Exploring Bioinspired Polymer Actuators via Electrospinning

Subjects: Polymer Science

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Nature has always been a source of inspiration for the development of novel materials and devices. In particular, polymer actuators that mimic the movements and functions of natural organisms have been of great interest due to their potential applications in various fields, such as biomedical engineering, soft robotics, and energy harvesting. The development and actuation performance of electrospun fibrous meshes with the advantages of high permeability, surface area, and easy functional modification, has received extensive attention from researchers.

electrospinning bioinspired actuators stimuli-sensitive hydrogels

1. Introduction

Nature has long served as a boundless source of inspiration for scientists and engineers seeking to develop innovative technologies. The realm of bioinspiration, specifically, aims to emulate and harness the extraordinary capabilities observed in biological systems [1][2]. One area of particular interest in biomimetics is the development of polymer actuators inspired by nature [3]. Polymer actuators can convert electrical, thermal, or chemical energy into mechanical motion. They are composed of polymeric materials that can undergo significant changes in shape, size, or stiffness in response to a stimulus. This unique property makes them ideal for use in a wide range of applications, including (soft) robotics, biomedical devices, energy harvesting systems, and artificial muscles [4][5][6]. A well-known example of a bioinspired actuator is the artificial muscle, which aims to replicate the contractile behavior of natural muscles. Natural muscles are composed of a network of protein fibers that can slide past one another to generate force and motion [7]. Other examples of natural actuations that have inspired materials scientists include the movement of plant tendrils [8] and the morphing of butterfly wings [9]. Tendrils are able to wrap around support structures by combining changes in turgor pressure with differential growth, while butterfly wings can change their color and shape through the controlled movement of scales and ridges [10][11].

Researchers have developed various bioinspired polymer actuators (BiPAs) with unique properties and based on various smart polymers such as stimuli-sensitive hydrogels, shape-memory polymers (SMPs), or electroactive polymers (EAPs) [12][13][14][15]. One of the most notable features of these materials is their ability to undergo large, rapid changes in shape and size in response to stimuli such as temperature, humidity, light, or electric fields [5][6][16][17][18][19].

In addition to their responsive properties, stimuli-sensitive polymers can also exhibit remarkable strength, flexibility, and durability [11][18][20][21][22]. This makes them highly desirable for applications such as soft robotics and wearable

devices, where flexibility and durability are key requirements [23]. In recent years, significant advancements have been made in the synthesis, characterization, and application of these smart polymers, propelling them into exciting new territories. However, despite the many promising features of BiPAs, there are also significant challenges associated with their development and use.

Electrospinning is a widely used technique for fabricating polymeric fibrous meshes, as it allows for precise control over the fiber diameter and alignment, as well as the incorporation of various functional components (**Figure 1**) [24] [25]. The use of nature as a source of inspiration for the design of electrospun polymer actuators has led to the development of devices that can replicate the movements and functions of natural organisms. For example, some electrospun polymer actuators have been designed to mimic the movements of muscle fibers [26], while others have been inspired by the motion of insects, plants, or other organisms. By controlling the parameters of electrospinning, such as the solution viscosity, flow rate, and applied voltage, it is possible to tune the morphology and mechanical properties of the resulting fibers [27]. One of the advantages of electrospun polymer actuators is their ability to exhibit multiple functions, such as responding to various stimuli and performing multiple tasks such as locomotion, sensing, color changing, etc. [28]. Moreover, electrospinning can be combined with other techniques such as 3D printing and microfabrication to create complex and functional structures.

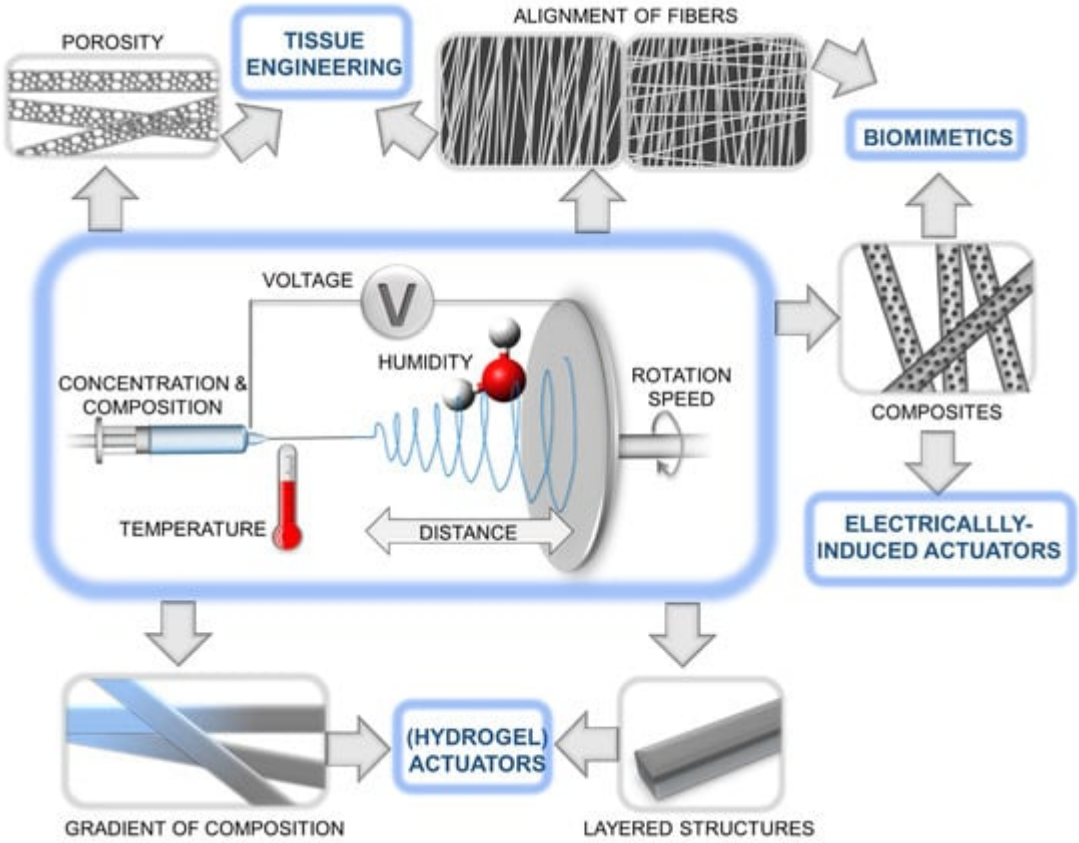

Figure 1. Schematic illustration of the electrospinning process along with various architectures of electrospun fibers and potential applications.

2. Biomimetic Inspiration for Synthetic Actuators

Biological systems, honed by millions of years of evolution, offer an extraordinary repertoire of intricate and adaptive movements that have inspired the development of cutting-edge synthetic actuators. As researchers have delved deeper into the mechanisms governing stimuli-sensitive locomotion and movements in living organisms, they have uncovered fascinating adaptations that not only showcase remarkable performance but also unparalleled energy efficiency [14][22]. For instance, animals rely on muscle contractions for various movements, such as walking, flying, and swimming [29]. Muscles are composed of bundles of specialized fibers called myofibrils, which are made up of proteins called actin and myosin. When stimulated by electrical signals from the nervous system, actin and myosin interact, causing the myofibrils to contract and generate force. This contraction allows organisms to produce a wide range of reversible movements, such as walking, grasping, or flexing muscles [30][31]. Tendons and ligaments are fibrous connective tissues that attach muscles to bones (tendons) and bones to other bones (ligaments) (**Figure 2**a). They are primarily composed of collagen fibers, which provide strength and flexibility. Tendons transmit forces from muscle contractions to bones, allowing movement at joints, while ligaments provide stability and limit joint movements to prevent excessive strain [32]. Marine invertebrates possess specialized fibrous structures that enable reversible movements. For example, certain types of tentacles in jellyfish or anemones contain fibrous proteins that can rapidly extend or contract, allowing these organisms to capture prey or withdraw from potential threats [33]. Tropic or nastic responses in plants enable directional growth or movements to adopt new environments.

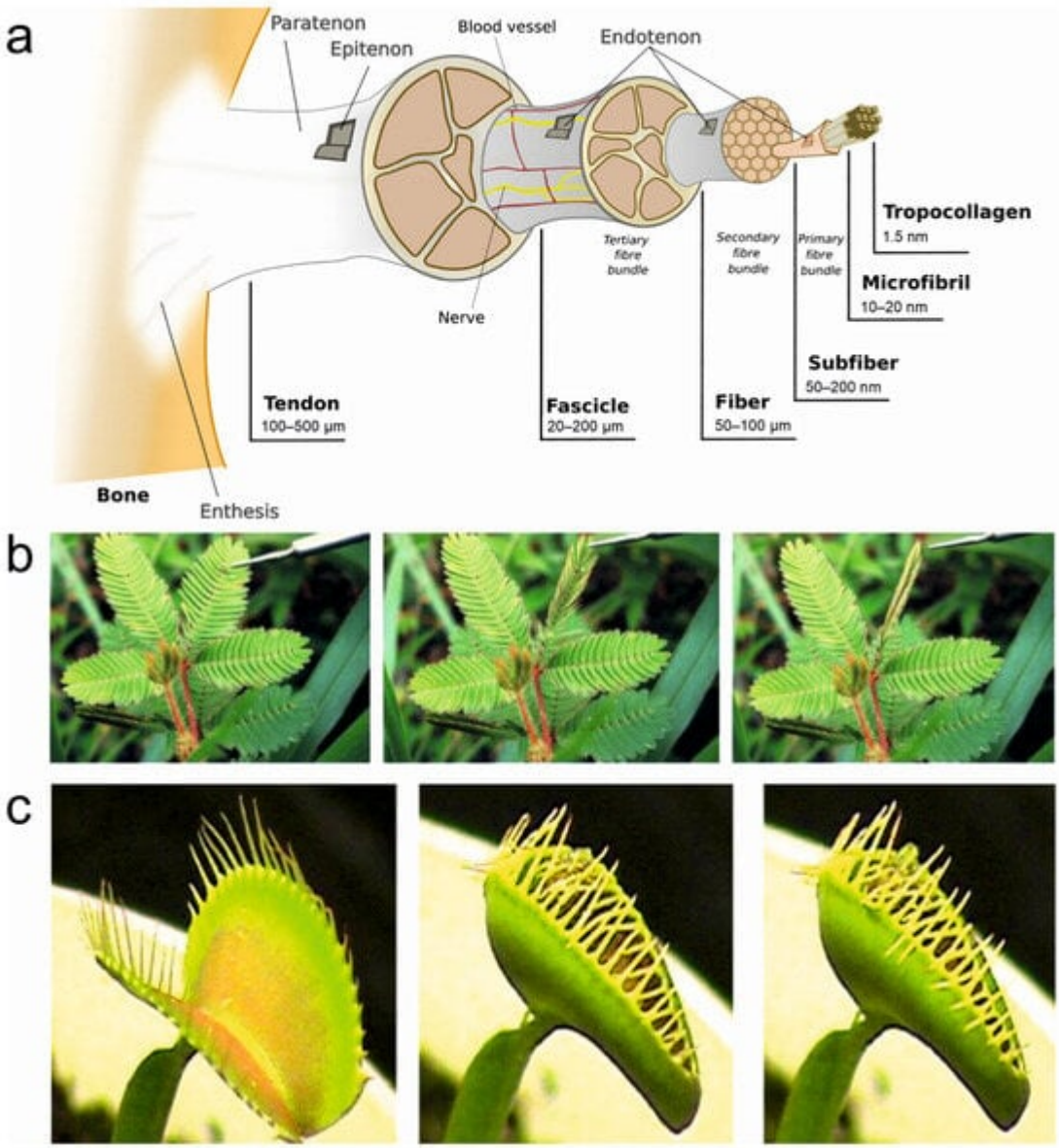

Figure 2. Representative actuating structures in living systems. (**a**) Hierarchical structure of the tendon/ligament. The tropocollagen crosslinked molecules are arranged in microfibrils, subfibrils, fibrils, fibers, and fascicles. Reprinted with permission from [34]. (**b**) Touch-induced folding/unfolding of mimosa leaflets. Reprinted with permission from [33]. (**c**) The snap–trap of the carnivorous Venus flytrap (*D. muscipula*) closes after the mechanical triggering of sensitive hairs, leading to a swift concave–convex curvature change in the two trap lobes. Reprinted with permission from [35].

Climbing plants, like vines, employ thigmotropism to sense and respond to physical contact [36]. They possess specialized fibrous structures, such as tendrils, which wrap around support structures when they come into contact with them [37]. By doing so, these plants can grow and climb upward, utilizing external structures for stability and support. The nastic movements in plants are reversible, non-directional responses to external stimuli that result in changes in the orientation of plant organs, e.g., rapid folding or drooping of leaves in the sensitive plant *(Mimosa pudica*) when touched. These movements are facilitated by specialized filaments or fibrous tissues within the plant structures, which undergo reversible changes in turgor pressure or cell elongation [35].

3. Hydrogel Actuators Created by Electrospinning

Many natural and artificial materials can show swelling and shrinkage behavior by responding to changes in environmental humidity. As examples, the skin of the human hands and feet forms wrinkles upon continued submersion in water [38] and pine cones can exhibit a folded shape on rainy days and an open shape when it is dry [39]. Especially in the case of pine cones, this motion relies on a bilayered structure of the individual scales that can change their conformation when the humidity is increased/decreased [40].

This phenomenon inspired the design of bilayer hydrogel actuators, in which one of the layers (called the active layer) can change its volume by means of swelling/deswelling effects [41]. The second layer (called the passive layer) is inert to the dimensional change. A macroscopic shape shift can be obtained as a result of generated stresses at the interface of the two layers. The resulting movements can be controlled by the variation in material types, thickness, mechanical characteristics in the bilayer system, sample size, and geometry. Electrospun hydrogel actuators are often based on thermoresponsive polymers (e.g., poly(*N*-isopropylacrylamide)—PNIPAM), which can uptake or release water as a function of temperature based on a phase separation upon heating (lower critical solution temperature—LCST) [42][43].

3.1. Hydrogel Actuators with Water and Temperature Sensitivity

Reversible movements of electrospun hydrogels were reported by a humidity-responsive bilayer actuator, which was created by combining an electrospun polyvinylpyrrolidone (PVP)/poly(acrylic acid) (PAA) active layer with a polyimide film as the passive layer [44]. This actuator showed bending movements when humidity was increased as result of swelling within the active layer and the created stress mismatch for the bilayer system. In this case, the properties of the active layer changed during actuation between a swollen hydrogel and a non-swollen polymeric layer, which presents the simplest concept for the design of reversible movements for electrospun hydrogel actuators.

A temperature-triggered swelling/deswelling response with increasing/decreasing sample volume was realized by electrospun hydrogels based on the copolymer of thermoresponsive NIPAM with a photoreactive 4-acryloylbenzophenone (ABP)—conjugated comonomer. The created crosslinked copolymer mats showed a rapid swelling behavior in an aqueous environment with a water content >60 wt%. As result of the LCST of PNIPAM, aggregates based on hydrogen bonding as additional temporary crosslinks can be created in hot water (deswelling). The prepared fibrous hydrogels showed a fast thermal response and a rapid self-recovery (74% within 10 s) after loading–unloading tensile cycles in water. Besides changes in material volume, real reversible movements were reported by hydrogels with a super-fast actuation behavior of less than one second [45].

One concept to adjust the bending movement for electrospun soft actuators is based on the variation in the thickness of the different layers as demonstrated for PNIPAM and cellulose nanocrystal (CNC) bilayer actuators [46]. The two layers included different amounts of CNCs, whereby the water uptake upon heating and cooling was influenced (decreased swelling with increased CNC content). A 3D geometry was obtained when the bilayer

system came into contact with water for the first time via anisotropic swelling of the two layers. Reversible shape shifts were observed by subsequent swelling/deswelling as a result of temperature changes between 20 °C and 40 °C. More interestingly, the direction of macroscopic shape shifts can be controlled.

As an alternative to that, the combination of electrospinning of a thermoresponsive PNIPAM membrane and 3D printing of different well-designed PNIPAM/clay patterns on electrospun membranes enables for the created internal stresses generated by swelling/deswelling effects to be guided [47]. Hence, complex shape geometries with controlled shape shifts could be obtained.

It has to be noted that most of the presented examples showed an actuation behavior based on swelling and deswelling effects, causing a stress mismatch in bilayer systems. Complex shape shifts can be obtained by cutting bilayer systems at different angles or by combining electrospinning and 3D printing, thus enabling macroscopic movements controlled by processing parameters (e.g., alignment of fibers). By contrast, SMPs can perform complex shape shifts by programming them into versatile temporary shapes (without requiring new synthesis). However, such electrospun hydrogel actuators, which provide shape-memory properties and are swollen during the whole shape-memory cycle, have not been reported so far. Shape-memory hydrogels often include hydrophobic crystallizable switching segments [48][49].

3.2. Light- and Electric Field-Responsive Hydrogel Actuators

Besides water and heat as stimuli to induce an actuation function, light-responsive electrospun hydrogel actuators inspired by the hierarchical structure of a whale baleen have been reported [50]. The actuators were designed via in situ polymerization of pyrroles on nanofiber-oriented electrospun and temperature-responsive P(NIPAM-ABP) hydrogels. The coating with polypyrroles on nanofibers enhanced mechanical strength (from 1.21 to 5.12 MPa of tensile strength) and enabled ultrahigh-efficiency of photothermal conversion. As a result of the porous structure of hydrogel nanofibers (high specific surface area), the speed of the light-responsive actuation could be accelerated. When the ultrathin hydrogel layer (15 ± 3 µm) was bonded to a polyethylene glycol diacrylate-cellulose nanofiber (PEGDA-CNF) composite hydrogel membrane by means of interfacial UV polymerization, an anisotropic bihydrogel actuator was obtained. This actuator showed various programmable complex deformations with a powerful force (it could grab up to 100 times its weight), rapid speed (1285.71°/s of folding, 32.73°/s of bending, and 434.36°/s of bending recovery), and was utilized to imitate a continuous crawling movement of a starfish.

3.3. Hydrogel Actuators with Multistimulus Response

In order to imitate the motion of soft materials such as living organisms, which act in an environment where multiple stimuli are simultaneously present, hydrogel actuators providing a multistimulus response were designed. When, e.g., a P(NIPAM-ABP) layer and a Fe_3O_4/polyacrylonitrile (PAN) layer are combined to obtain an anisotropic bilayer hydrogel actuator, multistimulus-responsiveness with programmable bifunctional synergistic movements can be realized [51]. Here, a bilayer structure was developed by the electrospinning of a PAN solution doped with Fe_3O_4 nanoparticles and a solution based on precursors for P(NIPAM-ABP). After crosslinking, a composite hydrogel, which was equipped with a thermoresponsive (P(NIPAM-ABP)) and a magnetoresponsive layer (Fe_3O_4/PAN), was

obtained. The Fe_3O_4/PAN layer could perform long-range directional navigation highly controlled by a magnetic field on account of the doping with magnetic nanoparticles. In addition, the efficiency of the Fe_3O_4 nanoparticles endowed the P(NIPAM-ABP) layer with fast remotely controlled photothermal-responsive deformations (178°/s) when NIR light was applied. Here, the resulting swelling/deswelling effects triggered macroscopic movements.

Depending on the functional groups in the hydrogel, the swelling behavior could also be dependent on pH. In this case, any pH-responsive group (e.g., acids, amines, or pyridines) in a hydrogel matrix can initiate pH-responsive swelling effects by deprotonation or protonation. As an example, thermo- and pH-responsiveness was realized in electrospun poly(NIPAM-co-AA) fibers, which were embedded within a passive TPU matrix [52]. The resulting composite had a gradient of the TPU along the thickness. At low pH value, the size of the demonstrator was controlled by the temperature (swelling at 6 °C, shrinkage at 40 °C). When the pH value was changed from pH = 3 to pH = 10, AA moieties were deprotonated and the generated charge repulsion increased the swelling. As a result, directed movements were obtained based on generated stresses in the composite and the angle, at which point fibers were embedded in the matrix that controlled the actuation direction.

4. Electrospun Shape-Memory Polymer (SMP) Actuators

A number of biological systems exhibit a shape change process when exposed to a wide variety of environmental changes, thus enabling sensing and responsive functionalities [12][53][54][55]. Synthetic materials can be programmed to intrinsically respond to environmental changes in a similar manner and have the potential to revolutionize materials science. One such example is shape-memory polymers, which can recover their original shape after being exposed to an external stimulus, such as heat, light, or a magnetic field [17][56][57][58]. These materials are unique as they can undergo a transition between a temporary shape and a permanent shape. The polymer is first programmed into a high-energy temporary shape by using a specific programming procedure. By exposure to an external stimulus, it reverts to its low-energy permanent shape. These polymers have attracted significant attention in recent years due to their potential use in a wide range of applications, including biomedical devices, aerospace, automotive, and textiles [17][48][56][59][60]. Recent studies have focused on the development of shape-memory electrospun fibrous meshes with actuation capabilities. These fibrous meshes have shown interesting advantages over bulk materials such as a faster recovery process, due to their high surface area (in the case of a thermally triggered process) and faster diffusion (in the case of a water-triggered process) [55][61]. They have also shown relatively high values of shape fixity and shape recovery ratios, with values ranging between 80% and somewhat higher than 90%. These benefits enable a versatile and customizable platform for developing advanced materials with enhanced mechanical, sensing, and actuation properties for various applications, including biomedical devices, smart textiles, and aerospace components [61]. However, most of these electrospun fibrous meshes are limited to a single, irreversible change in shape or pore size and the application of an external stress is required to program the sample [62]. Only few reports have dealt with reversible actuations or programmable pore size changes under stress-free conditions in covalently or physically crosslinked electrospun fibrous meshes.

4.1. Covalently Crosslinked Electrospun SMP Actuators

Electrospun SMPs based on covalently crosslinked poly(ε-caprolactone) (cPCL) fibrous meshes enabled a bidirectional reversible actuation and a temperature-controlled reversible change in porosity [63]. A two-step preparation procedure was used to achieved the cPCL fibrous meshes. In the first step, the electrospinning of a blend of PCL with triallyl isocyanurate (TAI) and benzophenone (BP) was carried out, while in the second step, the electrospun fiber meshes underwent a photoinitiated crosslinking process. To observe the actuation behaviour, the meshes underwent deformation at an elevated temperature and cooling while keeping the deformation strain.

4.2. Physically Crosslinked Electrospun SMP Actuators

To avoid the secondary crosslinking step by exposure to UV light, in situ crosslinking of electrospun fibers based on stereocomplexation was studied. Blending of a multiblock copolymer containing poly(L-lactide) and poly(ε-caprolactone) segments (PLLA-PCL) with oligo(D-lactide) (ODLA) in a one-step solution-casting process resulted in the formation of a stereocomplex [64]. This physical networking between the opposite enantiomers of PLA organized them into a periodic crystalline structure. The actuation behavior of the electrospun meshes and the bulk material was tested. The electrospinning process resulted in a higher molecular orientation, enabling an improved shape-memory actuation performance in the microfiber meshes compared to the bulk material. The actuation magnitude of ε_{rev} = 5.5 ± 0.5% in bulk PLLA-PCL/ODLA blends was increased to 7.8 ± 0.8% in fibrous meshes. Twisting the electrospun fibers into a yarn resulted in a further increase of actuation to 15 ± 1.8%. This was attributed to the improvement in the structural integrity of the fibers. The simultaneous orientation of polymer molecules and their crosslinking into a physical network opens a broad perspective for the development of actuating fiber meshes.

5. Electrospun Electroactive Actuators

Actuators based on electroactive polymers (EAPs) can operate when stimulated by an electric field. Due to the high surface-to-volume ratio of nanofibers and the porous structure of nanofibrous meshes, electrospun nanofibers have led to the fabrication of high-performance and versatile actuators [65][66][67]. One of the most promising applications of such devices is artificial muscles, which can mimic the function of natural skeletal muscles, and therefore, have potential applications in biomimetic robots and biomedical devices [5][7]. In recent years, various nanomaterials have been utilized to obtain artificial muscles and improve their mechanical, electrical, and electrochemical properties [68][69].

Actuation of such devices can happen according to two mechanisms based on electromechanical and electrochemical reactions. Electromechanical (electric) actuation is related to electric dipole rearrangements in electroactive polymers that cause dimensional changes, while electrochemical mechanisms utilize electrostatic forces, in which the ion exchange mechanism is responsible for volume changes in ionic electroactive EAPs [70][71]. In comparison to electromechanical, ionic EAPs offer a significantly lower voltage (1–2 mV); therefore, they can find applications in the medical field, especially in the preparation of artificial muscles.

Much attention has been paid to the fabrication of conductive polymer-based actuators having nanofibrous structures [72][73]. However, direct fabrication of conducting polymer nanofibers using the electrospinning process is challenging due to the fact that typically, polymers with a low molar mass that are produced show inherent brittleness, as often the corresponding monomers have poor solubility in common solvents [74]. Therefore, several alternative approaches have been utilized to incorporate conducting polymers (CPs) into fibrous structures. The most common are the following: co-axial electrospinning to produce core–shell nanofibers and preparation of electrospinnable blends of polymers with CPs, which can be processed by electrospinning [75][76][77]. However, they result in the formation of a nanofibrous layer with low electrical conductivity and poor electrochemical properties for use as an actuator. A direct polymerization of CPs on the surface of substrate nanofibers is a simple and versatile technique for producing CP nanofibers of a core–shell structure [78]. Therein, a conducting polymer layer is on the surface of the fibers, which provides an effective nanofiber-conducting polymer-based actuator [79].

Electroactive Actuators for Manufacturing Artificial Muscles

For the purpose of electrospun electroactive actuators, biopolymers such as cellulose [80], cellulose acetate (CA) [81], gelatin [82], chitosan [83], and silk [84] have been considered, particularly in biological and medical applications [85]. In most cases, biopolymer-based nanofibrous substrate is intended to increase the biocompatibility of an actuator. However, some biopolymers, such as CA, have naturally electrical actuation ability, which due to their synergistic effect with the active component, improve the final actuation performance of bioactuators [16][86]. Furthermore, due to their doping ability, CPs such as polypyrrole (PPy) [87][88], poly(3,4-ethylenodioxythiophene) (PEDOT) [79], and polyaniline (PANI) [82][89] can be used in conjunction with biopolymers to produce fibrous bioactuators for in vitro or in vivo applications, especially artificial muscles [90][91]. The chemical structure of CPs can expand and contract due to a flux of ions/solvent in and out of the polymer matrix when the conjugated backbone is electrochemically oxidized and reduced when low voltages are applied (1–2 V) in the presence of an electrolyte [92].

6. Electrospun Actuators Based on Liquid Crystalline Elastomers (LCEs)

LCEs constitute a class of materials that possess both elastic properties as conventional elastomers and anisotropic physical properties due to their liquid crystalline state of order. LCE-based microfiber actuators based on the nematic–isotropic phase transition of liquid crystal mesogens were reported to generate a large actuation strain of 60% with a simultaneous fast response <0.2 s and a high power density of 400 W/kg. Furthermore, when coated with a polydopamine layer, the actuation of the electrospun LCE microfiber could be precisely and remotely controlled by a near-IR laser through the photothermal effect. Krause et al. obtained electrospun crosslinked nematic fibers with a uniform alignment [19]. These highly oriented fibers exhibited a liquid crystalline state under ambient conditions.

7. Summary

Electrospinning has emerged as a modern and versatile fabrication technique, offering unique advantages for the production of advanced materials with diverse applications.

Through the ingenious combination of electrospinning and hydrogel technology, intricate fibrous structures are crafted, resulting in actuators that exhibit remarkable shape-changing abilities in response to external stimuli. The actuation in electrospun hydrogel actuators is inspired by the skin of human hands [38] and pine cones [39], which provide reversible movements based on swelling/deswelling effects in a bilayered structure. The active layer of the actuators can uptake water, resulting in volume increase and the passive layer is inert to dimensional change. These bilayer structures based on electrospun hydrogel meshes have enabled bending movements, which rely on internal mechanical stresses generated at the interface of the two layers.

SMP fibrous meshes have shown immense potential and exciting prospects for the cutting-edge technology in the field of soft robotics and beyond [55]. However, only a few studies related to electrospun SMPs enabling a reversible actuation have been reported. Electrospun actuators based on a crosslinked PCL resulted in an actuation performance of ε'_{rev} = 15%, while for PEVA-based actuators, their value of ε'_{rev} could vary in a range from 10 ± 1% to 17 ± 2% depending on the alignment of the fibers [63]. The post curing of PCL and PEVA fibers by exposure to UV light could be avoided by blending a multiblock copolymer based on PLLA and PCL (PLLA-PCL) with oligo(D-lactide) (ODLA). Here, the stereocomplex formation between the opposite enantiomers of PLA enabled physical crosslinks in the blend [93]. The fibrous meshes of the PLLA-PCL/ODLA blend resulted an actuation magnitude of εrev = 7.8 ± 0.8%, which could be increased to 15 ± 1.8% by twisting the electrospun fibers into a yarn [64].

Electrospun actuators harnessed from conductive polymers (CPs) leverage the unique electroactive properties of polymers, responding to electrical stimuli with dynamic shape changes. However, due to poor physical features induced by insolubility, infusibility, and brittleness, the applicability of CPs as actuators requires significant challenges to be addressed. As the utilization of electrospinning requires organic solvents for the preparation of solution, therefore, the synthesis of new CPs by the modification of existing CPs or synthesis of new derivatives with improved solubility and spinnability is mandatory. Furthermore, it is important to further improve the conductivity and thermal stability of electrospun CP fibers. This can be performed by the fabrication of CP-based electrospun composites containing a variety of nanofillers, such as inorganic metal oxides, CNTs, graphene, carbon nanotubes, metal or semiconductor nanoparticles, and quantum dots. It has been shown that preparation of polymer-based composites such as Au-doped poly PAN–PANI core–shell nanofibers [94], silver-doped PVDF fibers [95], or PVA/polyurethane/Au [96] can improve these properties and lead to better applicability due to better conductivity or thermal stability [97].

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