Review

Electrospinning Processing of Polymer/Nanocarbon Nanocomposite Nanofibers—Design, Features, and Technical Compliances

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Abstract: Polymeric nanofibers have emerged as exclusive one-dimensional nanomaterials. Various polymeric nanofibers and nanocomposite nanofibers have been processed using the thermoplastic, conducting, and thermoset matrices. This review aims to highlight the worth of electrospinning technology for the processing of polymer/nanocarbon nanocomposite nanofibers. In this regard, the design, morphology, physical properties, and applications of the nanofibers were explored. The electrospun polymer/nanocarbon nanofibers have a large surface area and fine fiber orientation, alignment, and morphology. The fiber processing technique and parameters were found to affect the nanofiber morphology, diameter, and essential physical features such as electrical conductivity, mechanical properties, thermal stability, etc. The polymer nanocomposites with nanocarbon nanofillers (carbon nanotube, graphene, fullerene, etc.) were processed into high-performance nanofibers. Successively, the electrospun nanocomposite nanofibers were found to be useful for photovoltaics, supercapacitors, radiation shielding, and biomedical applications (tissue engineering, antimicrobials, etc.).

Keywords: electrospinning; nanofiber; nanocarbon; nanocomposite; morphology; supercapacitor; photovoltaic; tissue engineering

1. Introduction

Polymer nanofibers have been developed as scientifically significant nanostructures [1]. Carbon nanoparticles or nanocarbon nanoparticles have been used as essential nanofillers for polymers [2]. The fullerene, graphene, carbon nanotube, and other nanofillers have been ranked as the vital carbon nanoparticles. Consequently, using these nanoparticles, polymer/nanocarbon nanocomposites and resultant nanofibers have been reported [3,4]. The nanocarbon nanoparticles have played a cooperative role with polymers to enhance the morphology profiles and physical features of the resulting nanostructure [5]. Subsequently, the polymer/carbon nanofiller nanofibers have been industrialized using appropriate techniques [6]. In this concern, electrospinning has been prominently used to form the polymer or nanocomposite nanofibers [7,8]. This technique demands precise control of the processing parameters to attain the desired nanofibers.

Numerous polymer/nanocarbon nanocomposite nanofibers have been fabricated and intended for industrial applications ranging from energy/electronic devices to biomedical [9,10].
This innovative article unfolds the fundamentals of the electrospinning approach and design and potential of polymer/nanocarbon nanocomposite nanofibers. Including nanocarbon nanofillers in polymers and electrospinning led to the development of high-performance nanocomposite nanofibers. The nanofiller may develop interfacial interactions with the matrix to cause synergistic effects on the resultant physical properties. Effects of matrix–nanofiller interactions and electrospinning processing have been observed in the form of high-tech solicitations in solar cells, supercapacitors, radiation shielding, and biomedical sides. To the best of our knowledge, this review is innovative as well as pioneering to portray the systematic progressions in the arena of polymer/nanocarbon nanocomposite nanofibers. Accordingly, this review can be very helpful for the researchers working in the field of nanocomposite nanofibers for future innovations.

2. Nanocarbon Nanofillers in Polymeric Nanocomposites

Considerable research attempts have been observed in this field of carbonaceous nanofillers [11]. Starting from a carbon nanotube, several unique nanostructures like graphene, fullerene, carbon dots, etc., have been developed. The important carbon nanofillers used as polymer nanofillers include a carbon nanotube, graphene, graphene derivatives, fullerene, nanodiamond, graphite, carbon black, etc. The addition of nanocarbon nanostructures in polymers may cause a significant change in the resulting physical properties and performance. The ensuing polymeric nanocomposites, with carbonaceous nanofillers, have a unique blend of the properties of polymers and nanoparticles [12]. The carbon nanostructures have distinct shape, dimensions, size, aspect ratio, and physical aspects. Depending upon the nanoparticle shape, dimensions (one-, two-, or three-), and inherent properties, the nanocomposite features will be affected [13]. Hence, the estimation of the nanoparticle structure, dimensions, etc., may reveal beneficial information regarding the final nanocomposite features. Consequently, the superior properties of carbon nanofillers have led to stimulating prospects of polymer/nanocarbon nanocomposites [14]. Carbon nanofillers have been filled in polymeric matrices through various facile techniques such as solution mixing, melt blending, and in situ polymerization, as well as sophisticated techniques like spinning methods [15]. The processing technique obviously determines the state of nanoparticle dispersion in the polymers. Accordingly, the nanofiller alignment in the matrices has been identified as an important factor in the nanocomposite formation. Here, the randomly oriented nanoparticles may negatively influence the electrical, mechanical, thermal, and other physical characteristics of the nanomaterials [16]. On the other hand, fine nanofiller dispersion in polymers has revealed superior properties and performance. To enhance nanoparticle scattering in polymeric matrices, various techniques have been adopted. A very common way is the stirring or the sonication of the nanoparticle suspensions. The electric and magnetic field effects may also enhance the nanoparticle orientation in the polymers [17]. In this regard, epoxy nanocomposites with well-dispersed nanocarbon nanofillers have been developed using magnetic field effects [18]. Consequently, the alignment and distribution of the nanofiller causes varying nanocomposite morphologies [19]. Another important method for a superior nanoparticle dispersion is the spin casting technique [20]. This approach has appropriate spinning steps and setup for better nanofiller configurations in the matrices [21]. Besides physical methods, nanoparticles have been modified through physical or chemical surface functionalization procedures prior to inclusion in polymers [22]. Modified nanofillers have developed compatible interfaces, interfacial interactions, and dispersion in polymeric matrices [23]. Interactions between nanocarbon nanofillers and matrices may involve weak van der Waals forces and electrostatic interactions [24]. On the other hand, appropriately functionalized nanocarbon nanofillers may form covalent bonding with polymer matrices [25,26]. Thus, both the physical or covalent interactions of nanofillers with polymers have been found to enhance the matrix–nanofiller compatibility. Henceforth, the electrical conductivity, load transfer properties, mechanical features, thermal constancy, and several other
properties of polymer/nanocarbon nanocomposites have been enhanced through adopting the appropriate processing technique for fine dispersion.

3. Nanofibers of Polymeric Nanocomposites

Polymeric nanofibers have been developed as nanostructures with a diameter of a few nanometers and length of quite a few millimeters [27]. Polymer nanofibers rendered superior structural properties and technical performance [28]. Polymer nanofibers have been fabricated through effective engineering practices. The ensuing nanofibers may have hollow, flat, crumpled, or solid structures. The nanofibers have been formed using thermostats, thermoplastics, as well as conducting polymer matrices like epoxy, polyamide, polyethylene, polystyrene, poly(vinyl alcohol), polyaniline, and countless other matrices [29–31]. A variety of procedures have been applied to form nanofibers such as solution or melt drawing, template and non-template practices, and spinning systems [32]. The diameter, surface texture, and morphology of polymer nanofibers have been affected by the processing technique used and the associated parameters [33]. In addition to a pristine polymer, reinforced polymers with numerous organic and inorganic nanoparticles have been processed to form nanocomposite nanofibers [34]. Carbonaceous nanofillers have been adopted as the essential reinforcements for polymer nanofibers [12]. Specifically, fullerene, graphene, and a carbon nanotube possess high surface area, structural, and physical features to enhance the final nanocomposite nanofiber topographies [13]. The resulting carbon nanoparticle-filled nanofibers revealed potential for wide-ranging fields from the energy or electronics to the medical sectors [35]. Here, the performance and properties of these nanofiber nanostructures directly rely on the manufacturing technique employed [36].

4. Electrospinning Technique for Nanofibers

Spinning methods have been prominently used to fabricate polymer and polymeric nanocomposite nanofibers [37,38]. Spinning techniques have been varied from the wet spinning [39] and melt spinning [40] methods to electrostatic spinning practices. Generally, spinning procedures have manageable process parameters. Here, solution blow spinning was applied for the polymers and nanocomposite nanofibers. This method combines the electrospinning and melt blowing approaches together [41]. The solution blow spinning setup has its own syringe, pumping system, nozzle, gas flow, and collector. The fiber diameter depends upon the variation in the parameters, polymer type, and matrix concentration [42]. Centrifugal jet spinning has also been used to form micro- or nanofibers. This setup has a spinning chamber, DC motor, and multiple fiber collector [43,44]. The electrohydrodynamic direct writing mechanano-electrospinning technique also forms nanofibers on micro- or nanoscales. This technique utilizes electrical as well as mechanical forces to develop viscous ink, resulting in the nanofibers [45,46]. The related setup has a variable nozzle-to-substrate distance and adaptable voltage sources [47]. Amid spinning approaches, the electrospinning technique has attained special attention to form nanocomposite nanofibers [48]. Polymers and polymer/nanocarbon nanocomposites have been processed into electrospun nanofibers with superior physio-chemical properties [49]. Electrospinning has been reported as a facile, reasonable, and versatile method to form nanofibers [50].

In the electrospinning method, the polymer solution or melt form is converted to the charged filaments in the presence of an electric field [51]. The general electrospinning setup comprises a syringe, the solution or melt pumping arrangement, a high voltage supply, and a collector for the nanofibers. As the polymer solution evicts from the syringe needle, it is converted to a charged strand under the effect of the applied voltage [52]. Owing to the electrostatic effects, the polymer strand elongates to form a nanofiber. The charged nanofiber continues to move towards the collector [53]. The process parameters such as the polymer type, amount of the nanofiller, melt or solution form, pumping or flow rate, voltage used, and several other electrospinning factors affect the nanofiber
texture, diameter, and length. The electrospinning setup has been reported with perpendicular as well as horizontal arrangements. The final nanofiber form demands the control and monitoring of facile electrospinning parameters. Both the polymer matrices and the nanocomposites have been processed, using the electrospinning technique, to form the nanofibers [54].

Coaxial and emulsion electrospinning techniques have been frequently employed for multifaceted applications. The coaxial electrospinning method involves two electrospinning tips and two solutions [55]. This technique has been used to produce core-sheath fibers through physical separation. Here, it is important to control the solution and processing parameters such as the solution flow rates, viscosities, and electrical conductivity. Coaxial electrospinning has been found to be successful for developing complex drug delivery systems. In a drug delivery application, varying core and sheath configurations have been utilized for better cell attachment and strength features of nanofibers [56]. A fine example can be nanofibers with a polyurethane core and collagen sheath [57]. Lee et al. [58] formed coaxial electrospun core-shell and hollow nanofibers of poly(styrene-co-acrylonitrile) (inner core) and poly(acrylonitrile) (outer sheath). Figure 1 depicts a coaxial electrospinning setup having a coaxial nozzle with two concentric cylinders. This system allows the formation of core-shell nanofibers. The inner and outer diameter of the core-shell nanofibers were also measured. Solution features like the concentration, flow rate, etc., have been found to affect the wall thickness and inner and outer diameter of the nanofibers. Field emission scanning electron microscopy and transmission scanning electron microscopy techniques were used to analyze the nanofiber morphology (Figure 2). The nanofibers have a perfectly uniform and hollow morphology. The micrographs have an outer smooth surface and elliptical cross-sectional shape, showing the effectiveness of this technique. Khalf et al. [59] developed core-sheath and hollow nanofibers of cellulose acetate. The coaxial electrospinning setup employs two syringes with acetone and dioxan solvents. The pumps were used to move the shell and core solutions for the formation of core-sheath nanofibers (Figure 3). From the obtained nanofibers, the core was detached through immersing the nanofibers in an octane solvent. Scanning electron microscopy revealed a uniform non-beaded nanofiber formation and fine fiber distribution. The perfect morphology depicted the effectiveness of the coaxial electrospinning technique applied.

Figure 1. Graphic of a syringe needle system for coaxial electrospinning. O.D. = outer diameter; SAN = poly(styrene-co-acrylonitrile); PAN = poly(acrylonitrile). Reprinted with permission from [58]. 2012, Springer.
Figure 2. (a) Field emission scanning electron microscopy and (b) transmission electron microscopy images of a hollow electrospun carbon nanofiber. Reprinted with permission from [58]. 2012, Springer.

Figure 3. Core-shell fiber formation: (a) schematic of coaxial electrospinning setup; (b) diagram of fiber core extrication; and (c) fiber size distributions of solid electrospun and hollow fibers. Reprinted with permission from [59]. 2015, Springer.
Emulsion electrospinning depends upon the chemical ways of separating an emulsion using surfactants [60]. The resulting nanofiber usually develops into the distinct phases upon solvent evaporation. This technique has also been used for a drug encapsulating application. Emulsion electrospinning has the advantage of using water (solvent) despite of harmful chemicals. On the other hand, coaxial electrospinning definitely varies from the emulsion-based method as it produces higher-mechanical-strength fibers. In tissue engineering, coaxial-produced nanofibers revealed better cell attachment and proliferation due to a core-sheath nanostructure [61]. However, both coaxial and emulsion electrospinning form nanofibers having an outer sheath and inner core. Gosh et al. [3] applied the emulsion electrospinning method to form poly(ε-caprolactone) nanofibers. For emulsion formation, two immiscible liquids were used. These solvents were stirred with a stabilizer. Figure 4 illustrates the setup and process for the formation of emulsion electrospun nanofibers. The stabilizer was used to stabilize the emulsion through reducing the surface tension between two phases. Moreover, mechanical stirring also prevented the droplet coalescence through reducing the barrier between two phases.

![Figure 4. Flowchart of emulsion electrospinning setup and process. Reprinted with permission from [4]. 2022, MDPI.](image_url)

The design principles of electrospun scaffolds can be easily controlled using the coaxial electrospinning method through the facile processing, controlled porosity, solution used, and environmental parameters. The literature has revealed the importance of polymer-solvent-processing relations to produce electrospun nanofibers for delicate scaffolds aiming for a controlled drug delivery and tissue formation [55]. Here, process parameters like the solution feed rates for the core and shell, applied voltage, tip to collector distance, and collector revolving speed have been found to be important for the desired end material. Then, solution parameters including the concentration, viscosity, conductivity, etc., matter for the formation of the required scaffold. Moreover, environmental parameters such as the temperature and humidity need to be controlled for a drug delivery application. All these factors affect the nanofiber structure, morphologies, and physical properties. In drug delivery, coaxial nanofibers have been found to be efficient to encapsulate various biomolecules, relative to emulsion nanofibers, due to a better core-sheath
nanostructural design [56]. However, a high drug release at the beginning occurs and so a long-term drug release has been found to be difficult. This initial drug release may result in lessening the effect of the drug dose; therefore, it is found as unsuitable for pharmaceutical applications. Here, managing the process parameters can limit in the desired drug release duration to enhance the effectiveness of the electrospinning technique.

Other spinning methods have also been employed for a polymer and nanocomposite nanofibers in the literature. The solution blow spinning practice has been employed using both melt blowing and electrospinning [62,63]. This procedure produces non-woven micro- and nanofibers [64]. In this method, the fiber production rate was found to be high; however, it has been considered as an expensive and complicated method compared with electrospinning. The centrifugal jet spinning method may help to form low-cost and high-throughput micro- or nanofibers [65]. However, the disadvantages relative to electrospinning involve the lack of controlled centrifugal forces, less managed solution viscosity, and mass transfer [66]. Moreover, it cannot be used for melt-processed nanofibers. Electrohydrodynamic direct spinning has been adopted for the programmable direct writing of nanofibers through combined effects of electrical and mechanical forces [67]. This method has benefits of a large-scale nanofiber production. However, electrospinning has more easily controllable processing conditions than electrohydrodynamic direct spinning. Therefore, the electrospinning technique has been favored in the literature for the majority of nanofiber designs.

5. Design and Characteristics of Electrospun Polymer/Nanocarbon Nanocomposite Nanofibers

Nanocomposite nanofibers own high surface area, alignment, and remarkable physical features [68]. Among nanocarbon nanostructures, fullerene molecules gained an essential stance [69]. Consequently, the fullerene exposed notable applications ranging from electronics/energy to biomedical fields [70,71]. Insuasty et al. [72] studied polymer/fullerene nanofibers having π–π stacking interactions. Conducting polymer matrices have been applied to form nanofibers with a fullerene nanofiller [73,74]. Pierini and researchers [75] developed poly[3-dodecylthiophene-co-3-(6-fullerenylhexyl)thiophene]- (a polythiophene copolymer with fullerene functionalities) and poly(ethylene oxide)-based electrospun nanofibers. According to an atomic force microscopy study of poly[3-dodecylthiophene-co-3-(6-fullerenylhexyl)thiophene]/poly(ethylene oxide) nanofibers, the nanofibers had a distinct nanostructure; however, it was slightly uneven after etching. Similarly, a scanning electron microscopy analysis revealed the uniform and textured surface of the electrospun nanofibers, even after etching. In addition, the nanofibers had a diameter of ~0.9 μm and considerably high elastic modulus in the range of 1.6–2.5 GPa. Owing to the donor-acceptor behavior of the conjugated polymer and fullerene molecules in the nanofibers, the nanocomposite nanofibers owned the photovoltaic efficiency of ~5.6%. Solanki and co-workers [76] used the electrospinning method to form poly(3-hexylthiophene-2,5-diyI):phenyl-C61-butyric acid methyl ester- ensuing nanofibers. Fibrous nanocomposite structures own an improved photovoltaic performance and so the power conversion efficiency was found as 2.16%. Jiang et al. [77] studied epoxy- and fullerene-based nanocomposite-coated carbon fibers. The inclusion of fullerene molecules upgraded the interface formation and matrix–fiber interactions of the epoxy resin and carbon fibers. The transverse fiber bundle tension test of the nanocomposites was performed to analyze the interface bond strength. The addition of fullerene up to 3 wt.% remarkably improved the transverse fiber bundle tension strength by 42%. The enhancement was accredited to fine matrix–fiber bonding tendencies due to the presence of fullerene.

Graphene is a unique two-dimensional one-atom-thick nanostructure made up of sp² hybridized carbon atoms [78]. It has large surface area and exclusive physical characteristics appropriate for constructing high-efficiency nanomaterials [79,80]. Polyamides or nylons have been adopted as important polymer matrices for nanocarbon-based nanofibers [81]. Lee et al. [82] manufactured nylon 6- and graphene flake-derived nanofibers. Leyva-
Porras and colleagues [83] industrialized electrospun nanofibers of nylon 6 and nitroxide-functional graphene oxide. Scanning transmission electron microscopy images of the functional graphene oxide as well as the nanocomposite nanofibers are given in Figure 5. The functional graphene oxide nanosheets seemed to be embedded in the nanocomposite nanofiber due to interactions with the matrix. Maccaferri et al. [84] reported nylon 6,6- and graphene-derived nanocomposite nanofibers through the electrospinning technique. Figure 6 displays the transmission electron microscopy images of the nanocomposite nanofibers. The nanofibers having 5 and 15 wt.% graphene loading levels revealed the diameter of 200 to 300 nm. The disposition of graphene nanosheets has been observed along the nanofiber surface. However, the graphene aggregation caused the bulging of the nanofiber surface.

Figure 5. STEM images showing (A) few layers of GOFT platelet (less than 4), and (B) nanocomposite nanofiber containing a thicker GO platelet. STEM = Scanning transmission electron microscopy; GOFT = nitroxide-functionalized graphene oxide layers; GO = graphene oxide. Reprinted with permission from [83]. 2014, Elsevier

Figure 6. TEM micrographs of nanofibrous mats with (A) 5 wt.% graphene (scale bar: 500 nm); (B) 15 wt.% graphene (scale bar: 300 nm); and (C) sketch of graphene disposition along the nanofiber surface. TEM = Transmission electron microscopy. Reprinted with permission from [84]. 2019, Elsevier.
Moreover, Weise et al. [85] formed nylon 6 and nylon 6/graphene nanocomposite nanofibers. The nanofibers were fabricated with 3–5 wt.% graphene loading. The nanofibers had a length-to-diameter ratio around ~2.0. Figure 7 depicts the differential scanning calorimetric curves for the pristine nylon 6 and 3 as well as 5 wt.% nanofiller-loaded nanofibers. In the case of the nanocomposite nanofiber, only an alpha crystalline peak appeared, while the gamma peak disappeared due to a change in the nanostructure upon the graphene addition. Actually, the inclusion of graphene decreased the distinction of the gamma peak. The higher concentration of the nanofiller caused more peak destruction. The result suggested that the graphene inclusion shifted the gamma phase towards the alpha phase. On the other hand, the unfilled polymer revealed two gamma and alpha peaks (~200 °C). The crystallization curves of neat nylon 6 and nylon 6/graphene nanocomposites were also studied. It was observed that the graphene nanofiller inclusion affected the crystallization behavior of the matrix, leading to a progressive enhancement in the crystallization peak. A high electron conduction of ~10 μSm⁻¹ has been perceived for nanocomposite nanofibers. Poly(vinyl alcohol) and poly(vinyl acetate) have also been applied as important matrices for a graphene nanofiller [86,87]. Consequently, electrospun nanofibers of poly(vinyl alcohol)/graphene and poly(vinyl acetate)/graphene nanocomposites have been reported [88,89]. The inclusion of graphene in the matrix has been found to enhance the optical, conducting, specific capacitance, and heat stability properties of the resulting nanofibers.

![Figure 7.](image)

**Figure 7.** (A) DSC thermograms of neat PA6- and graphene-filled PA6 nanofibers, and (B) crystallization curves of pure PA6- and graphene-filled nanofibers. DSC = differential scanning calorimetry; PA6 = polyamide 6. Reprinted with permission from [85], 2019, Elsevier.

Like fullerene and graphene, a carbon nanotube has been found as a unique one-dimensional nanocarbon nano-allotrope [90]. It has sp² hybridized carbon atoms and a hollow cylindrical nanostructure [91,92]. The unique nanostructure leads to marvelous properties and potential [93]. A carbon nanotube forms electrospun nanofibers with various polymers such as poly(ethylene glycol) and polyamide [94,95]. Electrospun poly(ethylene glycol)/carbon nanotube nanofibers have been reported with a fine morphology and
high-power density of 156 mWcm$^{-2}$ [96,97]. Kaynan et al. [98] designed pol(vinyl butyral)-and carbon nanotube-derived nanocomposite nanofibers. They explored the mean fracture energies of the pol(vinyl butyral) nanofibers with 0.5 to 5 wt.% nanofiller loadings (Figure 8). The mean values of the total fracture energy as the function of the delamination length have been studied. The fracture energy was calculated through monitoring the crack propagation and tracked load data. Consequently, the crack length of 24 mm was observed. According to the results, a crack growth resistance was found in reinforced nanocomposites. Thus, adding higher carbon nanotube contents to the matrix led to a considerable increase in the crack growth resistance of the nanomaterials. Polyaniline has also been used as an effective matrix for nanocarbon-based nanocomposite nanofibers [99,100]. In these nanofibers, remarkable properties of polyaniline have been combined with carbon nanoparticles to reveal superior properties and high performance [101]. In these nanofibers, the dispersion of nanocarbon nanofillers may alter the texture and features of these nanostructures [102]. Liao et al. [103] primed polyaniline/carbon nanotube nanofibers. Adding a carbon nanotube caused a high electrical conductivity of up to $10^{2}$ S cm$^{-1}$, due to the formation of a percolation network in the nanofibers.

![Figure 8. Mean fracture energies, $G_c$, with respect to crack length of reference and interlayered composites. PVB = pol(vinyl butyral); CNTs = carbon nanotubes. Reprinted with permission from [98]. 2018, Elsevier.](image)

6. Significance of Electrospun Polymer/Nanocarbon Nanocomposite Nanofibers

Polymeric nanofibers own remarkable features of a light weight [104], resilience [105], strength [106], toughness [107], and chemical constancy [108]. Polymer fibers have been applied in useful industrial materials such as coatings, membranes, textiles, packaging, and biomedical arenas [109–111]. In addition, including nanofillers in polymeric nanofibers has led to a rise in important physical characteristics and applications [112].

Carbon fillers or nanofillers having different dimensions and structural/physical aspects influence the final material properties. In a study by Kasgoz et al. [113], various carbon fillers like graphite, expanded graphite, carbon black, and carbon fiber were introduced to a cycloolefin copolymer matrix. Comparative effects were observed on the morphology, mechanical, and rheological features of the resulting composites. The difference in properties was attributed to the variance in size and physical aspects of the carbon fillers. Chen et al. [114] explored the comparative effect of carbon nanofillers (carbon nanotube, graphene oxide, graphite nanoplatelets, and carbon black) on the thermal
conductivity of epoxy matrix nanocomposites. Figure 9 shows the efficacy of various carbon nanofillers on the thermal conductivity of epoxy matrix nanocomposites. Pristine epoxy depicted a low thermal conductivity. Consistent with the results, graphene-based nanofillers were found to be more effective in enhancing the thermal transport properties of the epoxy matrix than other nanofillers like a carbon nanotube, carbon black, and a graphite nanoplatelet. The reason seemed to be the higher aspect ratio of a graphene nanofiller as compared to other carbon nanofillers used. Moreover, the epoxy/graphene nanocomposite had a higher interfacial thermal resistance in epoxy–graphene, leading to a high thermal conductivity.

The imperative principles to choose a nanofiller for designing polymeric nanocomposites include [115] (i) the aspect ratio, size, and dimensions according to the desired end application; (ii) inherent structural properties and physical aspects of the nanofiller; (iii) the price of the nanofiller; (iv) the facile preparation process; and (v) functionalization and property enhancement capability. According to the end use, the nanofiller dimensions and inherent properties must be considered to minimize agglomeration with the increasing nanofiller loading. This will also promote a better compatibility between the matrix and nanofiller. For example, a selected non-modified one-dimensional nanofiller can be more easily aggregated than a better dispersed and functionalized two-dimensional or zero-dimensional nanofiller. In other words, the aspect ratio, size, and dimensions of the nanofiller must be considered, because changing these factors significantly affects the surface interactions with the matrix, interface formation, dispersion, etc. Therefore, an appropriate choice of nanofiller may help to reduce aggregation problems and achieve a safe percolation threshold value at low nanofiller loading. The selection of a particular polymer for nanofiber formation mainly depends upon its cost and controllable properties [116]. There are various types of polymers available under the categories of thermoplastic and thermosets. While selecting a polymer, factors like the molecular weight, surface to volume proportion, elasticity, porosity, wettability, and surface charge of the resulting nanofiber are usually considered.

![Figure 9](image)

*Figure 9. Effect of various carbon nanofillers on the thermal conductivity of epoxy matrix nanocomposite at room temperature, relative to neat epoxy resin (0.22 W/(m·K)). Reprinted with permission from [114]. 2019, Elsevier.*

Various application areas have been identified for polymer/nanocarbon nanocomposite nanofibers [117]. Importantly, these nanocomposite nanofibers have been applied in
organic photovoltaic devices [118,119]. In bulk heterojunction, poly(3-hexylthiophene):phenyl-C_{61}-butyric acid methyl ester-derived nanofibers were applied and led to an impressive power conversion efficiency of >5% [120]. The high photovoltaic performance was accredited to the formation of a donor–acceptor interface along with a penetrating charge transportation network in the nanofibers [121,122]. Kurniawan and co-researchers [123] developed nanofibers of poly(3-hexylthiophene):phenyl-C_{61}-butyric acid methyl ester. Both thermally annealed and non-annealed nanofibers were prepared. Figure 10 illustrates current density–voltage (J-V) features of the thermally annealed and non-annealed nanofibers. The photovoltaic properties of the thermally annealed and non-annealed nanofibers were studied and compared. Accordingly, the short circuit current density of the non-annealed sample was found to be lower around ~4.56 mA/cm^2, which was increased to 8.57 mA/cm^2 after annealing. The annealed nanofiber-based device had higher J-V characteristics, due to a superior charge transportation. The results led to a higher power conversion efficiency of the annealed nanofiber-based solar cell (~3.57%), relative to the non-annealed one (~1.08%). Hence, the solar cell features of the thermally annealed nanofibers were found to be visibly increased, due to better molecular ordering and a high crystallinity attained after annealing, relative to non-annealed nanofibers.

Another important application of polymer/nanocarbon nanocomposites has been identified for energy storage devices, especially efficient supercapacitors having high charge storage capacities [124,125]. Carbon nanoparticles have been used as significant constituents in supercapacitor electrodes [126]. The resulting electrodes may have a high electron conduction, optimal porosity, and mechanical and chemical robustness. Almost all exclusive nanocarbons (graphene, carbon nanotube, etc.) have been encompassed to form supercapacitor components [127–129]. In this concern, numerous polymer/nanocarbon combinations have been considered to form nanocomposite electrodes [130]. Subsequently, Rose et al. [131] studied the polyaniline/poly(vinyl alcohol) matrix and graphene oxide-derived nanocomposite nanofibers for supercapacitor electrodes. These nanocomposite electrodes possess a high surface area, charge mobility, and high capacitance. Zhou and co-workers [132] made electrospun graphene-wrapped polyaniline nanofibers. They also formed neat polyaniline nanofibers for comparison. Figure 11 shows the specific
capacitance of polyaniline and graphene-wrapped polyaniline nanofibers vs. current densities. According to the results, the graphene-wrapped polyaniline nanofibers exposed a higher specific capacitance of the nanocomposite nanofibers (250 Fg\(^{-1}\)). On the other hand, the neat nanofibers revealed a lower specific capacitance of \(~175\) Fg\(^{-1}\). It was suggested that the synergistic effects between graphene-wrapped polyaniline significantly improved the electron transportation through the nanocomposite system, thus increasing the capacitance performance. In addition, the visibly higher capacitance values of the polymer/graphene nanomaterials pointed to a better polymer–matrix compatibility and the effectiveness of the spinning technique [133]. Nevertheless, comprehensive future surveys must be carried out to form advanced polymer/nanocarbon-derived nanofibers aiming for supercapacitor electrodes.

![Figure 11](image)

**Figure 11.** The specific capacitance of polyaniline (PANI) and graphene-wrapped polyaniline nanofibers (Gra100-wrap-PANI-NF) as a function of varying current densities. Reprinted with permission from [132]. 2013, Elsevier.

Some further applications of polymer/carbon nanoparticle nanocomposite-resultant nanofibers include electronics, radiation shielding, and biomedical arenas [134]. In the field of electronics, nanocomposite materials have found wide potential [135]. However, the functioning of electronic devices may hinder other devices, humans, and the environment due to the generation of harmful electromagnetic radiations [136]. Therefore, the applications of nanocomposites have also been extended to shield the harmful electromagnetic interference (EMI) radiations [137,138]. In this regard, conjugated polymers such as polyaniline-derived nanofibers have been applied to shield the EMI radiations [139,140]. Predominantly, polyaniline/carbon nanoparticle-based nanocomposite nanofibers revealed an application to develop the EMI shields [141–143]. A design of polyaniline/graphene nanocomposite nanofibers has been reported using the electrospinning method [144]. The polyaniline/graphene nanofibers depicted high conductivity, high strength (179 MPa), and considerably elevated EMI shielding effectiveness (30 dB) features. Nonetheless, more research attempts have been found to be desirable for efficient-radiation-shielding polymer/nanocarbon nanofibers [145,146].

Biomedical fields define other significant application areas of polymer nanofibers [147]. Various polymer and carbon nanoparticle-derived nanofibers have been produced for this purpose [148–150]. Electrospun poly(vinyl alcohol)/graphene nanocomposite nanofibers [151,152] and poly(D, L-lactic-co-glycolic acid)/graphene oxide nanocomposite nanofibers have been observed for the fabrication of tissue engineering scaffolds [153,154]. However, this field demands the explorations of more innovative design combinations of biodegradable polymers and nanocarbon nanoparticles [155,156]. The anti-microbial
features of electrospun chitosan/nanocarbon nanocomposite nanofibers have been observed [157,158]. These nanocomposite nanofibers need to be further explored in this area to reveal the technical biomedical potential [159].

Nanofiber-based materials have a number of advantages as compared to the polymeric or composite material in a film, precipitate, or other forms. Most importantly, nanofibers have high surface area, formability, and porosity properties. Consequently, spinning techniques may produce nanofibrous structures having various sizes and shapes to attain specific designs and functions, which have not been observed in nonfibrous polymeric materials. Electrospun as well as non-electrospun nanofibers have been utilized in water treatment technology due to a multitude of stimulating features like a high specific surface area, precise porosity, mechanical strength, functionalization aptitude, cost effectiveness, and energy reserves [160]. The surface engineering of nanofibrous membranes may further enhance the performance towards water purification. In addition, nanofibers possess multiscale topography, penetrability, and mechanical properties suitable for technical applications like tissue engineering scaffold formation [161,162]. Well-aligned nanofiber arrangement can effectively progress the strength and elasticity properties of the nanomaterial. Similarly, small-sized pores along with high surface area and surface properties of nanofibers led to an application in wound healing. Here, finely porous nanofibers allow for the water/oxygen exchange, hinder the infiltration of microorganisms, as well as eliminate metabolic wastes. Fine examples can be observed in the form of polymer nanofibers with silver and gold nanoparticles [163,164]. The application of optimally permeable nanocomposite nanofibers has also been observed in packaging applications especially for food and pharmaceuticals [165].

7. Future and Conclusions

In this state-of-the-art overview, the electrospinning approach has been well thought out as a major technique to form polymer and nanocarbon-derived nanocomposite nanofibers. Among various spinning and non-spinning nanocomposite and nanofiber formation techniques, electrospinning has been considered as the most efficient method to form well-aligned, homogeneously dispersed, and high-efficiency nanostructures for practical applications. In this regard, various combinations of the polymer and nanocarbon nanofillers processed using electrospinning have been surveyed. Electrospinning has been used to form nanofibers from a solution or melt precursors. Here, nanoparticles dispersion in the nanofibers defines the microstructure, homogeneity, scattering, and surface features. The nanofiller dispersion as well as electrospinning parameters (polymer solution concentration, flow rate, voltage, etc.) must be controlled to attain the desired properties of the nanocomposite nanofibers. The ensuing technical areas of the polymer and carbon nanoparticles have been recognized for supercapacitors, radiation shielding, and biomedical applications. The enhanced electron and charge transportation has been looked at for both energy storage and EMI shield-based devices. In this regard, the nanofiller network formation in the nanofiber matrix was found to support charge transportation features. Here, the formation and use of functional nanocarbon nanoparticles for supercapacitor electrodes may expose high specific capacitance values. Similarly, the functional nanocarbon in nanofibers may lead to a high electron conductivity to better interact with incoming EMI radiations for absorption or dissipation. Parenthetically, future attempts are desirable to develop novel advanced materials in the field of supercapacitors and radiation shields. In biomedical applications, few suitable polymer/nanocarbon designs have been observed for tissue engineering and antimicrobial materials. Above and beyond, several technical areas remain uncharted for polymer/nanocarbon nanocomposite nanofibers including space, auto, engineering, smart textiles, and so on. Here, major encounters have been found to be connected to the nanocarbon dispersal, functionalization, and controlling of electrospinning parameters.

Henceforth, this article offers a technical outlook on electrospun polymer/nanocarbon nanocomposite nanofibers. In this concern, the electrospinning approach as well as
the design, microstructure, and physical properties of nanocomposite nanofibers were discussed. The major applications of polymer/nanocarbon nanocomposite nanofibers were found in the sectors of energy storage, radiation shielding, and biomedical. Despite of the progress in this field so far, polymer/nanocarbon nanocomposite nanofibers must be further explored for optimum manufacturing parameters and new design possibilities to overwhelm the associated challenges.

**Author Contributions**: Conceptualization, A.K.; data curation, A.K.; writing—original draft preparation, A.K.; review and editing, A.K. and I.A. All authors have read and agreed to the published version of the manuscript.

**Funding**: This research received no external funding.

**Data Availability Statement**: Not applicable.

**Conflicts of Interest**: The authors declare no conflicts of interest.

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