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Electrospinning Functional Polyacrylonitrile Nanofibers with Polyaniline, Carbon Nanotubes, and Silver Nitrate as Additives

Nuray Kizildag and Nuray Ucar

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Abstract

Electrospinning of composite nanofibers has been attracting great attention as a way of producing functional nanofibers. Composite nanofibers are produced with the incorporation of the additives into the polymer melt/solution before electrospinning process and reported to show many superior properties such as high modulus, increased strength, improved thermal stability, or some new functionalities such as flame retardancy, antimicrobial properties, water repellency, soil resistance, decreased gas permeability, electromagnetic shielding, electrical conductivity, and so on. The availability of the wide range of additives makes it possible to produce a wide range of functional nanocomposite nanofibers that are promising for various applications. Polyaniline (PANI) as an inherently conductive polymer is being investigated as an additive for improving conductivity. Carbon nanotubes (CNT) are widely used for either their reinforcement ability or their superior electrical conductivity. Silver nanoparticles (AgNPs) are being incorporated into polymer matrices to obtain antibacterial activity. This chapter provides a comprehensive review about polyacrylonitrile (PAN) nanofibers with PANI, CNTs, AgNPs, and their combinations and highlights the synergistic effects obtained by their combined use.

Keywords: antibacterial, antistatic, semiconductive, multifunctional, nanocomposite, electrospinning, nanofiber, polyacrylonitrile, polyaniline, carbon nanotubes, silver nitrate

1. Introduction

Electrospinning is a process that uses electrostatic forces to produce nanofibers. The setup for electrospinning consists of a high-voltage power supply that is used to charge the electrospinning solution, a pump that is used to feed the solution through the needle and a grounded collector that is used to collect the nanofibers in the nanoweb form. In the electric field forming between the needle and the collector, a jet occurs when the electrostatic force overcomes the surface tension of the solution droplet and it undergoes bending and whipping instability as a result of which the solvent evaporates and nanofibers form [1, 2]. Electrospun nanofibers have attracted great attention due to their unique properties, ease of fabrication, and possibilities of functionalization [1]. They have high surface-area-to-volume ratio, low density, and high pore volume [3–5], which qualify them for a number of applications such as tissue engineering [6], wound healing [7], drug delivery [8], filtration [9], sensors [10], energy harvesting and storage [11], polymer reinforcement [12], and so on.

While nanofibers have already been providing unpaired properties, composite nanofibers made the way one step further and realized additional functionalities, which showed the potential of improving the applications of nanofibers [13]. The composite nanofibers are produced with the incorporation of some additives. It has been possible to produce semiconductive nanofibers with the addition of PANI [14], antibacterial nanofibers with the addition of AgNPs [15], and semiconductive nanofibers with improved mechanical properties with the addition of CNTs [16]. Furthermore, some synergistic effects have been reported to occur when the additives are used together.

This chapter provides a comprehensive review of the studies about electrospun composite polyacrylonitrile nanowebs produced using PANI, CNTs, and AgNPs as additives; highlights the synergistic effects obtained by their combined use; and shows that it is possible to produce multifunctional nanocomposite nanowebs with the combined use of the additives.

2. Polyacrylonitrile nanowebs with polyaniline (PAN/PANI)

PANI is one of the most widely investigated conductive polymer due to its environmental stability, low cost of raw material, ease of synthesis, and good compatibility with polymer supports, controllable electrical conductivity and interesting redox properties associated with its nitrogen chain [17–19]. Insolubility of PANI has been a big problem retarding its applications. In this regards, the counter-ion-induced solubility of PANI has been a successful attempt that made polyanilines in conducting form to be soluble in some ordinary organic solvents [20]. Since then, solution blending of PANI with polystyrene [21], polyimide [22], polyamide [23], polyacrylonitrile [24], so on has been reported. The method of solution blending has also been adapted to prepare electrospinning solutions of different polymers with PANI with the aim of producing conductive nanofibers which may be used in sensor [25], tissue engineering [26], supercapacitor [27], flexible solar cells [28], hydrogen storage applications [29], and so on.

PANI exists in various levels of oxidation such as fully reduced leucoemeraldine base form, the half-oxidized emeraldine base form (EB), and the fully oxidized pernigraniline base form [30, 31]. The EB oxidation state of PANI can be doped with a protonic acid to form emeraldine salt (ES), which transforms the electronic structure of the chain into a polaronic lattice and results in an electrically conductive state [30]. For doping, nonvolatile acid dopants, such as camphorsulfonic acid (CSA) and dodecylbenzylsulfonic acid (DBSA), are widely used since they overcome the evaporation disadvantage of smaller molecular organic and inorganic acids, which cause conductivity depression of the acid-doped PANI [32]. The properties of the dopant, such as molecular weight, molecular size, acidity, and so on determine the doping ability of the dopant [33, 34] and thus the conductivity of the solutions, which has a direct influence on the electrospinning process and the properties of the nanowebs. Solvent selection is also important since it primarily determines the solubility of the polymers and electrospinnability [35]. The studies about PAN/PANI composite nanofibers are mainly focused on the effects of PANI content, dopant types, solvent types, solution preparation procedures, and redoping on the properties of composite nanowebs [14, 19, 32, 35–37].

Raeesi et al. [19] investigated PAN/PANI nanowebs with different composition ratios using N-methyl-2-pyrrolidone (NMP) as the solvent. Horizontal electrospinning setup with stationary collector was used for nanofiber production with various contents of PANI (up to 30 wt%) at various electrospinning temperatures. While bead-on-string structure with nonuniform morphology was observed at the PANI content of 30%, drops instead of fibers were observed at the PANI content above 30%. Average nanofiber diameter decreased with increasing PANI content. The electrical conductivity of the nanowebs was measured as 10^{-1} S/cm for nanofibers with 30% PANI after a doping process with HCl vapor [19]. Qavamnia et al. [36] electrospun PAN nanofibers with CSA-doped PANI using NMP as the solvent and investigated the effect of PANI content on the morphological, electrical conductivity, and mechanical properties of the blend nanofibers. PANI content was varied as 0, 10, 20, 30, and 40 wt%. Composite nanofiber diameters were in the range of 59 to 234 nm and decrease was observed in nanofiber diameter with the increase in PANI content. Beads were observed at 40 wt% PANI content. Tenfold increase in tensile modulus and 3-fold increase in tenacity were observed at the PANI content of 30 wt%. The electrical conductivity was reported to be between 10^{-10} S/cm and 10^{-1} S/cm depending on the amount of PANI added to nanofiber structure [36]. Kizildag et al. [14] electrospun nanofibers of PAN- and CSA-doped PANI using dimethyl sulfoxide (DMSO) as the solvent and investigated the effect of PANI content and the application of different dissolution methods on the morphology, chemical structure, conductivity, crystallinity, mechanical, and thermal properties of nanowebs. PANI content was varied as 1, 3, 5, 7, 10, and 30 wt%. For the investigation of the effect of dissolution process, three samples with 10 wt% PANI were prepared using different preparation procedures. Two different PANI solutions, which were stirred magnetically for 2 and 10 days, and another solution, which was exposed to homogenization with an ultrasonic probe for 1.5 h after magnetic stirring, were prepared. The diameters of the composite nanofibers increased until the PANI content of 5% and then decreased as the PANI content was further increased. The composite nanofibers were generally uniform except the nanofibers with 30 wt% PANI which had nonhomogeneous fiber structure. PAN/PANI composite nanowebs

with 1, 5, 10 wt% PANI appeared to have improved crystallinity values in comparison to neat PAN nanofibers. Breaking stress decreased with PANI addition, while breaking elongation increased as PANI content increased until the content of 7 wt% and then decreased. The conductivity of the composite nanofibers was improved, reaching a value higher than 10^{-6} S/cm with 3 wt% PANI which was in the range for electrostatic discharge applications. Thermal stability of the nanofibers was improved with PANI addition. Increase in dissolution time and application of ultrasonic homogenization affected the diameter, mechanical properties, crystallinity, and thermal properties of the nanofibers, while they had negligible effects on conductivity [14]. Kizildag et al. [35] also investigated the effects of different dopants such as camphorsulfonic acid (CSA), dodecylbenzene sulfonic acid (DBSA) in isopropanol, and dodecylbenzene sulfonic acid sodium salt (DBSANA⁺), and different solvents such as NMP and *N,N*-dimethylformamide (DMF) on the structure and properties of PAN/PANI composite nanowebs. It was shown that the solvents and dopants had significant effects on morphology, average nanofiber diameter, mechanical properties, while they had less effect on conductivity of the composite nanofiber webs. The fibers produced from NMP solvent generally had larger fiber diameters than the fibers produced from DMF, while the use of DBSANA⁺ resulted in the formation of larger diameters in comparison to other dopants. The use of NMP as the solvent resulted in higher breaking stress values for the reference samples and the composite samples, which contained CSA-doped PANI. The conductivity values of the composite nano/microfiber webs were around 10^{-8} and 10^{-9} S/cm [35]. In another study, comparing the effects of the solvents such as DMF and DMSO, and the dopants such as CSA and DBSA in isopropanol and DBSANA⁺, Kizildag et al. resulted that the composite nanofibers of PAN/PANI produced from DMSO generally had larger fiber diameters than nanofibers produced from DMF. While the diameter of composite nanofibers with the dopants CSA and DBSA (in isopropanol) decreased compared to 100% PAN nanofiber, the diameter of nanofiber with DBSANA⁺ drastically increased. Increased breaking elongations were observed for the samples electrospun from DMSO, while decrease was observed for the samples electrospun from DMF. CSA used with DMSO resulted in the highest conductivity of 10^{-6} S/cm, which is in the range suitable for electrostatic discharge applications [37]. Ucar et al. [32]. investigated the effect of different solvents (DMSO, NMP, and DMF) and solvent mixtures, application of dispersion and mixing techniques during solution preparation and redoping process on PAN/PANI composite nanofibers using CSA as the dopant. The morphology, average nanofiber diameters, crystallinity, mechanical properties, thermal properties, and electrical conductivity were all affected by the solvents used. Mechanical dispersion technique resulted in higher tensile breaking stress values than the corresponding magnetic stirring. While redoping did not affect the morphology and the diameter of the nanofibers significantly, it affected the tensile properties of the nanowebs by increasing the breaking stress values and decreasing the elongation values. The conductivity was improved 10 times and reached 1.2×10^{-5} S/cm after redoping [32].

As seen from the literature, polyaniline addition affected the morphology, nanofiber diameter, crystallinity, mechanical properties, electrical properties, and thermal properties of the nanofibers [14, 19, 32, 35–37].

3. Polyacrylonitrile nanowebs with carbon nanotubes (PAN/CNTs)

CNTs are widely used as additives in nanofiber production for either reinforcement or functionalization. They possess special properties such as high strength and aspect ratio, good thermal and electrical conductivities, and a low density, which are all important in the preparation of polymer composites [38–40]. They can have diameters ranging from 1 to 100 nm and lengths of up to millimeters. Their densities can be as low as 1.3 g/cm^3 and their Young's moduli are greater than 1 TPa. The weakest types of CNTs have strengths of several GPa [41]. Their electrical conductivity can be as high as 10^6 S/m [42]. In most cases, the addition of only a few percentages of CNTs to the nanofiber structure results in enhanced tensile properties, thermal stability, electrical properties and dimensional stability [38–43]. Nevertheless, to be able to fully benefit from their reinforcing properties, a uniform dispersion, and orientation of CNTs in the polymer matrix are important [16]. The strength and elongation are adversely affected by the addition of CNTs especially when the CNTs are not well dispersed and aligned along the fiber axis. The agglomerates can act as stress points instead of reinforcing and result in a decrease in both tensile strength and breaking elongation [43]. For better dispersion, several approaches, which can be roughly classified as mechanical and chemical methods, can be seen in literature. While the mechanical methods such as ball milling, ultrasonication, and high shear mixing contribute to better dispersion by altering the surface energy of the solids, chemical methods such as surface functionalization improve the chemical compatibility between the CNTs and the solvents and the polymer matrixes, enhance wetting characteristics and reduce their tendency to agglomerate [16]. Ultrasonication is the most common method applied for dispersion of the CNTs [16, 44]. CNTs are ultrasonicated in either the solvent or the polymer solution. In many studies, CNTs are chemically treated before ultrasonication [40, 45, 46]. Besides all the efforts to better disperse the CNTs in polymers, electrospinning is reported to be a process that greatly contributes to the alignment and dispersion of CNTs by charge, confinement, and flow effects [47–49]. Dror et al. established a model to explain how the CNT-polymer composite nanofibers were formed by electrospinning. The randomly oriented MWCNT rods in the electrospinning solution were oriented along the streamlines of the electrospinning solution due to elongation of the fluid jet [49]. In addition, it has been shown that significant interactions exist between PAN chains and CNTs, which lead to better dispersion of CNTs in PAN. DMF, which is widely used as a solvent for PAN provides another advantage. It is a good solvent for suspending oxidized CNTs [35].

Ge et al. [50] prepared PAN/CNT nanofibers on an electrospinning setup with a rotating collector using acid treated CNTs. The CNT content was changed as 3, 5, 1, 20 wt%. UV-visible spectroscopy indicated that there was a strong interfacial bonding between the CNTs and PAN macromolecules. The orientation of the CNTs within the nanofibers was observed to be much higher than that of the PAN polymer crystal matrix. Incorporation of CNTs has been demonstrated to enhance electrical conductivity, tensile modulus, thermal deformation temperature, and decomposition temperature of composite nanowebs. At the CNT content of 20 wt%, the electrical conductivity the composite nanofibers was measured as 1.0 S/cm [50]. Hou et al. [45] produced composite nanofibers of PAN with oxidized MWNTs. While the surfaces of the pure PAN nanofibers and composite nanofibers with low amount of

CNTs were smooth, they became rough with the increase in CNT content. Increase was observed in tensile modulus and tensile strength, while decrease was observed in breaking elongation with CNT addition. The tensile modulus reached 4.4 GPa at 20 wt% of MWCNT with a 144% improvement. The maximum tensile strength was 80.0 MPa at about 5% MWCNT with a 75% improvement. It was shown that a higher concentration of MWCNTs effectively resisted heat shrinkage of the composite nanowebs during carbonization [45]. Heikkilä and Harlin [44] electrospun pure, salt-containing, and CNT-containing nanofibers using different nozzle sizes, spinning voltages and distances. PAN and additive concentration were selected as 13 and 0.25 wt%, respectively. Composite nanofibers with CNTs showed more pronounced surface roughness and markedly larger fiber diameters than pure PAN and salt-containing nanofibers. The electrospinnability was improved with the addition of CNTs. They resulted that the solution composition had a greater effect on nanofiber diameter than process parameters [44]. Saeed et al. [46] used 1 and 2 wt% MWNTs functionalized by Friedel-Crafts acylation to produce PAN/CNT nanofibers. Functionalization provided better dispersion of the CNTs, which resulted in nanofibers with less beads and higher mechanical properties. Specific tensile strength and the specific modulus increased while breaking elongation decreased at CNT content of 1 wt%. Increase was observed in the degradation temperature with CNT addition [46]. Chen et al. [40] functionalized CNTs by grafting with PAN through the process of plasma-induced grafting polymerization before incorporating into PAN nanofibers. PAN grafted CNTs provided stable and well-dispersed solutions due to the chemical affinity between the polar-modified groups and the organic solvent. TEM observations showed the CNTs were generally parallel and oriented along the axes of the nanofibers. The surfaces of the composite nanofibers became rough with the increase in CNT content. Raman results indicated enhanced growth of graphitic crystals in the carbonized PAN due to the presence of the CNTs. The sheet resistance of the CNT/carbon nonwoven fabrics was appreciably enhanced by increasing CNT concentration. Carbonized PAN/CNT nanowebs had a significant SE of more than 30 dB at 30 MHz, and the SE was around 10–15 dB between 900 MHz to 3.0 GHz, even for the small thickness of 150 μm . The results indicated that carbonized PAN/CNT nanowebs were promising for use as effective and practical EMI shielding materials due to their lightweight, good mechanical properties, low cost, and high shielding performance [40]. Yousefzadeh et al. [47] dispersed MWNTs in DMF using probe sonicator for about 1 h. Magnetic stirrer was used to mix the polymer with CNT dispersion until the polymer was uniformly dissolved in the solvent. The CNT content was varied as 0.01, 0.05, 0.1, 0.3, 0.5, 1, and 2 wt%. According to the SEM images of dispersed nanotubes, mixing for about 1 h with 30% amplitude was found to be sufficient to achieve a well-dispersed solution. To improve the dispersion of nanotubes at high concentration, MWNTs were refluxed in HNO_3 and stirred at 15°C for 8 h to attach functional groups of carboxyl and hydroxyl groups onto MWNTs. As the CNT content increased, the surfaces of the composite nanofibers became rough. They obtained thicker fibers with the addition MWNTs compared to CNT-free ones. The highest tensile strength, tensile modulus, and breaking elongation were obtained with 1% CNT addition [47]. Qiao et al. [51] functionalized the SWNTs by polymer wrapping, dispersed them in DMF through mild bath sonication for 2 h, added PAN, and mechanically stirred overnight at 40°C using a

magnetic stirrer to yield a homogeneous solution. The SWNT content was varied as 0.25, 0.5, 0.75, and 1 wt%. While the surfaces of the nanofibers became rough, the diameters of the nanofibers became larger with CNT addition. The introduction of SWNTs improved the modulus and tensile strength of the PAN nanowebs. The tensile strength of the nanocomposites at about 0.75 wt% SWNTs was increased by 58.9%. In addition, the tensile modulus showed a peak value of 4.62 GPa with 66.8% improvement. While the electrical conductivity increased to 2.5 S/cm, T_g increased by about 3°C by incorporating 0.75 wt% SWNTs into the PAN matrix [51]. Wang et al. [52] functionalized MWCNTs by Friedel–Crafts acylation. They used *in situ* and *ex situ* solution polymerization systems to obtain composite solutions with 0.5, 1, 3, and 5 wt% CNTs and an electrospinning setup with a stationary collector to produce composite nanofibers. While the tensile modulus, tensile strength, thermal stability, crystallinity were improved with CNT addition regardless of the incorporation method, the *in situ* polymerization resulted in better dispersion, finer fiber formation, higher orientation and crystallinity, larger crystal size, higher tensile modulus and tensile strength, higher thermal stability [52]. Almuhammed et al. [16] dispersed MWNTs (0.2, 0.4, 0.5, 0.7, 1.0, and 1.5 wt%) in the solvent by high shear mixing using a homogenizer device and ultrasonication, added PAN to the dispersions and stirred magnetically until dissolution of PAN. While PAN nanofibers had a mean diameter of 568 nm, the composite nanofibers had average diameters ranging from 325 to 795 depending on the percentage of MWNTs. The composite nanofibers possessed an electrical volume percolation threshold at very low loading percentage of MWNTs corresponding to 0.5 wt%. While the volumetric electrical conductivity increased by five orders of magnitude from 1.85×10^{-11} S/m at CNT content of 0.4 wt% to 4.15×10^{-6} S/m at 0.5 wt%, the surface electrical conductivity was not very much affected by CNT addition. The composite nanowebs were suggested for use as pressure sensors as an exponential relationship was observed between the mechanical pressure applied and the volume conductivity [16]. Eren et al. [53] investigated the effects of differently functionalized (carboxyl, amine, and hydroxyl functionalized) MWNTs on the structure and properties of composite PAN nanofibers produced by horizontal electrospinning setup with a rotating collector. CNTs were dispersed in DMF by ultrasonic tip followed by the application of ultrasonic bath for 45 min. The concentration of PAN and CNTs were 7 and 1 wt%, respectively. Slight increases were observed in nanofiber diameters with CNT addition regardless of the functionalization process applied. Among the three differently functionalized MWNTs, amine-functionalized nanotubes provided the highest tensile strength, tensile modulus, and crystallinity. The conductivities of the composite nanowebs were measured as around 10^{-7} S/cm regardless of the functional groups of CNTs [53].

According to the literature, significant differences are reported to occur in properties of PAN/CNT nanowebs depending on the types of CNTs used, functionalization processes applied to the CNTs, solution preparation methods, additive contents, and electrospinning conditions. The studies show that improvement in electrospinnability, crystallization, mechanical properties, thermal properties, thermal stability, and electrical conductivity can be obtained with the addition of CNTs if the optimum conditions are ensured.

4. Polyacrylonitrile nanowebs with silver nanoparticles (PAN/AgNPs)

Silver has been the most widely used material to fight against broad range of microorganisms since ancient times [54]. AgNPs are expected to show better performance than micro-particles due to their increased surface area. Moreover, they have been found to exhibit remarkable catalytic activity, and high electrical conductivity [55]. The incorporation of AgNPs into nanofibers is reported to result in an improved mechanical properties and desirable functionalities, such as antistatic and antibacterial properties [56], which offer great potential in various fields such as filtration, protective textiles, medical textiles, biomedical applications, and so on [4]. The studies in literature have demonstrated the antibacterial activity of nanowebs containing AgNPs against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus Subtilis*, *Bacillus cereus*, and *Pseudomonas aeruginosa* [4, 15, 57, 58]. For antimicrobial performance of the nanofibers, the rate and the amount of silver release are important factors [4, 57]. A steady and prolonged release of silver cations can inhibit the growth of bacteria when their concentration is above 0.1 ppb [59].

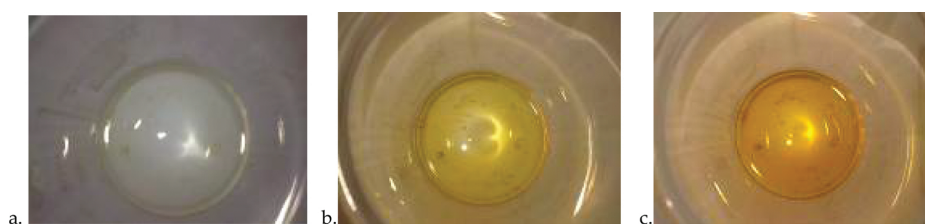


Figure 1. Photographs of PAN/10 wt% AgNO₃ solution: (a) without any treatment; (b) after exposure to xenon-arc lamp for 15 min; (c) after exposure to xenon-arc lamp for 30 min.

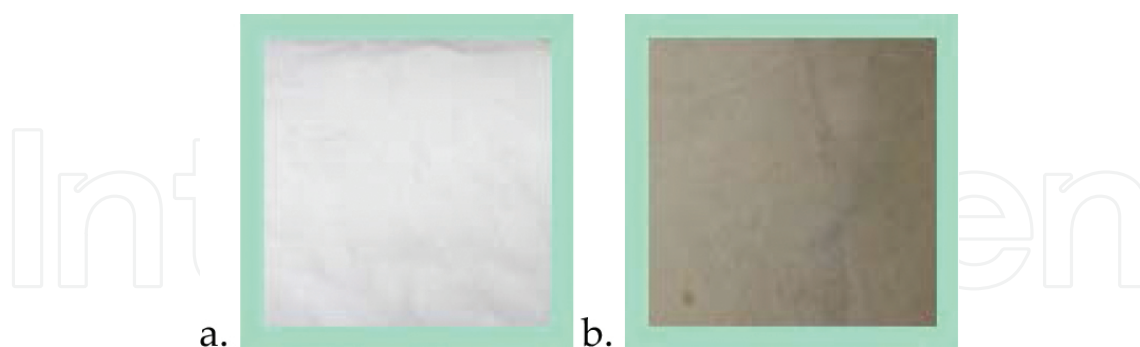


Figure 2. Photographs of PAN/10 wt% AgNO₃ nanoweb: (a) before; (b) after chemical reduction process performed by immersing the nanowebs into aqueous solution of hydrazinium hydroxide.

There are two general approaches in the preparation of polymeric nanowebs with AgNPs such as *ex situ* and *in situ*. In the *ex situ* methods, AgNPs are synthesized before their incorporation into the polymer that is used as the dispersion medium; whereas in *in situ* methods, the polymer is used as the reaction medium and AgNPs are synthesized in the polymer. Providing better dispersion of AgNPs, *in situ* methods have attracted more atten-

tion than *ex situ* methods in preparing polymeric matrix with AgNPs [60, 61]. Chemical reduction by the solvent [15], or aqueous solutions of sodium borohydride (NaBH_4) [15], and hydrazinium hydroxide ($\text{N}_2\text{H}_5\text{OH}$) [62], photo reduction [57, 62] and heat treatment [15] are some of the methods used for *in situ* synthesis of AgNPs [15, 57]. With the formation of AgNPs, electrospinning solutions and nanowebs change color from yellow to brown [63]. The photographs showing the color changing in the solutions and nanowebs after reduction process are presented in **Figures 1** and **2**, respectively.

PAN [56], cellulose acetate [64], chitosan [65], gelatin [60], polyvinyl alcohol [66], and so on have been used in nanofiber formation as host polymers for *in situ* formation of AgNPs. PAN is an excellent polymer for *in situ* synthesis of AgNPs since coordination bonds forming between silver ions and cyano nitrogen of PAN avoid aggregation of AgNPs [55].

Lee et al. [67] prepared 7 wt% PAN/DMF solution with silver nitrate (0.05, 0.2, and 0.5 wt% of the amount of PAN) and aged the solutions for 10 days before electrospinning, thereby using DMF as the reducing medium. AgNPs were spherical in shape and had an average diameter of 5.8 nm. UV-Visible spectra showed that the amount of AgNPs increased in time during aging without any change in their sizes. When the concentration of PAN was increased, the generation of AgNPs were slower. They concluded that DMF successfully reduced the Ag^+ ions and PAN acted as a stabilizing agent to inhibit the agglomeration of the Ag nanoparticles. Decrease in nanofiber diameter was observed with increase in AgNP amount which was attributed to the increased conductivity of the electrospinning solutions [67]. Wang et al. [68] prepared composite PAN nanofibers with AgNO_3 and applied chemical reduction in $\text{N}_2\text{H}_5\text{OH}$ aqueous solution. AgNPs with average diameters of 10 nm were dispersed homogeneously in PAN nanofibers. D and G peaks in Raman spectrum of the composite nanowebs indicated that the structure of PAN became similar to the PAN-based carbon fiber after being doped with AgNPs. This was attributed to the AgNPs acting as a catalyst for the dehydrogenation of hydrocarbon compound at room temperature [68]. Sichani et al. [57] added 0.05, 0.2, and 0.5 wt% AgNO_3 to PAN/DMF solutions and used xenon arc lamp in order to *in situ* synthesize AgNPs in these solutions. The average size of silver nanoparticles was around 10 nm. Improvement in electrospinning process, decrease in the number of the beads and fiber diameter were observed with the addition of up to 0.5 wt% AgNO_3 . The crystallinity increased with the addition of AgNO_3 . The composite nanofibers had steady and good antibacterial activity, especially against *P. aeruginosa*. The antibacterial activity against *S. aureus* and *E. coli* was lower [57]. Rujitanaroj et al. [63] prepared 10 w/v% PAN/DMF solutions with different contents of AgNO_3 (0.5, 1.5, 2.5 wt%) and aged the solutions for 5 days before electrospinning. The composite nanowebs were exposed to UV-irradiation to enhance the reduction process. UV treatment resulted in the formation of larger AgNPs on the surface of nanofibers. The diameter of the nanofibers decreased dramatically with increase in the AgNO_3 amount and decreased further slightly with the UV treatment. The amount of AgNPs increased with aging time without any change in their size. While the tensile strength increased slightly, elongation at break decreased slightly with AgNO_3 addition. The cumulative amounts of the silver release increased as the submersion time, the initial AgNO_3 concentration and the UV irradiation time interval increased. The antibacterial activity of the membranes against *S. aureus* and *E. coli*

bacteria increased with the increase in AgNO_3 concentration and UV irradiation time [63]. Lee et al. [69] prepared composite PAN nanofibers with AgNO_3 and performed chemical reduction in $\text{N}_2\text{H}_5\text{OH}$ aqueous solution. AgNPs with diameters of less than 5.8 nm were dispersed homogeneously in PAN nanofibers and the nanofibers were effective against *S. aureus* and *E. coli* [69]. Shi et al. [4] added AgNO_3 (0.5 and 1.25 wt%) to 8 wt% PAN/DMF solution and performed atmospheric plasma treatment for the reduction of silver ions in the PAN/ AgNO_3 /DMF solutions. AgNPs with diameters ranging between 3 and 6 nm were found to be uniformly dispersed in the nanofiber. The composite nanofibers showed excellent antibacterial activity against both Gram-positive and Gram-negative microorganisms [4]. Mahapatra et al. [15] prepared composite nanowebs of PAN with 8 wt% AgNO_3 and applied three different reduction methods such as refluxing the solution before electrospinning, treating the composite nanoweb with aqueous solution of sodium borohydride (NaBH_4), and heating the prepared composite nanofibers at 160°C . Distinct absorption band at 410 nm on UV-Visible spectra confirmed the formation of AgNPs. TEM micrographs showed that the AgNPs were dispersed homogeneously on the surface of PAN nanofibers, and particle diameter was about 5–15 nm. They concluded that refluxing resulted in smaller nanofiber diameter than chemical reduction applied to the nanoweb and attributed this to the increased conductivity of the electrospinning solution during refluxing. All three methods resulted in good antibacterial activity against *S. aureus*, *E. coli*, and *B. subtilis*. The size of the silver nanoparticles were smallest and length of inhibition zone was the highest against *S. aureus* bacteria for the composite membrane that was prepared by refluxing Ag^+ ions in DMF solvent [15]. Ucar et al. [56] prepared PAN/AgNP nanofibers with and without stabilizer and applied four different reduction methods (refluxing in DMF, chemical reduction by hydrazinium hydroxide, xenon arc reduction in solution and nanoweb form) in order to compare their effects on the properties of the composite nanowebs. 10 wt% AgNO_3 was added to 10 wt% PAN/DMF solution. Horizontal electrospinning setup with a rotating collector was used. Higher absorbance values were obtained for PAN/10 wt% AgNO_3 nanowebs reduced with hydrazinium hydroxide. While the xenon arc reduction applied to the solution resulted in thicker nanofibers, chemical reduction process resulted in finer nanofibers. Composite nanowebs electrospun from the composite solution exposed to xenon-arc displayed the lowest breaking strength values. The nanowebs which were chemically treated with aqueous solution of $\text{N}_2\text{H}_5\text{OH}$ displayed the highest breaking strength. Electrical conductivity was measured as 10^{-7} S/cm for the composite nanowebs reduced by chemical reduction and xenon arc application. With the addition of the stabilizer, fiber diameter increased while conductivity decreased [56]. Demirsoy et al. [62] investigated the effect of dispersion technique, reduction method, and AgNP amount on the properties of PAN/AgNP nanofibers. AgNO_3 (1 wt%, 3 wt%, and 10 wt%) was added to 7 wt % PAN/DMF solution and stirred for 1 h. The nanowebs were produced on a horizontal electrospinning setup with a rotating collector. Two different reduction methods such as chemical reduction by $\text{N}_2\text{H}_5\text{OH}$ solution and xenon arc reduction were applied. While the reduction process by $\text{N}_2\text{H}_5\text{OH}$ applied to the nanowebs resulted in a decrease, reduction by xenon arc applied to the electrospinning solution resulted in an increase in the nanofiber diameters. The crystallinity of PAN/10 wt% AgNO_3 nanoweb was lower than that of PAN/1 wt% AgNO_3 nanoweb. The highest tensile strength was obtained at the AgNO_3 content of 1

wt% after chemical reduction by N_2H_5OH . The tensile strength decreased with the increase in additive amount. Application of an additional dispersion process by ultrasonic homogenizer and bath generally provided higher breaking strength values than only mixing with a magnetic stirrer due to better dispersion of particles. The electrical conductivity of PAN/AgNP nanowebs was around 10^{-7} S/cm at 3 wt% $AgNO_3$ content and a decrease was observed with the increase in $AgNO_3$ content. Excellent antibacterial activity against *S. aureus* was obtained at the $AgNO_3$ content of 3 wt% after the chemical reduction process [62].

According to the existing literature on PAN/AgNP nanofibers, it can be concluded that concentration of the AgNPs, the dispersion and reduction methods applied, addition of a stabilizer are important factors that affect the final properties of the composite nanowebs.

5. Composite PAN nanowebs with the combined addition PANI, CNTs and AgNPs

A recent approach for functionalization of nanofibers is the combined use of additives. There are studies about composite electrospun nanowebs and films showing improved mechanical properties, thermal stability, crystallization and antimicrobial activity [70], electrical properties [71, 72], and biocompatibility [72] with the combined use of CNTs and AgNPs. Besides there are also some studies reporting about the synergistic effects obtained by the simultaneous use of the conductive polymers, CNTs and AgNPs [73, 74].

Ucar et al. [75] produced PAN composite nanofibers adding PANI and CNT simultaneously. While the diameters of nanofibers increased, the effect of PANI on diameter was higher than that of CNTs. The breaking of the composite nanofibers with 1% CNT and 3% PANI was 25% higher than that of pure PAN nanofibers. Conductivity of the composite nanowebs was in the semiconductive range regardless of the additive content. The crystallinity of PAN/PANI/CNT composite nanofiber was higher than that of pure PAN, PAN/CNT, and PAN/PANI composite nanofibers [75]. Eren et al. [76] incorporated various amounts of CNTs, AgNPs, and PANI into PAN nanofibers in order to see the synergistic effect of the additives on the final properties of the composite materials. Increase in the amount and types of additives generally resulted in an increase in the diameter of nanofibers and decrease in mechanical strength. Composite nanofibers with AgNPs displayed higher breaking strength and electrical conductivity than the composite nanofibers with CNTs. Generally, PANI improved the crystallinity of the composite nanowebs more than the nanoparticles. The use of the additives (PANI, CNT, AgNPs) at low concentration resulted in an increase in the temperature and enthalpy for cyclization compared to pure PAN nanofiber. Even though each of the nanoparticles was used in low concentrations, the composite nanowebs of PAN/1 wt% CNT/1 wt% $AgNO_3$ and PAN/3 wt% PANI/1 wt% $AgNO_3$ exhibited antimicrobial properties due to the synergistic effect of additives. It was suggested that PAN composite nanofibers with 3 wt% PANI and 1 wt% $AgNO_3$ generally presented better performance than the other samples in terms of electrical conductivity, antimicrobial activity, mechanical strength, crystallization, and thermal stability [76]. Kizildag et al [70] produced composite nanofibers from a solution of PAN, MWNTs,

and AgNO_3 in DMSO by the electrospinning method. They immersed the composite nanowebs into aqueous solution of hydrazinium hydroxide for the chemical reduction of silver ions. PAN/f-MWNTs/AgNPs nanowebs displayed enhanced conductivity and antimicrobial properties particularly when the chemical reduction process was applied. Besides, they showed improved crystallinity. While the reduction process made the highest contribution to the ultimate tensile strength, elongation, and conductivity of the nanowebs, MWNT content had negligible effect on conductivity of the nanowebs. PAN with 1 wt% MWNTs and 1 wt% AgNO_3 was suggested for use as antistatic and antibacterial nanowebs [70].

6. Conclusions

The composite nanofibers have been attracting great interest, as they display many improved properties such as high modulus, increased strength, improved thermal stability, electrical, barrier properties, and/or new functionalities such as flame retardancy, antimicrobial properties, water repellency, conductivity, and so on. Polyaniline, carbon nanotubes, and silver nanoparticles are widely used additives in the production of composite nanofibers. While their incorporation into the nanofiber structure is reported to affect morphological properties, chemical structure, crystallinity, conductivity, thermal properties, mechanical properties, and so on, polyaniline is mainly added to improve the conductivity; carbon nanotubes for improving strength, conductivity and thermal properties; and silver nanoparticles for developing antibacterial properties. The studies on the combined use of these additives are promising since it has been possible to obtain some synergistic effects as well as multifunctionality. With the improvements in the processing that will ensure especially uniform dispersion of the additives and higher production rates, the potential applications of functional composite nanofibers will soon turn into reality.

Author details

Nuray Kizildag* and Nuray Ucar

*Address all correspondence to: kizildagn@itu.edu.tr

Textile Engineering Department, Istanbul Technical University, Istanbul, Turkey

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