



Graphene-embedded electrospun polyacrylonitrile nanofibers with enhanced thermo-mechanical properties

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Abstract Nanofibers have gained significant consideration due to their unique structural properties and applicability in a wide range of sectors. This study aimed to develop polyacrylonitrile (PAN)/graphene co-electrospun nanofibers at different nanofiller loadings. The electrospinning conditions were prior optimized for potential difference, dope solution feed rate, and needle-collector distance to get bead-free electrospun fibers. The prepared composite nanofibers were characterized using various instrumental techniques. The results demonstrated that prepared composite electrospun were hydrophilic (water contact angle—WCA—7.9°) as compared to control PAN nanofibers (WCA: 135.9°). The nanofibers diameter of control PAN (611 nm) decreased to 515 nm after graphene loading under the same electrospinning conditions. The tensile strength of the control PAN fibers (2.95 MPa) increased to 4.37 MPa, whereas the respective elongation at the break decreased from 96 to 44%. The FTIR analysis expressed a strong bonding of cyanide functional groups in the PAN with the polar

groups at the graphene nanoplates in the composite electrospun fibers. The finding of the study is the successful development of PAN/graphene composite electrospun nanofibers with tuned thermomechanical properties.

Keywords Electrospun · Graphene · Hydrophilic · Nanofibers · Nanocomposites · Polyacrylonitrile

Introduction

Polymer-based materials have mostly replaced the metals based on lightweight, controlled structures, reasonable market prices, and tunable physicochemical properties [1]. Polyacrylonitrile (PAN) expresses exceptional properties in terms of mechanical strength, elasticity, fiber stability, thermal stability, chemical resistivity, and degradation resistivity even under ultraviolet (UV) irradiation. It is a thermoplastic polyester and is commonly synthesized via nitrile polymerization [2]. PAN, although polar, dissolves in organic polar media including ethylene carbonates, dimethylformamide (DMF), and dimethylacetamide [3]. The PAN is used to produce novel carbon-based fibers, gas filters, flame retardants, and sensors [4, 5]. The cyanide (-CN) group at the PAN enables its effective interaction with nanofillers like carbon nanotubes, graphene, and graphene oxide (GO) during its nanocomposite's formation with tuned tensile, electrical, and thermal properties [6]. The PAN-based nanofibers could find remarkable applications in the fabrication of composites, defensive

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materials, filtration films, hardware materials, wound dressings, and lithium-polymer batteries [7].

Extensive research work has been done on investigating the physical attributes of graphene-based nanocomposites [8, 9]. Graphene possesses interconnected microstructure, high surface area, flexibility, quick ion transport, and electron conductivity. Such extraordinary properties make it applicable in electrochemical storage, charge transformation, semiconductors, catalysis, and polymeric composites [10]. The homogenous dispersion of graphene-based nanostructures in a polymer matrix is a challenging problem in the nanotechnology industry. Such a uniform dispersion of graphene-based nanostructures could enhance the thermal, and mechanical properties and the performance of the polymer-based nanocomposites. There are various techniques to make a uniform distributed dispersion of NPs in the polymer matrix including salinization, ultra-sonication, direct mixing, or making NPs hydrophobic if the polymer matrix is non-polar, to improve dispersibility [11]. However, the dispersion of nanomaterials does not necessarily improve the nanocomposite but also depends on the concentration, size, shape, compatibility, and type of NPs in the polymer matrix [12].

Electrospinning is a powerful technique that can be used to fabricate fibers with unique properties by carefully controlling various parameters. Electrospun PAN/graphene fibres are one such example, where the incorporation of graphene into the polymer matrix can significantly enhance the mechanical, electrical, and thermal properties of the resulting fibers [13]. The high surface area of electrospun fibers makes them ideal for applications such as sensors, energy storage, and reinforcement of composites. The incorporation of graphene into PAN fibers also leads to improvements in the mechanical properties, such as increased tensile strength, modulus, and toughness, making them an ideal candidate for structural applications [14].

Kaur et al. [15] fabricated carbon nanotubes-PAN nanofibers via electrospinning and studied the structural morphology at various electrospinning parameters. Wang et al. [16] prepared PAN/GO nanofibers via an electrospinning process for enzyme immobilization and studied the mechanical properties, such as elasticity and frictional forces. Wang et al. [17] modified the surface of zirconium oxide using polyethyleneimine and then fabricated PAN-based modified

zirconium oxide nanofibers to eliminate fluoride from underground water. Abdel-Mottaleb et al. [18] prepared PAN/GO nanomembrane via electrospinning and enhanced the mechanical performance of the PAN nanomembrane water filter by incorporating a GO nanofiller. However, there is a variety of studies being performed on the formation and application of nanocomposites [15, 16].

The present study is devoted to fabricating, characterizing, and studying the thermo-mechanical properties of PAN-based graphene-embedded electrospun composite nanofibers. The developed composite nanofibers were characterized using scanning electron microscopy (SEM) to ascertain the surface morphology, Fourier transforms infrared spectroscopy (FTIR) to investigate interfacial bonding, water contact angle (WCA) to analyze hydrophilicity, single fiber strength tester to examine mechanical enhancements, and thermogravimetric analysis (TGA) to study thermal properties.

Materials and methods

Materials

Materials used for the fabrication of composite nanofibers include the PAN (\overline{M}_w 150000, Sigma–Aldrich), graphene nanoplatelets (2 to 10 nm thick and 5 μm wide, TCI, Japan) and DMF (99.5%, Dukson Chemicals).

Fabrication of PAN/graphene composite nanofibers

A homogeneous PAN solution was prepared in DMF using magnetic stirring at 50 °C for 24 h. Desired amount (0 to 3 wt%) of graphene nanoplatelets was dispersed into DMF and sonicated (Biotechnology Medical Services, UC-D06, USA) for 90 min 1.5 h at 40 °C. A desired amount of PAN solution was poured into the prepared graphene dispersion and magnetic stirred for 18 h at 40 °C at 500 rpm. A syringe with a G-18 needle was filled with the prepared dispersion and placed vertically for a few minutes to remove any air bubbles. The syringe was affixed to a computerized pump to switch the solution ejection. The prepared electrospinning dispersion was electrospun and deposited on the aluminum foil placed over a grounded stationary collector. Electrospinning conditions were optimized at a potential difference of 15

kV, feed rate of 1.5 mL/h, and needle-to-collector distance of 15 cm, to get uniform fiber formation. During the electrospinning process, the solvent DMF evaporated as the jet of nanofibers traveled to the stationary collector due to its volatile nature, spinning velocity, and large deposition time over the collector. So, the developed composite nanofibers were formed in a dried state and separated from the aluminum foil using a forceps tool.

Characterization of PAN/graphene composite nanofibers

The SEM micrographs were obtained using FEI Nova 450 electron microscope to study the surface morphology of PAN/graphene composite nanofibers. FTIR scan was performed using Tensor 27 IR Bruker Netherland and obtained transmission spectra in the range 4000–600 cm^{-1} . A Theta Lite optical tensiometer (Attention TL 100, Finland) was employed to measure the WCA of the fabricated electrospun composite nanofibers. Mechanical testing was performed using a single fiber strength tester (Tensiometric 2.5). Thermal stability of the composite nanofibers was ascertained using TGA TG209 F1 Libra NETZSCH by examining the weight loss during a constant heating rate (10 $^{\circ}\text{C}/\text{min}$) with a scanning range of 28–600 $^{\circ}\text{C}$ under a nitrogen flow environment.

Results and discussion

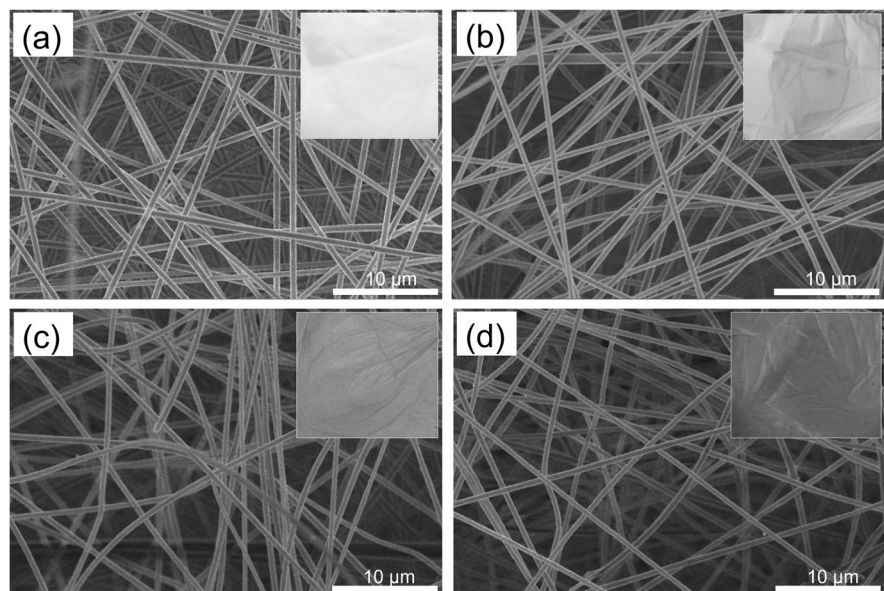
SEM analysis

On increasing the contents of graphene nanoplates in the PAN matrix, the color shade of the composite nanofibers turned darker (insets of Fig. 1), confirming the presence of graphene nanoplates [19]. The mean diameter of the developed nanofibers reduced from 611 ± 01 to 515 ± 01 nm with the increment of graphene nanoplates within the PAN matrix (Fig. 2) [16, 18].

FTIR analysis

The FTIR analysis was performed to probe any associations between the graphene nanoplates and PAN polymer framework to check the first details of the comonomers included in the antecedent nanofibers (Fig. 3). The composite nanofibers spectra peaks at 2922 cm^{-1} and 2243 cm^{-1} demonstrated the stretching vibration in alkanes and extending the nitriles vibration, respectively [20]. The band at 1664 cm^{-1} was referred to as carbonyl elongation and the carbonyl peak appeared to verify the occupancy of methacrylate moiety. The bending at 1453 cm^{-1} was due to vibrations of the methylene group [19]. The bands presented from 1290 to 900 cm^{-1} were due to C–H stretching; the carbonyl peak verified the probable presence of a corrosive comonomer [14]. The FTIR peaks

Fig. 1 SEM images of electrospun nanofibers at 5000 \times magnification for **a** control PAN, and PAN/graphene composite nanofibers with graphene contents of **b** 0.5 wt% **c** 1 wt%, and **d** 3 wt%. The inset is a respective digital photo in each part



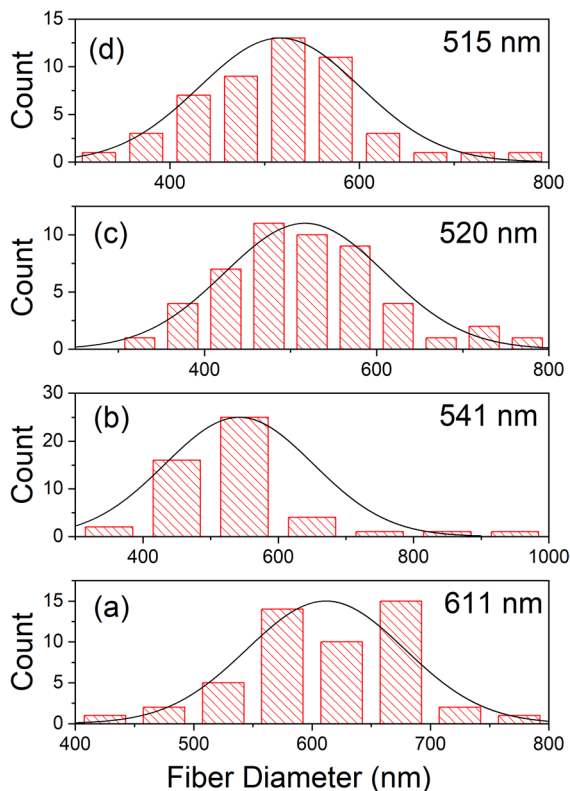


Fig. 2 Histograms of SEM images of electrospun **a** control PAN, and PAN/graphene composite nanofibers with graphene contents of **b** 0.5 wt% **c** 1 wt%, and **d** 3 wt%

at 2852 cm^{-1} and 760 cm^{-1} indicated the occupancy of C–H bonds and C–C vibrations, respectively. The characteristic peak at 656 cm^{-1} , indicates C–C bonding of PAN/graphene composite nanofibers.

Water contact angle analysis

The water contact angle measurement is an effective tool to determine the wettability of test surfaces. A lower WCA value indicates higher hydrophilicity of the surface under consideration. Figure 4 shows the captured WCA images of the developed composite electrospun nanofibers. The WCA of control PAN was measured as 135.9° , which decreased to 119.1° on adding 0.5 wt% graphene nanoplates. The WCA value further reduced to 64.2° on adding 2 wt% graphene into the PAN matrix and to 7.9° with 3 wt% graphene loading. Table 1 shows that the WCA decreased on increasing the graphene nanoplates contents. Such a hydrophilic trend is required when

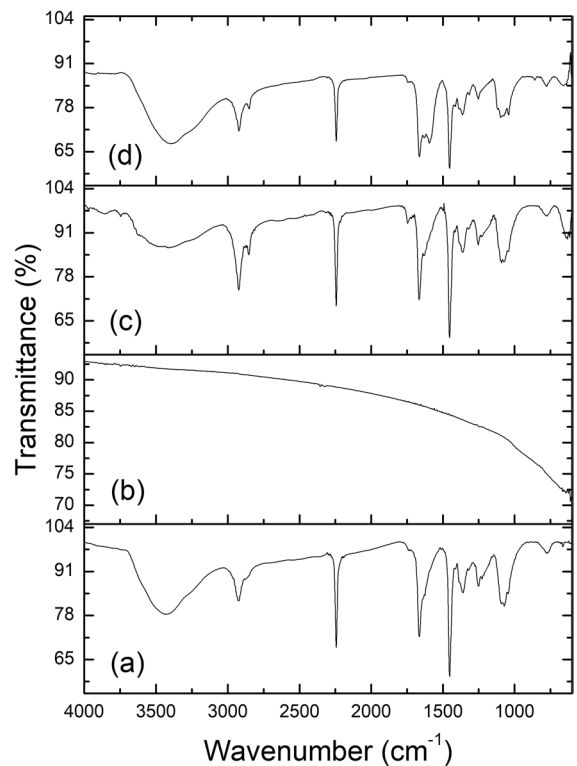


Fig. 3 FTIR spectra of **a** control PAN, **b** graphene nanoplates, and PAN/graphene composite nanofibers at **c** 1 wt%, and **d** 3 wt% graphene loadings

working in polar environments like water filtration. The graphene nanoplates loading into the PAN matrix could enhance the surface area and porosity of the resultant nanofibrous mats [21, 22].

Mechanical analysis

It is attractive to fabricate composite nanofibers with elevated mechanical characteristics to extend their application zone, like water filtration, optoelectronic gadgets, and sensors. The addition of graphene nanoplates causes an enhancement in the mechanical properties of the PAN-based nanofibers. The graphene incorporation (0.5 wt%) into the PAN matrix enhanced the tensile strength from 2.95 to 3.47 MPa (Fig. 5). The tensile strength of 3.69 MPa was obtained for 1 wt% graphene loadings, which reached 4.37 MPa by adding 3 wt% graphene nanoplates. SEM analysis showed a decrease in the thickness of composite nanofibers on increasing contents of

Fig. 4 Water contact angle of **a** control PAN, and PAN/graphene nanofibers at various loadings of **b** 0.5 wt%, **c** 1 wt%, and **d** 3 wt% graphene nanoplates

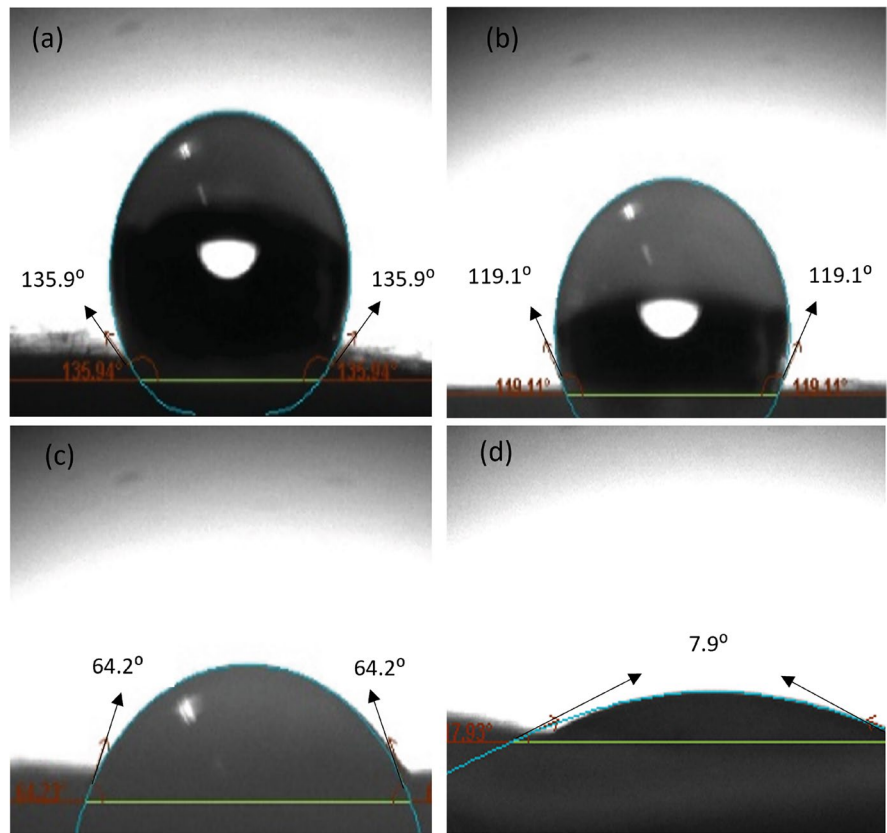


Table 1 Water contact angle of electrospun control PAN and PAN/graphene composite nanofibers

Sample	Water contact angle
Control PAN	135.9°
PAN/graphene (0.5 wt%)	119.1°
PAN/graphene (1 wt%)	64.4°
PAN/graphene (3 wt%)	7.9°

graphene nanoplates; the trend of increasing tensile strength with decreasing thickness is following the literature [23]. The increase in tensile strength is due to good dispersion of graphene nanoplates into the PAN matrix, strong interfacial adhesion with the matrix, a uniform diameter of nanofibers, the orientation of nanofibers in the load direction, and strong intrinsic mechanical strength as well as the large surface area of graphene nanoplates [24–26]. The insertion of graphene nanoplates could improve the mechanical profile of the PAN-based nanofibers. The results also

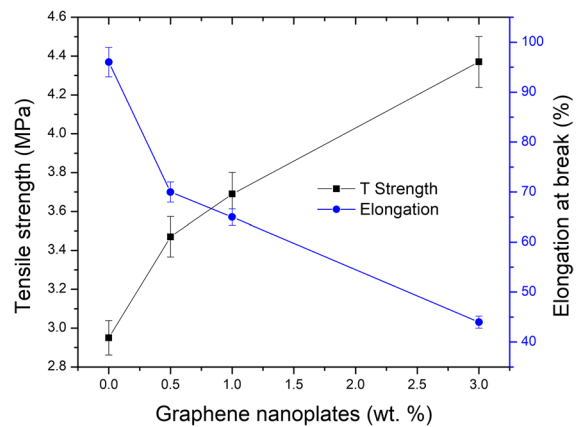


Fig. 5 Tensile strength and elongation at break (%) of control PAN and PAN/graphene composite nanofibers at various graphene loadings

showed that graphene incorporation (up to 3 wt%) enhanced brittleness in the composite nanofibers as the elongation at break decreased, accordingly.

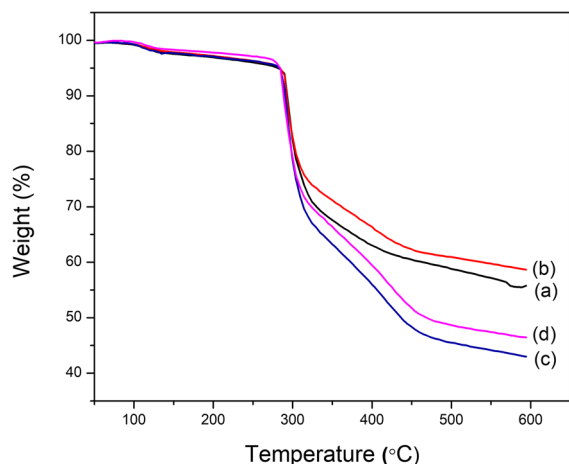


Fig. 6 Thermogravimetric curves of **a** control PAN, and PAN/graphene composite nanofibers at **b** 0.5 wt%, **c** 1 wt%, and **d** 3 wt% graphene loadings

Thermal analysis

The thermal stability of the control PAN and PAN/graphene composite nanofibers was examined (Fig. 6). Under pyrolytic situations, the control PAN and graphene-incorporated PAN nanofibers were degraded. TGA was performed to investigate the thermal behavior of the composite nanofibers, and the results were reported closer to the literature [27]. The TGA curves showed that the PAN and PAN composite nanofibers experienced weight (%) loss with increasing temperature at different graphene nanoplate loadings. The weight reduction for the prepared composite nanofibers was observed at about 5% for lower temperatures to 250 °C and might be due to the elimination of residual solvent and moisturization [28]. Composite nanofibers displayed less weight reduction in this region. At about 270 °C, carbonation occurs, resulting in a rapid mass loss of 20 wt% because of elimination of non-carbon factors including N_2 , NH_3 , HCN , CO_2 , and CO . The temperature of carbonation was increased within the composite nanofibers. The decomposition of the PAN nanofibers occurred at above ~ 300 °C. In the composite nanofibers, the backbone degradation temperature additionally increased. So, thermal stability of the PAN-based composite nanofibers with graphene contents was enhanced appreciably at higher temperatures. The robust interfacial interaction and uniform dispersion of the graphene nanoplates in the PAN matrix increased the thermal stability of the composite nanofibers compared to that of the control.

Compared to the PAN nanofibers, the decomposition temperature was raised for graphene-incorporated composite nanofibers. Therefore, it could be inferred that the thermal stability of composite nanofibers was attained by incorporating graphene nanoplates. The obvious improvement in thermal stability might be influenced by homogeneously dispersed graphene nanoplates.

Conclusions

Herein, PAN/graphene composite electrospun nanofibers have been fabricated, and their surface chemical, structural, and thermo-mechanical properties have been investigated and analyzed. The SEM analysis expressed that beads-free porous PAN/graphene composite electrospun fibers were formed with uniform nanoscale diameter distribution. FTIR analysis expressed covalent interactions among the components of graphene-loaded PAN electrospun fibers. The prepared PAN/graphene nanofibers expressed hydrophilic behavior, and improved tensile properties including tensile strength and elongation at the break as compared to control PAN electrospun fibers. The thermal analysis showed the enhanced thermal stability of graphene incorporation PAN composite nanofibers. Based on all results, the PAN/graphene composite nanofibers could be promising candidates for water filtration applications, especially desalination processes. This, however, needs extensive research in water permeability and flow profiles of the PAN/graphene electrospun nanofibrous filters. The antibacterial, toxicity reusability and regeneration profiles of such nanofibrous filters could also be extensively studied before recommending for practical water treatment applications.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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