

Nanofiber Polymers for Biomedical Applications

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The features of the nanofibers (NFs) that are used to coat biomedical Ti-based implants are predominantly dependent on the type of polymer employed. Applicable polymers are categorized as either natural or synthetic based on their source and composition. Natural polymers, namely cellulose, collagen, gelatin, chitosan, chitin, dextrose and silk fibroin, have been electrospun into NF scaffolds.

nanofibers

polymers

titanium implants

1. Introduction

The features of the NFs that are used to coat biomedical Ti-based implants are predominantly dependent on the type of polymer employed ^[1]. Applicable polymers are categorized as either natural or synthetic based on their source and composition ^{[2][3][4]}. Natural polymers, namely cellulose, collagen, gelatin, chitosan, chitin, dextrose and silk fibroin, have been electrospun into NF scaffolds ^{[4][5][6]}. Kadavil et al. ^[7] report on gelatin providing cellular attachment and adhesion of human stem cells, which is typical of most natural polymers. However, natural polymers are limited in their clinical application due to being immunogenic, exhibiting batch-to-batch differences, limited availability, expensive production and vulnerability to cross-contamination ^{[3][7]}. Moreover, natural polymers lack mechanical strength and have a relatively rapid degradation rate due to their hydrophilic nature, limiting their use in long-term clinical processes. These limitations of natural polymers may be remedied through the use of synthetic polymers ^{[2][3][7]}.

Synthetic polymers have numerous advantages in comparison to their natural counterparts, namely cost-effectiveness and durability, and the majority of them have stable mechanical properties for applications in load-bearing tissue engineering scaffolds ^{[2][3][7]}. Owing to their ease of processing and biocompatibility, the most popular synthetic polymers include poly(ϵ -caprolactone) (PCL), poly(lactic acid) (PLA), poly(lactic-co-glycolic acid) (PLGA), poly(glycolic acid) (PGA), poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA) ^{[5][7][8]}. These polymers have been approved by the United States Food and Drug Administration (FDA) for use in human medical devices, which emphasizes their in vivo applicability and that their toxicity factor has been evaluated ^{[3][4][9][10][11][12][13]}.

In addition to biocompatibility, biodegradability and lack of toxicity are common properties among synthetic polymers relevant for coating surfaces of biometals ^{[14][15]}. Biodegradation may be defined by hydrolysis in physiological conditions (as in the human body) ^{[14][15]}. Boia et al. ^[12] greatly emphasized the slow degradation of PCL-based implants, which is supported by Perumal et al. ^[13], who reported that PCL has been said to gradually

degrade when compared to PLGA and PLA. The degradation rate is dependent on the hydrophilicity of the monomeric units, and basically, the comparative degradation rates of the polymers may be summarized in terms of length of the degradation period as [3][13][16]: PCL > PLA > PLGA > PGA > hydrophilic polymers (such as PEO and PVA). **Table 1** lists the distinguishing properties of synthetic polymers used in the biomedical field.

Table 1. Overview of the characteristics of synthetic polymers.

Polymer	Properties	Applications	Degradation Rate	Ref.
Poly(ϵ -caprolactone) (PCL)	Hydrophobic aliphatic polyester; slow degradation rate; bioactive; flexible mechanical properties; effectively entraps bactericidal material; semi-crystalline; semi-permeable	Long-term implants; bone graft material; tissue engineering scaffolds; drug-delivery systems	2–4 years	[3] [17] [18]
Poly(lactic acid) (PLA)	Hydrophobic aliphatic polyester; slow degradation rate; bioactive; tunable mechanical properties; crystalline; porous; stereoisomers: poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLLA)	Biomedical coating; load-bearing applications; orthopedic fixation devices; tissue engineering; three-dimensional (3D) printed scaffolds; drug-delivery systems	>24 months	[3] [17] [18]
Poly(lactic-co-glycolic acid) (PLGA)	Hydrophobic/hydrophilic balance; intermediate/adjustable degradation rate; PLA/PGA copolymer; crystalline; semi-permeable; low osteoinductivity	Copolymer for development of bone substitute constructs; bone regeneration; orthopedic implants; tissue engineering	6–12 months	[2] [3] [7] [18]
Poly(glycolic acid) (PGA)	Hydrophilic aliphatic polyester; fast degradation rate; tunable material properties; crystalline; low solubility; semi-permeable	Implants, tissue engineering; drug delivery; biological adhesives; open soft tissue wounds	2–4 weeks	[2] [3] [18] [19]
Poly(ethylene oxide) (PEO)	Hydrophilic; synthetic hydrogel	Composite functional materials; hydrogel coatings;	-	[1] [11]

Polymer	Properties	Applications	Degradation Rate	Ref.
		blood contact		[20] [21]
Poly(vinyl alcohol) (PVA)	Hydrophilic; fast degradation; gel-forming properties; good film-forming; good chemical resistance; semi-crystalline	Implants; tissue engineering	-	[7] [9] [11] [22]

devices [4]. In addition, water-soluble synthetic polymers, such as PVA, exhibit poor mechanical properties [7]. Studies indicate that one of the most effective strategies applied to subdue the limitations of polymer groups is the production of novel composite fibers through the combination of various polymers [1][6][7][23]. The results of Jahanmard et al. [24] indicated that the biological properties of bi-layered PCL/PLGA composite NFs far exceeded those of the single layers. Synthetic polymers are often fused with natural polymers to form fibers with optimized mechanical properties, degradation rates and bioactivity while maintaining the similarity to the ECM and promoting cell attachment [4][7]. Examples of single and hybrid electrospun NFs are illustrated by the scanning electron microscope (SEM) images in **Figure 1**.

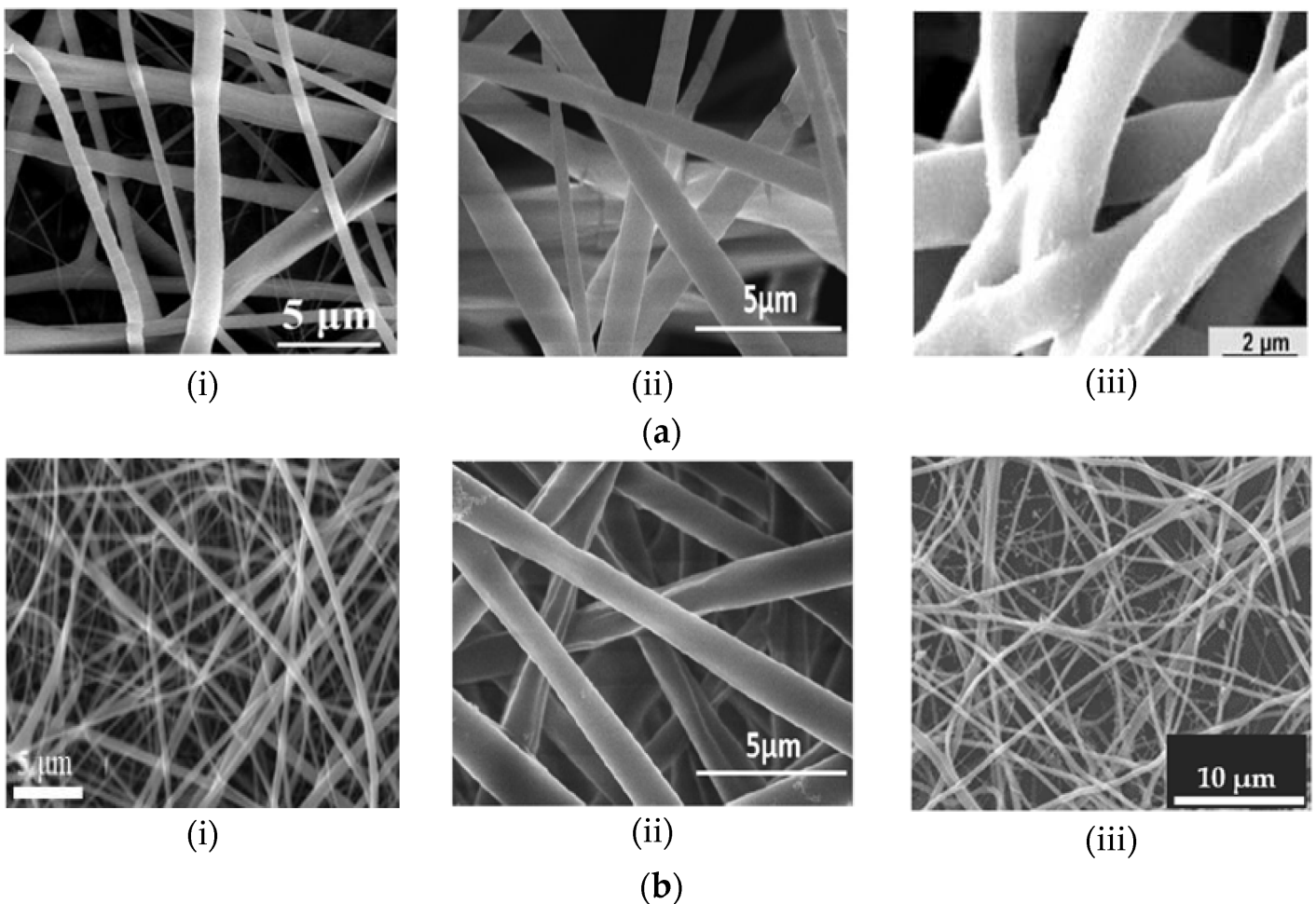


Figure 1. Scanning electron microscope (SEM) micrograph illustrations of nanofibers (NFs) composed of (a) pure synthetic polymers (i) PCL [6], (ii) PLLA [25] and (iii) PLGA [24]; and (b) synthetic and natural polymer composites of (i) PCL/Collagen [26], (ii) PLLA/Chitosan [25] and (iii) PEO/Chitosan [1].

3. Electrospinning Technique

Electrospinning is a common nanotechnology used to fabricate scaffolds of aligned polymeric NFs with diameters varying between 3 nm and greater than 5 μm [19][27]. The engineered 3D porous scaffolds serve as a pattern to provide mechanical and biochemical support to the surrounding cells relative to the tissue type [28][29]. A simple electrospinning setup (**Figure 2**) consists of a high voltage power supply (typically between 5 to 30 kV), a piece of feeding equipment (usually a syringe), a spinneret and a collector [5][22][30]. The collector for electrospun fibers is usually on a grounded plate and is usually a metallic material; hence, coating a Ti implant using the electrospinning method is relatively straightforward [27][31][32]. Important factors that govern the quality NFs produced using the electrospinning process include solution parameters (such as polymer structure and viscosity), processing parameters (such as flow, voltage and distance) and ambient conditions [4][26]. By altering these parameters, multiple experimental arrangements of the process, including coaxial, solution and melt electrospinning, are achievable [6][24][33]. Deviations from the basic electrospinning process are necessary to modify the primary properties of NFs and realize a tunable coating towards desired structural and functional properties [6][7][24]. The flexibility of the electrospinning technique is convenient for application in Ti implants intended for the complex human body environment. Several researchers have successfully applied electrospinning to coat Ti [8][28][31][34] and Ti-6Al-4V [1][31][35][36] samples intended for use as human implants. Kadavil et al. [7] notes also that polymers such as PCL and PVA have gained popularity as readily electrospinnable polymers and have been used as a template for the preparation of non-electrospinnable polymers. A specific amount of PEO was used as a fiber-forming additive by Nitti et al. [37] to improve the electrospinnability of chitosan. Therefore, technique modifications allow for the accommodation of the various biopolymer solutions.

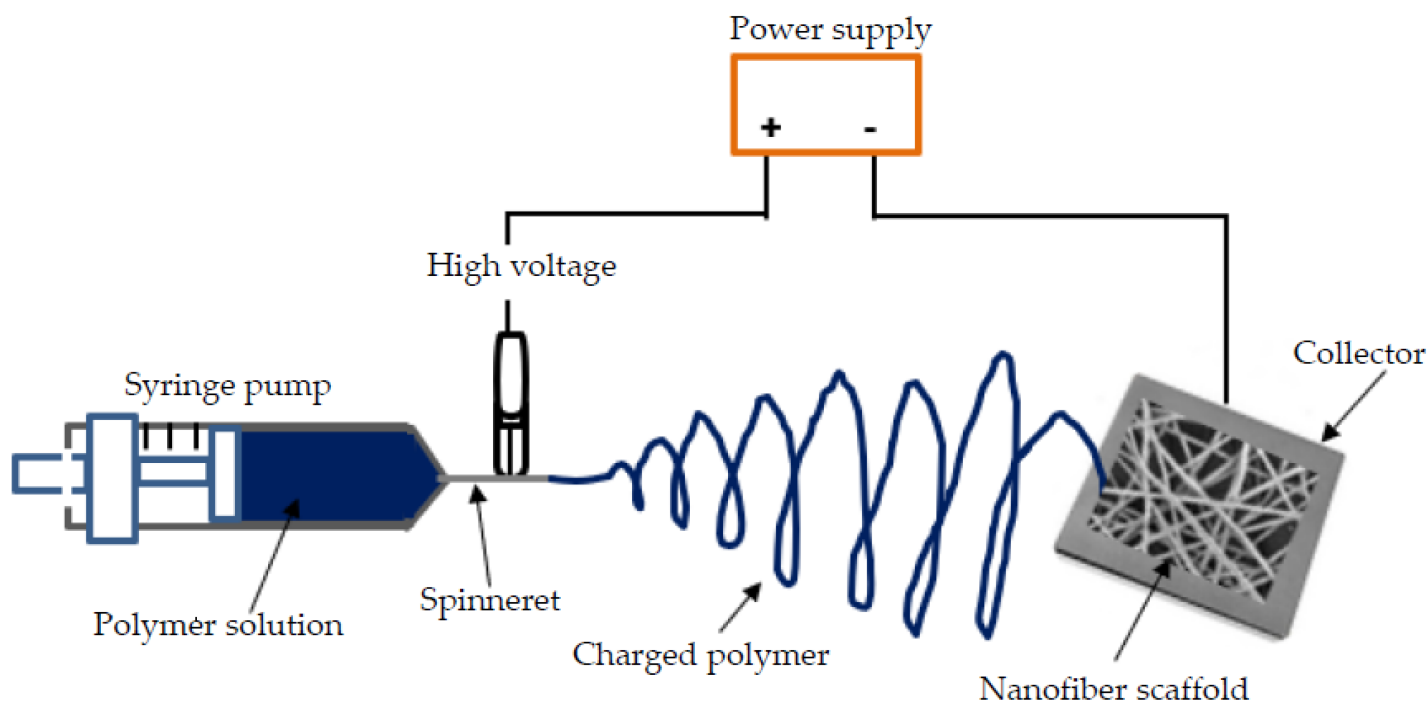


Figure 2. Schematic representation of a basic electrospinning horizontal set-up.

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