb structure [61].

Yalcinkaya et al., measured the jet current and jet life in roller electrospinning of PU (molecular weight 2000 g/mol, Larithane LS 1086; Novotex, Italy) in their study. They analyzed the relationships between jet current and jet life and number of Taylor cones/m² (NTC/m²), spinning performance (SP), and fiber properties (diameter, non-fibrous area) and determined the effects of PU and TEAB concentrations on jet current and jet life. They observed that jet current increases with PU and TEAB concentration, while jet life decreases. NTC/m² and spinning performance increased with jet current and decreased with jet life, and they observed that jet current movement gives an idea about jet life [62].

Among above the traditional electrospinning method, an uncommon laser-heated electrospinning which is represented in (**Figure 5**), was used by Takasaki et al. and they investigated the effect of the spinning conditions including the applied voltage, the laser power, the laser irradiation point, and the laser beam width on the diameter of TPU microfibers. The average diameter of electrospun TPU fibers decreased with decreasing applied voltage and increasing laser power. A narrower laser beam reduced the variation in the fiber diameters. A PU microfiber with an average diameter of 2.4 μm and a coefficient of variation of 8% was obtained using a 0.9 mm wide laser beam [63].

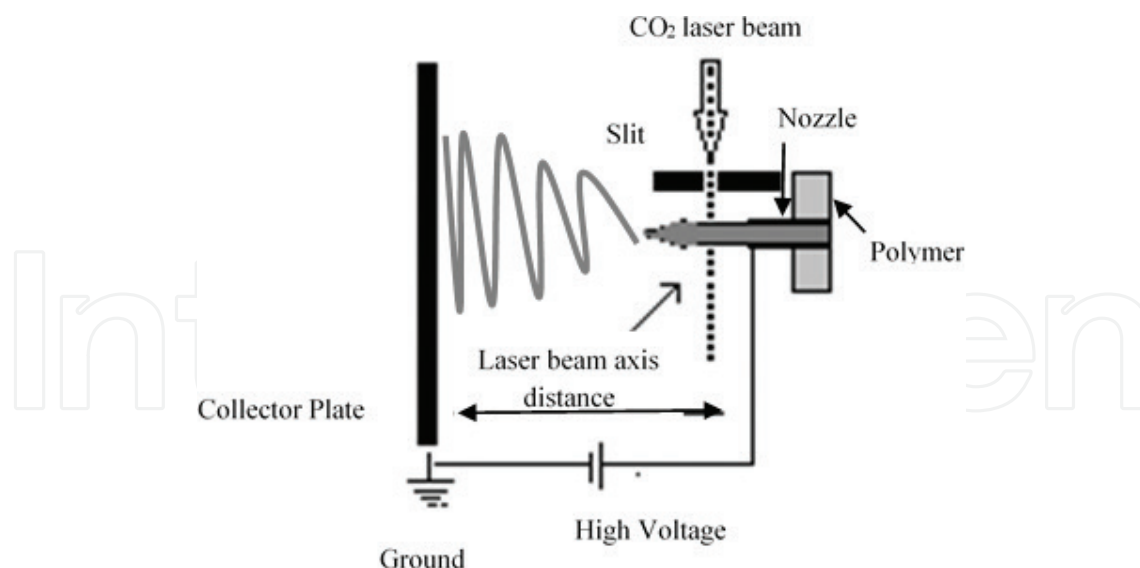


Figure 5. Schematic diagram of laser-electrospinning system. Modified from Takasaki et al. [63].

4.2.1. Melt electrospinning

Although most electrospinning researches are based on polymer solutions, there are also several researchers that use polymer melts. Generally, most electrospinning conditions also affect the molten polymer in electrospinning [9]. Melt electrospinning is especially attractive for tissue engineering scaffold manufacturing process, because it is possible to eliminate potentially cytotoxic solvents in contrast to electrospinning from a polymer solution. However, there are some technical challenges related to the need for a well-controlled high-temperature setup and there is a difficulty in developing an appropriate polymer. In the study of Karchin et al., a biodegradable and thermally stable PU, produced from 1,4-butanediamine and 1,4-butanediol, (CH₂)₄-content diisocyanates and polycaprolactone. These aliphatic PU formulations were used in the melt electrospinning [42]. A catalyst-purified PU based on 1,4-butane diisocyanate, polycaprolactone, and 1,4-butanediol in a 4/1/3 M ratio respectively, yielded a non-toxic polymer that could be electrospun from the melt. The authors concluded that this electrospun polymer contained point bonds between fibers and its mechanical properties were analogous in vivo soft tissues.

4.3. Collectors for electropun PU nanofibers

In most electrospinning setup, the collector plate is made out of a conductive material and covered by a piece of aluminum foil, which is electrically grounded so that there is a stable potential difference between the source and the collector [9]. Rotating drum with different diameters [47, 59, 64–69], parallel electrodes [70], rotating wire drum collector [71], rotating tube collector with knife-edge electrodes below [66], disc collector [72–74] array of counter-electrodes [75], rotating drum with sharp pin inside [76], ring collector placed in parallel [77] could be also used for different purposes [13]. Despite the random and centered collection of nanofibers on the collector plate, the most basic form of getting aligned nanofiber deposition is through the

use of a rotating mandrel. Schematic representation is given in **Figure 6**. Beside aligned nanofibers, the texture of the fiber mesh may also be varied by using patterned collectors.

Andrews et al. deposited the PU nanofibers onto 3 mm diameter stainless steel mandrels that were pre-coated with a saturated NaCl solution to facilitate fiber formation and subsequent removal of the scaffold [59]. Pedicini and Farris used a grounded flat aluminum foil target for isotropic TPU fiber mats for tensile tests and infrared spectroscopy experiments, oriented electrospun TPU nanofiber samples for IR dichroism studies were collected onto a rotating stainless steel drum [64]. Two types of electrodes with tines were used in the study of Banuskeviciute et al. [79]. The electrode consists of eight separate plates. In every plate, tines were set at equal distances. Tines were different by the width and shape of every electrode. They showed that the type of electrode had an influence on the structure of the electrospun TPU mats, but not on the diameter of formed fibers. Rotating mandrels could be used for electrospun vascular graft for the regeneration of blood vessel (**Figure 6b**). Theron et al. [65] spun small diameter vascular graft prototypes (1.6 mm nominal ID) using the apparatus including rotating/translating mandrel. Tubes were removed from the mandrels by swelling in EtOH and dried. Thandavamoorthy et al. [80] self-assemble electrospun PU nanofibers into honeycomb patterns on the collector surface. Residual charges on the collected fibers and the electrical property of the collector screen influenced the self-alignment of fibers. They electrospun PU nanofibers over these substrates while keeping all other process parameters constant. When cotton, a natural fiber with very poor electrical conducting properties, was used as the collecting surface, a 3-D honeycomb pattern deposition was produced (**Figure 7**). Similar results were observed with the glass substrate.

4.4. Electrospinning of PU/blends and PU nanocomposite nanofibers

In electrospinning, it is sometimes useful to combine the properties of two or more polymers to achieve a new structure. This can be obtained either by physical mixing to form a blend or through polymerization to form a copolymer [9]. Addition of a second component could also facilitate the electrospinning process. For example, it was difficult for most of the natural polymers to be electrospun; however, addition of a synthetic polymer could improve the

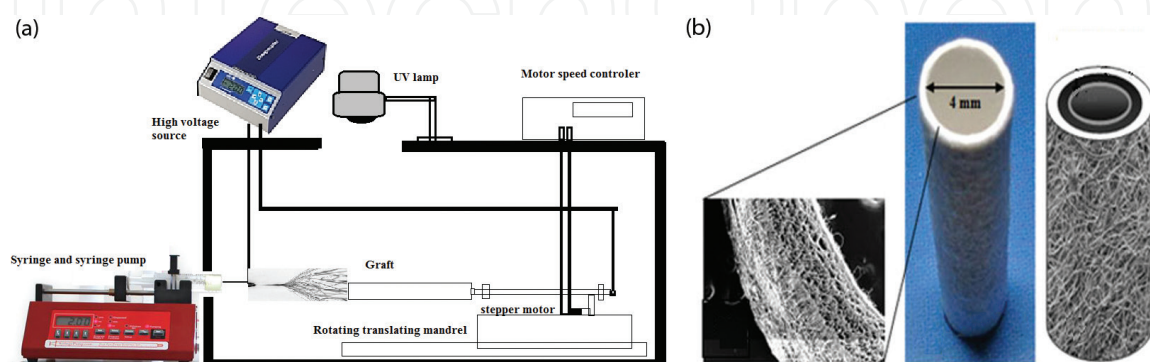


Figure 6. (a) Schematic representation of the reactive electrospinning apparatus with UV light using a rotating mandrel. Modified from Theron et al. [65]. (b) Electrospun vascular graft for regeneration of blood vessel [78].

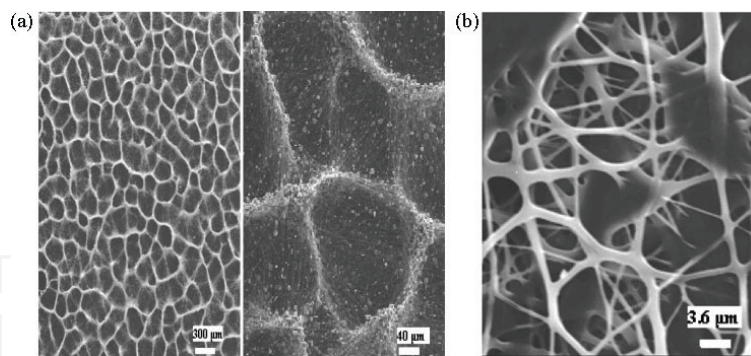


Figure 7. SEM images of self-assembled polyurethane electrospun nanofibers [81].

processability of these polymers [82]. PUs are easy to electrospin and they can be mixed either with a natural polymer or with a synthetic polymer [83, 84, 87] for special applications such as collagen [88], dextran [43], and hydroxypropyl cellulose (HPC) [41].

Buruaga et al. [83] dissolved a water-soluble polymer [poly(ethylene oxide) (PEO)] in the PU dispersion and fibers were obtained from electrospinning of the resulting mixture. The template polymer (PEO) was removed from electrospun fibers by water extraction, then they obtained pure PU fibers. The authors offered a new perspective for the preparation of micro and nanofibers by using aqueous dispersions for the preparation of water-insoluble PU fibers by electrospinning. Lee et al. [84] dissolved various polyblends of poly(vinyl chloride) and PU (Pellethane 2363-80AE) in a mixture of THF and DMF. They produced nanofibers in different ratios, with several electrospinning conditions and investigated the relationship between morphology and mechanical behavior of the resulting fiber mats. Point-bonded structures in the PU fiber mats increased with increasing PU composition and the mechanical properties of the fiber mats. In the study of Hong et al. [44], PU/organically modified MMT (O-MMT) nanocomposites were prepared via a solution intercalation method and electrospun. The authors investigated the effect of O-MMT on the morphology and physical properties of the PU/O-MMT nanofiber mats. To prepare the PU and PU/O-MMT nanofibers, 11 wt% of PU and PU/O-MMT solutions in a mixed solvent of DMAc/THF (7/3 w/w) were electrospun. Increasing the content of O-MMT resulted in the linearly increase of conductivities of the PU/O-MMT solutions and this decreased the average diameters of the PU/O-MMT nanofibers. Produced PU and PU/O-MMT nanofibers were uniform and not microphase separated. They achieved a well distributed and oriented MMT layers within the PU/O-MMT nanofibers. When the PU/O-MMT nanofibers were annealed, the exfoliated MMT layers hindered the microphase separation of the PU. Incorporation of MMT layers into PU nanofibers improved Young's modulus and tensile strength of PU/O-MMT nanocomposites. Akçakoca Kumbasar et al. [85] loaded β -CD into TPU nanofibers (**Figure 8**). They observed that TPU/CD nanofibers had higher fiber diameters compared to pure TPU nanofibers and fiber diameters increased with the increase in β -CD concentration. The authors also proved the inclusion complex formation capability of TPU/CD nanofibers by the phenolphthalein test method.

Hu and Yu [86] prepared shape stabilized bio-phase change material (PCM) by encapsulating the wax inside the PU nanofibers using coaxial electrospinning. The encapsulated bio-PCMs

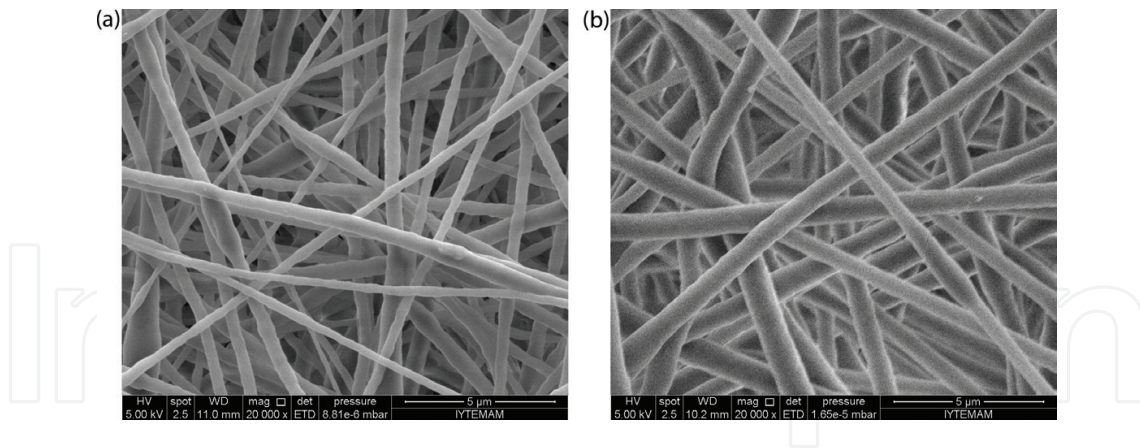


Figure 8. 30% β -CD loaded (a) 8% TPU, (b) 10% TPU nanofibers.

can potentially be used for thermal storage and thermal protection areas, which has appealing environmental advantages. The authors encapsulated the soy wax into PU fibers without being miscible with PU fibers and adjusted the wax content either by the concentration of wax/chloroform solution or flowing rate. Results of thermal analysis showed that the enthalpy increased as the wax content increase. The authors conducted 100 heating-cooling cycles and the thermal properties of the fibers were unaltered. The outer PU layer prevented the leakage of the bio-wax like a reservoir and it also enhanced the modulus and lowered the tensile strain. They produced uniform fiber morphology with a core-shell structure and a homogeneous wax distribution throughout the core of the fibers.

Vlad et al. [41] synthesized PU from hexamethylene diisocyanate (HDI), polytetramethylene ether glycol (PTMEG), and butanediol (BD). They mixed PU with different proportion of hydroxypropyl cellulose (HPC) for biomedical applications. Increase of HPC amount of sample provoked a decrease of contact angles. Similar behavior was observed for fibrinogen adsorption, which confirms that PU/HPC nanofibers are suitable in biomedical applications. Unnithan et al. [87] combined PU with two biopolymers, cellulose acetate (CA) and zein to produce an antibacterial electrospun nanofibrous scaffolds. In another study, they used a solution composed of dextran, PU, and ciprofloxacin HCl (CipHCl) drug for wound dressing applications [43]. They investigated the viability, proliferation, and attachment of fibroblasts to the PU-dextran and PU-dextran-drug scaffolds. Their results indicated that the composite mat has a good bactericidal activity and the cells especially interacted with the drug containing scaffolds.

Chen et al. [88] produced collagen functionalized-TPU nanofibers (TPU/collagen) by coaxial electrospinning technique (**Figure 9**) with a goal to develop biomedical scaffold. 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) was used as solvent for collagen and TPU. The authors carried out the cross-linking process by placing electrospun membrane (collagen (shell)/TPU (core) (8 wt%/3 wt%) together with a supporting aluminum foil in a desiccator using glutaraldehyde (GTA) (25% water solution) with different process time. Feasibility of PU/collagen core-shell construct as an optimal tissue engineering scaffold materials was supported by its high porosity and adequate pore size. Pig iliac endothelial cells proliferation in vitro demonstrated the feasibility and efficacy of using TPU/collagen composite nanofibers for improving cell-scaffold

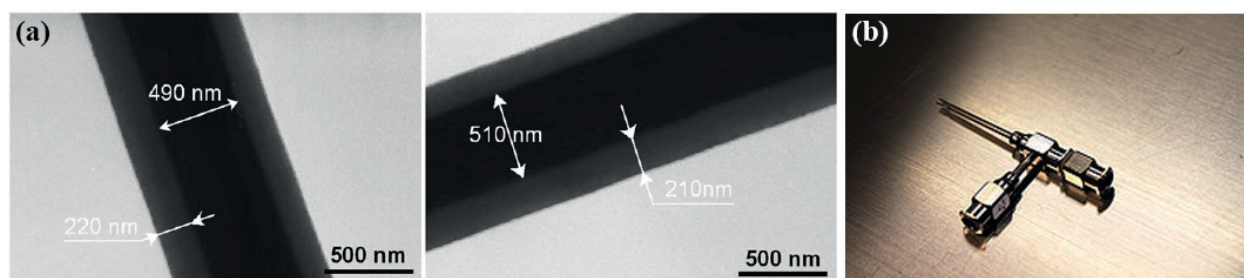


Figure 9. (a) Transmission electron microscopy image of the core shell nanofibers, (b) coaxial nozzle for electrospinning [89].

interactions pore size and these composite nanofibers had the characters of native extracellular matrix and may be used effectively as an alternative material for tissue engineering and functional biomaterials.

Huang et al. [90] electrospun random and aligned nanofibrous scaffolds based on collagen-chitosan-TPU blend to mimic the componential and structural aspects of the native extracellular matrix. They also investigated the optimal proportion to keep the balance between biocompatibility and mechanical strength. The scaffolds were cross-linked by GTA vapor to prevent them from being dissolved in the culture medium. The mechanical properties of the scaffolds were found to be flexible with a high tensile strength. Cell viability studies with endothelial cells and Schwann cells demonstrated that the blended nanofibrous scaffolds had good biocompatibility and aligned fibers could regulate cell morphology by inducing cell orientation. Chen and Chiang grafted collagen to PU fiber surface by low temperature oxygen plasma treatment, which could improve surface hydrophilicity to promote wound healing and facilitate covalent binding of collagen molecules to the plasma-treated PU surface [91]. After modification, the nanofibrous membrane's antimicrobial activity improved to ~100% inhibition of bacterial growth. Water absorption ability of membrane was increased, which facilitates its use as a functional wound dressing. Also, their results demonstrated that the nanofibrous membrane was better than gauze and commercial collagen sponge wound dressing in wound healing rate.

4.5. Mechanical properties of electrospun PU nanofibers

The electrospinning technique have the advantages of being simple, convenient, and inexpensive in comparison with conventional methods such as wet, dry, and melt spinning. Unfortunately, the practical applications have been limited because produced electrospun fiber mats have poor mechanical properties, low molecular orientation, and broad distribution of fiber diameter. Hence, an enhancement in both mechanical and physical properties of the electrospun fiber mats is very important from an industrial point of view [92]. TPUs present a class of polymers that possess a range of very desirable properties: they are elastomeric, resistant to microorganisms and abrasion, and have excellent hydrolytic stability and many commercially available TPUs can be used to make good electrospinning solutions [64]. Earlier studies on the electrospinning process have been more focused on the basic principles [2–4] and processing parameters like the voltage applied, tip-to collector

distance, and viscosity of solution [20, 26–28, 48]. The future use of electrospun PU materials in practical applications will require good mechanical properties. Thus, several authors recently investigated the mechanical properties of electrospun PU fiber mats [19, 40, 64, 65, 92–94].

Lee et al. [92] used Pellethane 2363-80AE and solved it in a mixture of THF and DMF (60/40, v/v) at room temperature at a concentration of 8 wt%. The authors investigated the mechanical behaviors of TPU by cyclic tensile tests. Produced electrospun TPU mats were composed of randomly oriented sub-micron fibers, where each fiber was restricted by physical netting and entanglements. They have seen almost linear elastic behavior until the fiber mats undergo breaking. Major cause of energy loss and stress softening at relatively low strains was the slippage of the electrospun fibers. At higher strains, the breaking of electrospun fiber at point-bonding junctions, as well as the slippage crossed fibers occurred as a further source of the dissipation energy. Pedicini and Farris [64] prepared the Pellethane 2103-80AE in DMF at room temperature at a concentration of 7% by weight and bulk samples by thermally processing plaques from polymer pellets. The uniaxial tensile tests results indicated that the behavior of the electrospun Pellethane 2103-80AE to be distinctly different from the bulk. Qualitatively, the electrospun mat is also elastomeric in nature, but the shape of the stress-strain curve for the electrospun material is not sigmoidal in contrast to bulk material. The curve is monotonic and its slope has not got an inflection. When they applied a strain to the electrospun mat, they got oriented fibers. They also concluded that the apparent molecular orientation in the electrospun fibers leads to the pronounced reduction in elongation to failure of the electrospun mat, relative to the bulk.

Cha et al. [93] synthesized shape-memory PU block copolymers to prepare electrospun non-wovens. The authors prepared PU solutions in a mixture of DMF and THF, and electrospun PU non-wovens with hard-segment concentrations of 40 and 50 wt%. The average diameter of low viscosity (ca. 130–180 cPs) beaded electrospun fibers was about 800 nm. In contrast, the average diameter of high viscosity (ca. 530–570 cPs) electrospun fibers was about 1300 nm. The mechanical properties of the electrospun PU non-wovens were investigated and found the increase in the hard-segment concentration increased the tensile strengths as well as the viscosities. Also, because of a difference in the velocities of the drum collectors, the tensile strength in the machine direction was higher than that in the transverse direction. Prepared PU non-wovens have a shape recovery of more than 80% that included hard-segment concentrations of 40 and 50 wt%.

The main weakness of electrospun nanofibrous membrane structures seems to be their poor mechanical properties caused by relaxation processes occurring immediately after fiber formation, at which a certain degree of molecular orientation is lost. With the aim to overcome this problem, some researchers combined single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) (**Figure 10a**) [94] to prepare PU nanocomposite fibers and achieve a significantly enhanced Young's modulus [19, 40, 95].

Sen et al. [19] demonstrated the effect of the chemical functionalization of SWNTs on the mechanical properties of SWNT-reinforced composites of electrospun PU nanofibers. The tensile strength of ester functionalized and as-prepared SWNT-PU membranes is enhanced

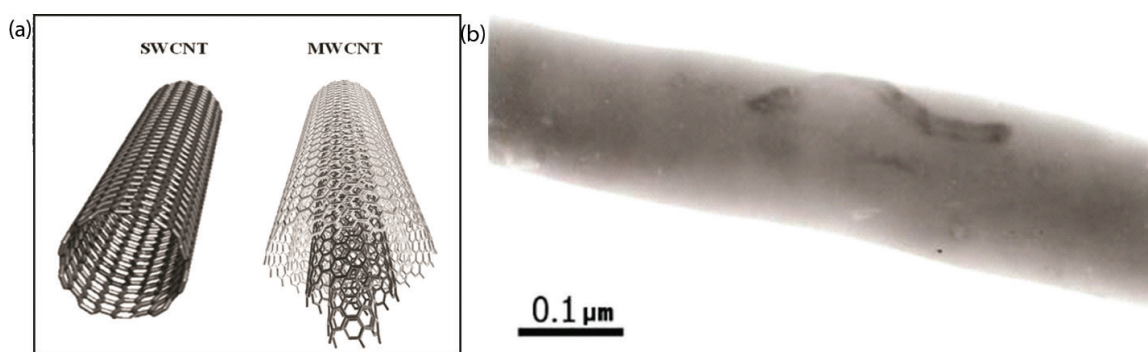


Figure 10. (a) TEM images of MWNTs/PU nanofibers and multi-wall carbon nanotube (MWCNT) [94]. (b) Schematic diagrams of single-wall carbon nanotube (SWCNT) [95].

by 104 and 46%, respectively as compared to electrospun pure polyurethane membranes. The tangent moduli of as-prepared and ester functionalized SWNT-PU membranes were also higher than the control PU membranes and were 215 and 250%, respectively.

Liu and Pan [95] produced MWNTs/PU composite nanofibrous membranes (**Figure 10b**). They used a thermal treatment method to improve the comprehensive properties of the membranes. They reported that the proposed thermal treatment method effectively improved the conductivity and mechanical properties of the nanomaterials, with 3 wt% of MWNTs, the conductivity of the membranes reached $8.29 \times 10^{-5} \text{ Scm}^{-1}$, which was nearly three orders higher than that of the untreated sample and the tensile strength and the modulus increased more than 50% after thermal treatment. PU and PU/multi-walled carbon nanotube (MWCNT) nanocomposite nanofibers, both with diameters of 350 nm, were prepared by Kimmer et al. as well [40]. The appearance of smaller nanowebbs in PU/MWCNT nanofiber structures with diameters of 20–40 nm was observed. They attributed the existence of these structures to the occurrence of strong secondary electric fields, which were created between individual conducting MWCNTs (distributed in the PU/MWCNT nanocomposites). From the TEM images individual and very well aligned MWCNTs can be seen in the outer surface of the main nanofiber from which nanoweb fiber was created. However, the authors did not investigate the mechanical properties of the prepared electrospun fiber mats.

Cross-linking the nanofibrous mats is another way to improve the mechanical properties. Theron et al. [65] modified a medical standard TPU (Pellethane 80A) with latent cross-linkable groups; and they determined the effect of subsequent cross-linking on viscoelastic properties and degradation resistance. They confirmed the successful cross-linking by insolubility of the materials. Pellethane was cross-linked with containing an increasing number of pentenoyl groups. Cross-linking decreased (up to 42%, $p < 0.01$) the hysteresis and creep (44%, $p < 0.05$), and significantly improved the degradation resistance in vitro. Modified Pellethane was also electrospun into tubular grafts and with UV irradiation they were cross-linked to make them insoluble. Prototype grafts had a burst pressure of $>550 \text{ mmHg}$, and for uncross-linked and cross-linked samples, it was 12.1 ± 0.8 and $6.2 \pm 0.3\%/100 \text{ mmHg}$, respectively. They concluded that the modification of Pellethane with PCL occurred on the carbamate nitrogen and cross-linking resulted in improved viscoelastic properties. Although there were some

decrease in tensile strength and strain, the polymers had sufficient strength and extensibility. They suggested to use these cross-linked materials such as vascular grafts where repetitive and relatively low stresses is encountered.

5. Potential applications of electrospun PU nanofibers

PU nanofibers prepared by electrospinning technology may have almost circular cross-sections, smooth surfaces, and diameters ranging from a few nanometers to several micrometers. Electrospun nanofibers have great applicability for drug delivery applications [16, 96–101], medical implants [102], nanocomposites for dental restoration [103], preservation of bioactive agents [104, 105], tissue engineering [12, 106], wound dressing [21, 43, 82], biosensors [107, 108], molecular separation [109], filters [45, 110, 111], and protective clothing [112–114]. Potential applications of electrospun PU nanofibers are discussed in depth below.

5.1. Biomedical applications

The importance of electrospinning, in general, for biomedical applications like wound dressing, drug release, tissue engineering, medical implants etc. is emphasized in this part of the chapter. The focus is on the active substances combined with PU and blends of PU that have been electrospun and also on the modifications that have been carried out in conventional electrospinning apparatus.

PU, due to their structure/property diversity, are considered one of the most bio- and blood-compatible materials known today. Properties like durability, fatigue resistance in tensile, compression or shear, elasticity, compliance, “elastomer character,” and propensity for healing became attainable via PU. Furthermore, modification via hydrophilic/hydrophobic balance or by attachments of biologically active species to the PUs is possible [37].

Due to their higher surface area to volume ratio, nanofiber mats have been studied for applications as drug delivery carriers. The blending (or mixing) technique is a common choice for the nanofiber functionalization [9]. Verreck et al. [96] prepared PU nanofibers containing model drug itraconazole and ketanserin, using DMF and dimethylacetamide (DMAc) as solvent, respectively. The collected non-woven fabrics released the drugs at various rates and profiles based on the nanofiber morphology and drug content. They used a specially designed release apparatus based around a rotating cylinder for release studies. They loaded 10% ketanserin and 10 and 40% itraconazole to the PU nanofibers. At low drug loading, itraconazole was released from the nanofibers as a linear function of the square root of time. They did not observe initial burst release. They explained the faster initial release of ketanserin versus itraconazole with (1) higher drug solubility of the ketanserin in the polymer and (2) increased drug diffusivity in the polymer. They also observed that the obtained fiber diameters did not significantly influence the initial release rate. Fiber diameters for the ketanserin loaded samples were between 0.5 and 2 μm , 10% itraconazole loaded were 2 μm and 40% loaded samples were 0.3–0.7 μm . They observed a biphasic release pattern for ketanserin in which

two sequential linear components. The authors correlated these release phases temporally with (1) drug diffusion through the polymer and (2) drug diffusion through formed aqueous pores.

Akduman et al. [99] prepared nanofiber mats of TPU containing naproxen (NAP) from 8 to 10% (w/w) TPU/DMF solutions. The amount of NAP in the solutions was 10 and 20% based on the weight of TPU and the collection periods were changed to 5, 10, and 20 h. The diameters of the nanofibers were significantly affected by the TPU concentration; however, the NAP loading and percentage of NAP did not have a significant effect on the fiber diameters. They investigated the release characteristics of fiber mats by the total immersion method in the phosphate buffer solution at 37°C and performed the characterization of the produced NAP-loaded TPU mats. They observed that the diffusion paths correlated to the nanofiber collection period has a significant effect on the release characteristics of the drug. Short collection periods resulted burst release of the drug. Beside, higher drug loading (20% w/w_{polymer}) caused higher drug release rate. The drug that had previously leached from the nanofiber mat formed channels through the matrix and that these channels lead to higher release rates of the drug. As a result, the authors suggested that in drug-loaded electrospinning studies, the produced mats should be collected for at least 20 h for a one needle electrospinning system, and drug loading should not exceed 10% for better controlled release rates (**Figure 11**).

Polymeric nanofiber matrix has similar structure with the nano-scaled non-woven fibrous extra cellular matrix (ECM) proteins, thus it can be considered as potential candidate for ECM-mimetic material [115]. A successful tissue engineering nanofibrous material should allow cell attachment and proliferation. Most of the surface modifications are related to the biocompatibilities of polymeric tissue engineering scaffold and to the immobilizations of biomolecules that can be specifically recognized by cells on the biomaterials [9]. In the study of Unnithan et al. [43] prepared an antibacterial electrospun scaffold by electrospinning of a solution composed of dextran, polyurethane (PU), and ciprofloxacin HCl (CipHCl) drug. They used dextran, which is a versatile biomacromolecule. Dextran can be used by blending with either water-soluble bioactive agents or hydrophobic biodegradable polymers for biomedical applications for preparing electrospun nanofibrous membranes. They investigated the interaction

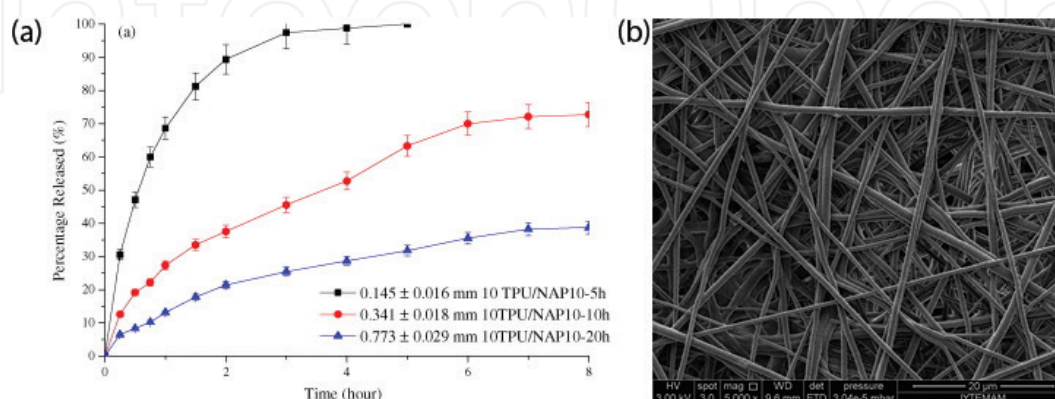


Figure 11. (a) Percentage release of NAP from (■) 5 h collected-, (●) 10 h collected-, and (▲) 20 h collected 10TPU/NAP10 mats by the total immersion technique during (b) SEM image of a NAP-loaded TPU nanofibers [99].

parameters between fibroblasts and the PU-dextran and PU-dextran-drug scaffolds such as viability, proliferation, and attachment. Their results indicated that the cells interacted favorably with the scaffolds especially the drug containing one. The authors concluded that the introduced scaffold might be an ideal biomaterial for wound dressing applications.

Amoroso et al. [116] utilized two fabrication modalities to induce controlled alterations in fiber network topology. They investigated the variation of collecting mandrel translation velocity, and concurrent electrospaying of cell culture medium with or without cells or rigid particulates to emulate the maximum possible micro-inclusion stiffness. Once, they electrospun poly(ester urethane) urea (PEUU) without modifications to the process, then electrospun it "wet" by concurrently electrospaying cell culture medium onto the target. The authors studied the effect of cell and particulate inclusion into the fiber scaffold matrix. Authors used either vascular smooth muscle cells or polystyrene microspheres. They electrospayed the cells at concentrations of 2 and 6 million/mL and electrospayed the microspheres at 7 million/mL into the cell culture medium. The inclusion of cell culture medium into the construct resulted in a dramatic change in scaffold microarchitecture. Particulates and cells would act as additional fiber bonding sites, increasing the effective fiber intersection density and consequently raising the level of mechanical anisotropy. Practically, wet processing and mandrel rastering can be successfully implemented as tools to reliably modify scaffold microarchitecture without altering fiber alignment.

In the study of Carlberg et al. [117], electrospun fibrous PU scaffolds have been studied as substrate for embryonic stem cells cultivation and neuronal differentiation. The authors prepared electrospun scaffolds composed of biocompatible PU resin (Desmopan 9370A) with a vertical electrospinning setup. They showed that the embryonic stem cells displayed favorable interaction with the substrate, spreading outgrowths, establishing connections to adjacent cells and attaching to individual fibers. Immunocytochemistry results showed that fibers can support neuronal differentiation in embryonic stem cell cultures. Their results indicated that physical cues induced by the fibrous scaffolds affect stem cells toward a neuronal cell fate. Hence, they claimed that these scaffolds are potential cell carriers in neural tissue engineering repair and rehabilitation of the adult human nervous system.

Grasl et al. [118] *in vitro* studied the mechanical homogeneity of electrospun small diameter polyurethane grafts as well as spontaneous attachment, proliferation, and adhesion molecule expression of endothelial cells. They prepared the prostheses from 5% (w/w) PU (Pellethane 2363-80A; DOW Plastics) in 1,1,1,3,3,3-hexafluoro-2-propanol and used a mandrel with the diameter of 2.1 mm and the length of 170 mm. It was rotated at 200 rpm and oscillated 150 mm in the transverse direction at a speed of 8 mm/s. The authors measured the axial and circumferential tensile strengths and they found that they were two-fold higher in the circumferential direction. They fabricated highly uniform small diameter polyurethane grafts and easily achieved the endothelial cells attachment without precoating the fiber matrix. They also observed that the synthetic graft surface neither impaired the endothelial response toward IL-1b stimulation nor did it adversely affect the regulation of expression of endothelial adhesion molecules.

To assess mesh architecture sensitivity to manufacturing parameters, Mitchell and Sanders [119] developed a system for controlled electrospinning of fibro-porous scaffolds for tissue

engineering applications. Their intent was to achieve scaffolds with well-controlled fiber diameters and inter-fiber spacing. They used a custom, closed-loop controlled, electrospinning system. With their system, they were capable of producing TPU meshes with fiber diameters ranging from 5 to 18 μm with variability less than 1.8%; inter-fiber spacing ranged from 4 to 90 μm with variability less than 20.2%. They concluded that their system has potential use in biomedical applications where meshes with controlled fiber diameter and inter-fiber spacing are needed.

Antibacterial and antimicrobial agents such as silver (Ag) nanoparticles [120], 4-vinylpyridine (4VP) [36], or streptomycin sulfate [87] loaded electrospun PU nanofibers were also developed for biomedical applications. Some of these studies combined the antibacterial properties of PU nanofibrous membranes with wound dressing applications.

Yao et al. [36] developed a novel antibacterial material by surface modification of electrospun PU fibrous membranes, using a plasma pretreatment, UV-induced graft copolymerization of 4-vinylpyridine (4VP), and quaternization of the grafted pyridine groups with hexylbromide. Poly(4-vinyl-*N*-hexyl pyridinium bromide) was grafted to the surfaces to achieve antibacterial activities. They showed that the morphologies of PU fibrous membranes changed slightly during the modification process. The tensile strength of PU fibrous membranes decreased after surface modification. After the modification, the tensile strength of PU fibrous membranes from 7% (w/v) decreased from 3.27 to 1.99 MPa, losing almost 40% of tensile strength. They observed smaller decreases in the tensile strength with the increasing solution concentration. The largest diameter of fibers belongs to a concentration of 11% (w/v) and the loss of tensile strength was approximately 16%. They carried out the antibacterial assays with surface modified PU fibrous membranes electrospun from 10% (w/v). Their modified PU fibrous membranes possessed highly effective antibacterial activities against Gram-positive *Staphylococcus aureus* (*S. aureus*) and Gram-negative *Escherichia coli* (*E. coli*) and the authors claimed that these fibrous membranes may have a wide variety of potential applications in high-performance filters, protective textiles, and biomedical devices.

Sheikh et al. [120] synthesized PU nanofibers containing silver (Ag) nanoparticles. They carried out the synthesis of silver nanoparticles by exploiting the reduction ability of DMF, which is used mainly to decompose silver nitrate to silver nanoparticles. Typically, a sol-gel consisting of AgNO_3 /PU was electrospun and aged for 1 week. Ag nanoparticles were created in/on PU nanofibers. They examined the durability of the silver NPs on the PU nanofibers by harsh successive washing. Their results confirmed the good stability of the nanofiber mats. The authors used *E. coli* and *Salmonella typhimurium* to check the antimicrobial influence. Consequently, antimicrobial tests indicated that the prepared nanofibers have a high bactericidal effect and they have potential for using as antimicrobial agents.

In the study of Unnithan et al. [87], an antibacterial electrospun nanofibrous scaffolds with diameters around 400–700 nm were prepared by physically blending PU with two biopolymers, cellulose acetate (CA) and zein. They used PU as the foundation polymer, blended it with CA and zein to achieve better hydrophilicity, cell attachment, proliferation and blood clotting ability. They incorporated an antimicrobial agent, streptomycin sulfate into the electrospun fibers and characterized the interaction between fibroblasts and the PU-CA and

PU-CA-zein-drug scaffolds. They investigated the viability, proliferation, and attachment of the fibroblasts on the nanofiber scaffolds and observed that the produced composite nanoscaffold has better blood clotting ability than pristine PU nanofibers. They found that the incorporation of CA and zein to the nanofiber membrane enhanced the bioactivity of nanofiber mats, as well as the hydrophilicity. CA and zein also provided a moist environment for the wound.

Nanofibrous materials provide a realistic representation of the native tissue than any other substrate with respect to general cell culture. An advantage of using nanofibrous material is they can also be produced in a highly aligned orientation. The orientation of the nanofibers plays an important role in the study of cell behavior whose native environments consist of highly aligned ECM [121]. Most researchers carried out cell culture tests to characterize the developed nanofibers for wound dressing and scaffold purposes. In **Figure 12**, representative cell-cultured images of nanofibers were given.

Khil et al. [21] prepared PU nanofibrous membrane and evaluated its performance as a wound dressing. They saw that the produced nanofibrous wound dressing showed controlled evaporative water loss, good oxygen permeability, and promoted fluid drainage ability due to porosity of nanofibrous membrane. Neither toxicity nor permeability to exogenous microorganism was observed with the nanofibrous membrane. They also observed that the epithelialization rate was increased confirmed by histological examination, and they were able to control the exudate in the dermis by covering the wound with the electrospun membrane. Thus, they claimed that nanofibrous PU membrane prepared by electrospinning could be properly employed as wound dressings.

Kim et al. [39] prepared a blended nanofiber scaffold using synthetic and natural polymers, PU and gelatin, respectively, to prepare a material for wound dressing. They produced a gelatin/PU blended nanofiber scaffold and examined these scaffold by contact angle, water uptake, mechanical property, recovery, and degradation tests, and cellular response. They observed that, with the decreasing amount of gelatin in the blended solution, the contact angle increased, in the meanwhile water uptake of the scaffold decreased. The mechanical tests showed that, the blended nanofibrous scaffolds had an elastic character, as expected, and the elasticity of the scaffold increased with the increasing amount of PU. Beside, gelatin

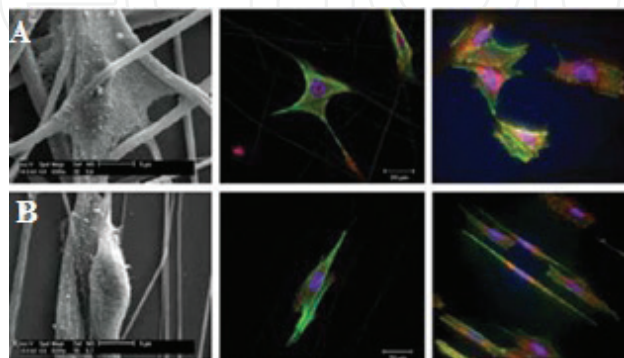


Figure 12. SEM images of (a) cells on randomly oriented nanofibers, (b) cells on aligned nanofibers and their fluorescence images [121].

amount increased the cell proliferation with the same amount of culture time. These results indicated that produced gelatin/PU blended nanofiber scaffold has a potential for wound dressing applications.

Lee et al. produced nanofiber-based artificial renal microfluidic chip by electrospinning method [122]. Authors have developed polyethersulfone and PU-based nanofibers and combined these webs with the poly(dimethylsiloxane)-based microfluidic platform top to create a chip-based portable hemodialysis system. They measured the filtration capability of this dialyzing chip and found that during the filtration and the transportation of the blood cells, they were not mechanically affected.

5.2. Other applications

In addition to biomedical applications, other application fields such as filtration, sensors, nanoweb lamination based on electrospun PU polymer nanofibers have been steadily extended in recent years. One main interest of electrospun polymer nanofiber non-woven mesh is for filtration application and it is best represented by relevant academic researches, in which many applications are in the field of filtration systems.

Filtration efficiency is closely associated with the fiber fineness and it is one of the most important concerns for the filter performance [10]. In general, due to the nanodimensions of the nanofiber, nanofiber mats have very high surface area to volume ratio and which results in high surface cohesion. Hence, tiny particles of the order of <0.5 μm can be easily trapped in the electrospun nanofibrous-structured filters. Thus, it is possible to improve the filtration efficiency with nanofibrous materials. In this manner, PU-based electrospun nanofibers could also be used as a filtration material because they are resistant to microorganisms and abrasion, and also have high hydrolytic stability [40].

Sambaer et al. [45], synthesized a PU based on 4,4'-methylenebis(phenylisocyanate) (MDI), poly(3-methyl-1,5-pentanediol)-alt-(adipic, isophthalic acid) (PAIM) and 1,4-butanediol (BD) in molar ratio 9:1:8 at 90°C for 5 h. They used needleless electrospinning apparatus and a supporting polyester fabric for collecting nanofibers with a speed of 0.16 m/min. Nanofibers were collected on the fabric with square ordering of electroconductive 9601 of fiber resistant, 95 g/m^2 of area mass, electroconductive 5 mm of thread distance. They evaluated the filtration efficiency of the nanofibers by experimental particle penetration efficiency according to EN 779 standard at the constant air flow rate 5.7 cm/s with aerosol particles. They also created 3D structure model from SEM image of the filter and compared this 3D structure model representing real filter structure with the corresponding experimental data. They obtained good agreement between both datasets.

In addition to fulfill the more traditional purpose in filtration, the nanofiber membranes fabricated from some specific polymers or coated with some selective agents can also be used as, for example, molecular filters or affinity membrane applications. Such filters can be applied to the detection and filtration of chemical and biological weapon agents [10].

Air filters separate particles mainly by the physical entrapment but also electrokinetic capture plays an important role in the air filter [46]. Through the filtration process particles collide

with the filter medium. The filter medium that has an electrical charge and has attractive forces on the surface capture the particles. Due to attractive forces between charges or induced forces, particle deposition can occur on the surface. PU cationomers (PUCs) containing different amounts of quaternary ammonium groups were synthesized and successfully electrospun into non-woven nanofiber mats for use in antimicrobial nanofilter applications in the study of Jeong et al. [46]. The PUCs showed antimicrobial activities against *S. aureus* and *E. coli*. Due to the increased charge density of the PUC solutions, the average fiber diameters decreased with increasing quaternary ammonium group content. The PUC nanofibers showed adhesion between nanofibers with various bonding sites, yielding mats with a film-like character and structural integrity. The authors specified that, particle deposition could occur due to attractive forces between charges or induced forces. Therefore, they expected that the developed PUC nanofiber mats can exhibit a better performance as air nanofilters due to their surface electrical charges.

Ouyang et al. [123] reported the preparation of PU filled with carbon nanotubes and Ag nanoparticles (PU-MWCNT-AgNP) and the subsequent fabrication of a novel non-enzymatic amperometric biosensor for analytical determination of hydrogen peroxide. They conducted cyclic voltammetry experiments to indicate PU-MWCNT-AgNP nanofiber-modified electrodes have high electrocatalytic activity on hydrogen peroxide. The authors also carried out chronoamperometry measurements to illustrate developed electrospun sensor has high sensitivity for detecting hydrogen peroxide. Their study confirms that there is a remarkable synergistic effect of MWCNTs and AgNPs on the significant improvement of the conductivity of electrospun nanofibers. MWCNTs and AgNPs filling also affect the electrocatalytic activity, and the sensitivity of the fabricated non-enzymatic sensor. Their results indicated that the created biosensor for detecting hydrogen peroxide has a sensitivity of $160.6 \mu\text{A mM}^{-1} \text{cm}^{-2}$, a wide linear range from 0.5 to 30 mM and a detection limit of $18.6 \mu\text{M}$ ($S/N \geq 3$) and they claimed that PU-MWCNT-AgNP nanofibers have wide potential applications in bio-analysis and detection.

In most electrospinning setup, a conductive material is used as a collector, then produced nanofiber mat is removed from this material. But for some applications it is possible to use a nonwoven or casual fabric as supporting material. US20100304108 describes a stretchable, non-woven nanofiber fabric. It allows vapor transport, capable of conforming to body parts but is impermeable to water. This breathable fabric could be useful in high-performance apparels and personal care products [124]. Inventors combined the fabric with different substrates to form a laminate (**Figure 13a**). Illustration of a composite breathable fabrics with electrospun membrane is given in **Figure 13b** [125]. Ahn et al. [24], electrospun PU nanofibers on to a water repellent nylon fabric and compared its waterproof and breathable properties with sole nylon fabric and polytetrafluoroethylene laminated nylon fabric. The aim of the authors is to develop an outdoor clothing with increased performance. A nanoweb laminate was prepared by laminating a PU electrospun nanoweb to the face fabric followed by heat treatment at 160°C in a tenter. The authors evaluated the water resistance and water vapor transmittance of the fabrics were under simulated microclimate. They examined the clothing microclimate and subjective sensations under normal and rainy atmospheric conditions. Their results indicated that the nanoweb laminate compared to the polytetrafluoroethylene laminate, had a higher water

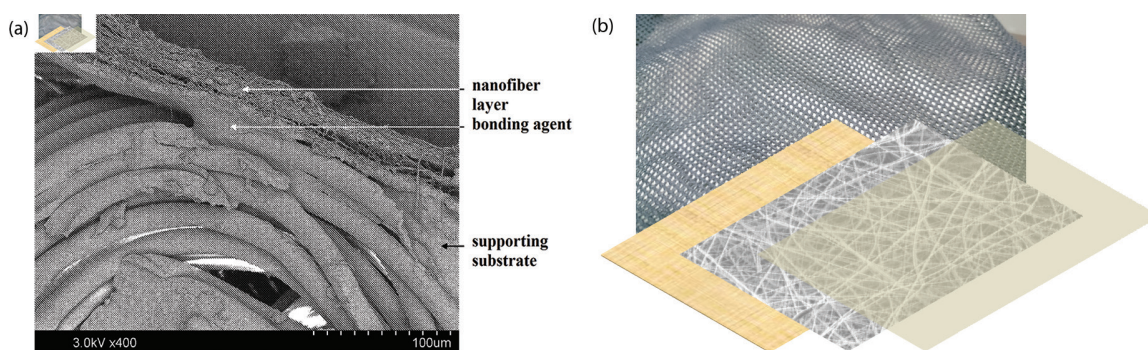


Figure 13. (a) A non-woven layer laminated fabric (US20100304108). (b) Illustration of a composite breathable fabrics with electrospun membrane [125].

vapor transmission rate but lower water resistance. They conducted wearing tests in a normal, warm environment to simulate exercising or sweating, to reveal the PU nanoweb-laminated clothing provided a more comfortable clothing microclimate than polytetrafluoroethylene-laminated clothing. In the rainy test conditions, they did not observe any difference between the polytetrafluoroethylene and the nanoweb-laminated clothing.

6. Conclusions

The main advantages of electrospinning process are the production of nanometer scale fibers with large surface areas, good mechanical properties, easy functionalization of these fibers for various purposes such as protective clothing, drug release material, or an air filter. These advantages provide many opportunities for their use in wide range of different applications [126]. PU is often chosen as a material for composing a nanoweb due to its chemical stability, mass transport, good mechanical properties, and also excellent nanofiber forming characteristic. Main reason for choosing PUs in electrospinning is that, the properties of PUs can vary in a wide range, so it is possible to adopt PUs to many applications by varying the structure of PUs. Electrospun PU nanofiber mats exhibiting good mechanical properties may have a wide variety of potential applications in high-performance air filters, protective textiles, wound dressing materials, sensors, in biomedical applications, drug delivery, as well as in wound dressing studies because of its good barrier properties and oxygen permeability. For these applications, electrospinning assembly can be varied in different ways for combining materials properties with different morphological structures. PUs can also be mixed either with a natural polymer or with a synthetic polymer for special applications such as collagen, dextran, and hydroxypropyl cellulose (HPC). Beside, from an industrial point of view, an enhancement in both mechanical and physical properties of the electrospun fiber mats is very important and it is possible to mix the PUs with SWCNTs or MWCNTs to overcome this problem.

Although there is ever increasing literature on use of PU nanofibers for various applications but still the field is in its infancy. For example, there are also lots of questions for biomedical applications, like interaction of scaffolds with biological systems, toxicity, in vivo studies etc.

There is no doubt that PU electrospun materials are going to take major place in future for above mentioned applications. Thus, all these applications have to be thoroughly investigated before the technology can be used for any real practical application.

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