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CHEMICAL AND THERMAL INVESTIGATIONS OF ELECTROSPUN POLYACRYLONITRILE NANOFIBERS INCORPORATED WITH VARIOUS NANOSCALE INCLUSIONS

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ABSTRACT

Thermal behaviors of electrospun polyacronitrile (PAN) fibers incorporated with graphene nanoplatelets and multiwall carbon nanotubes (MWCNTs) were evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques. DSC was used to determine the glass transition temperature (T_g), melting temperature (T_m) and heat flow of the polymeric fibers, while TGA was used to determine the stages of thermal breakdown, weight loss in each stage, thermal stability, and threshold temperatures. Glass transition temperature is an especially important property during the processing of polymers, applications, and storage. Pure PAN fiber has a T_g of 104.09°C; however, in the presence of 2 and 4 wt.% of graphene in PAN fibers, T_g values were increased to 105.07°C and 105.75°C, respectively, and then decreased to 102.82°C at 8 wt. % of graphene. Similarly, T_g values of PAN fibers were increased to 105.08°C and 108.19°C in the presence of 2 and 4 wt. % of MWCNTs, and then decreased to 104.98°C at 8 wt. % MWCNTs. The TGA curves of pure PAN and PAN fibers with different weight percentages of graphene nanoplatelets and MWCNTs exhibited a four-step weight loss.
In FTIR spectra, the intensities between 2,400 and 2,200 cm^{-1} for all samples of PAN having different weight percentages of MWCNTs and graphene nanoplatelets corresponded to the C≡N band for saturated nitrile groups.

Keywords: *Electrospun Nanocomposite Fibers, MWCNTs, Graphene, Thermal Analysis, Properties*

INTRODUCTION

General Background

Polyacrylonitrile (PAN) is a widely used precursor for the production of carbon fibers; therefore, its degradation has been a topic of research for many decades due to its commercial importance in the production of high-performance carbon fibers. The glass transition temperature (T_g) and melting temperature (T_m) of PAN are 85–95°C, and 317–320°C, respectively. Thermal analysis such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are common tools in the study of PAN degradation [1]. DSC and TGA techniques are used to characterize polymer thermal stability, and have been further employed to assess the comparative thermal stability of various polymeric materials and the prediction of material lifetimes. Most researchers have focused their attention on physical and chemical changes during thermal degradation and stabilization of PAN. Those physical changes are entropy, crystallinity, density, and tensile strength, while those chemical changes are nitrile polymerization, chain scission, evolution of volatile gases (NH_3, CH_4, CO, CO_2, and H_2O), and formation of carbonyl, carboxyl, and peroxide groups [2]. Alarifi et al. [3] studied the thermal properties of PAN electrospun fibers by DSC and TGA methods. The test results showed that the glass transition temperature (T_g) of pure PAN is 104°C by DSC analysis. The TGA analysis also indicated that the weight loss in the first stage is negligible, while in the second stage and fourth stage they are 18% and 80%, respectively.

Grassie and McGuchan [4] studied the thermal degradation of polyacrylonitrile by thermal volatilization analysis (TVA) and determined that hydrogen cyanide and ammonia were the main constituents of the degradation.

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Coleman et al. [5] proposed a cyclic structure with polymeric imine and enamine as the degradation constituents, and studied the tautomeric exchange between the two structures. They found that the degradation (or intramolecular cyclization reaction) initially starts at 160°C under a vacuum [5]. The intramolecular cyclization of the nitrile groups present in PAN polymer is an exothermic reaction, and some gases evolve during this time. The cyclization reaction occurs due to the nucleophilic attack on nitrile. The cyclization reaction in PAN consists of several factors: impurities present in PAN, residual polymerization products, chain end groups, transformation of nitrile to azomethine, random initiation of hydrogen atoms to nitrile, the presence of ketonitrile, hydrolysis products from keteneimine formed during the polymerization, the hydrolysis of nitrile to acids in polymerization, and structural randomness or abnormalities present during polymerization [6]. In PAN fibers, there are strong internal chains and interactions through secondary bonding because of the high dipole moment of the nitrile groups, which is why PAN undergoes degradation just before melting [5]. Because of these factors, PAN Electrospinning requires a high polar solvent, such as N, N-dimethylformamide (DMF), dimethylacetamide (DMAc), or dimethyl sulfoxide [7].

Thermal analysis is an important evaluation step in understanding the structural and properties relationship of a polymer material [8]. By using thermal analysis, it is also possible to quantify the amount of moisture and volatile compounds present in polymeric materials, which will weaken their physical and chemical properties [8]. The applications of PAN nanofibers in many industries are impeded due to their poor strength and manufacturability, which can be attributed to their small diameter and un-optimized molecular orientation and crystallinity [10]. TGA is one of the generally accepted methods of studying the thermal properties of polymeric materials. TGA results show a number of stages of thermal breakdown, weight loss of the material in all stages, threshold temperature, extent of degradation, and nature of degradation. DSC determines the heat flow rate associated with thermal changes that can be measured as a function of temperature and time. DSC can also be used to study the melting mechanism and phase transition phenomena [8]. The chemical and physical properties of polymeric materials mainly depend on thermal stability and crystallization. Fourier transform infrared spectroscopy (FTIR) is a spectroscopic method in which the sample is irradiated with infrared light from a spectrometer. An infrared spectrum is obtained when molecules in the sample absorb a certain frequency from the infrared light. FTIR is essentially a non-destructive method and is employed to differentiate between crystalline and amorphous phases, and to study structural changes and chemical bonds (covalent bonds).

Electrospinning is a technique used to generate multiwall carbon nanotubes (MWCNTs) and graphene-embedded-reinforced PAN nanofibers. In order to enhance the thermal properties of electrospun nanofibers, MWCNTs and graphene are considered due to their outstanding thermal, mechanical, and electrical properties [11]. Polyacrylonitrile was chosen in this study since it is the main precursor of carbon and carbon fibers, and also soluble in many solvents such as dimethylformamide and dimethyl acetate [12]. The properties of nanocomposites depend not only on the type of nanoparticles but also their shapes. The spherical shaped nanoparticles are limited for many industrial applications. Because of this reason, non-spherical shaped nanoparticles have been chosen in this study [33].

In this study, PAN nanofibers embedded with 0, 2, 4, and 8 wt. % of MWCNTs and graphene nanoplatelets were produced by electrospinning and characterized by means of DSC, TGA, and FTIR, in order to study phase transition, changes in glass transition temperature due to filler materials, weight loss, degradation mechanisms, and chemical bonds.

ELECTROSPINNING

Electrospinning is a process of generating high surface area submicron and nanosize fibers very quickly. Electrospinning is related to the principle of spinning polymer solutions in a high electric field [10]. Electrospinning uses a high direct current (DC) electric field or high electrostatic force on the surface of a polymeric solution to overcome the surface tension and viscoelastic forces of the polymeric solution, and produce a very slim charged jet [13]. Mutual charge repulsion creates shearing forces the intensity of which increase with the applied electric field. Finally, these forces overcome surface tension and viscoelastic forces, and a fine jet erupts from the tip of the capillary tube. The jet is initially stable and then enters into a bending instability region where plastic stretching, bending, pirouetting motion, evaporation of the jet, and looping pattern with growing amplitude cause the generation of an ultrafine nonwoven mesh of fibers on a collector screen that has been placed some distance from the capillary tube [14]. The jet follows a spiral path in three dimensions and becomes thinner with the increase in loop circumference, as shown in the schematic view of the electrospinning process in Figure 1.

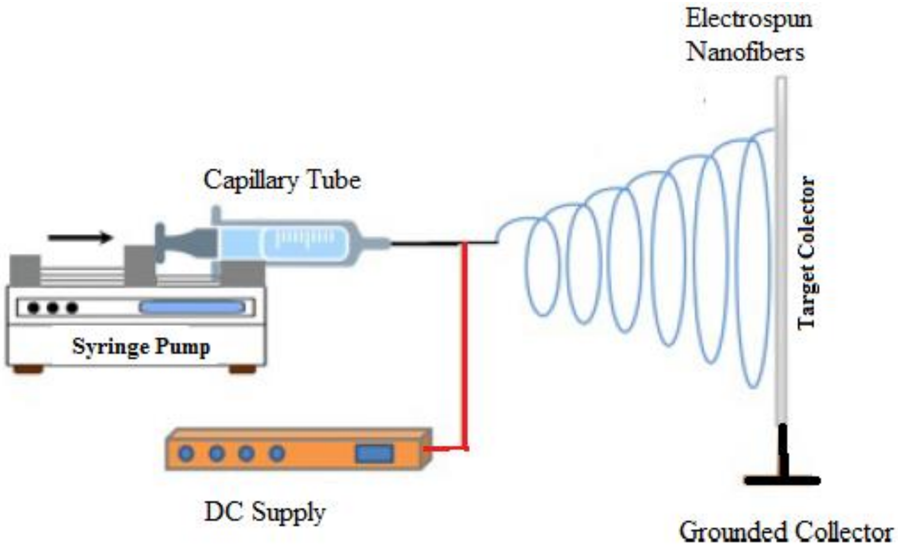


Figure 1. Schematic view of electrospinning process

The spiral or whipping motion, referred to as "bending instability," is primarily a thinning mechanism in the electrospinning process. The major advantage of the electrospinning process is to produce nanofibers in a short period of time. Electrospun nanofibers have diameters in the range of 500 nm to 3 nm. Many different polymers have been electrospun to form various diameters based on the processing parameters [15]. A wide variety of shapes and sizes of electrospun fibers can be produced from various polymers after dissolving them in appropriate solvents. Electrospun fibers have more than a hundred different applications in various fields. Through current research development, the electrospinning technique will be a driving force in the advancement of various fields in the near future [16-18].

EXPERIMENT

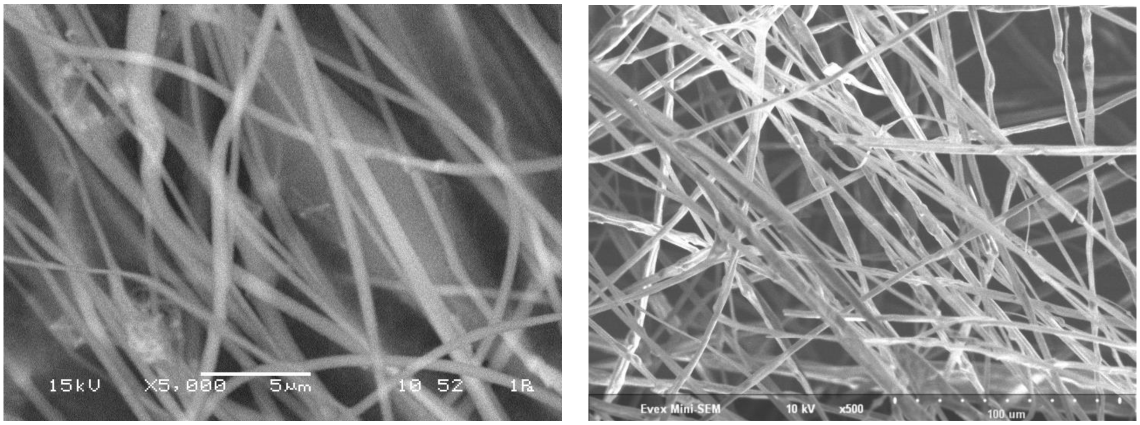
Materials

Polyacrylonitrile (PAN) having molecular weight of 150,000 g/mol and Dimethylformamide (DMF) were purchased from Sigma-Aldrich. Multiwall carbon nanotubes (MWCNTs) having diameters of 140 (±30) nm and lengths of 7 (±2) μm were purchased from Fisher Scientific. Graphene nanoplatelets with average X and Y dimensions equal to 6 μm and the Z dimension less than 10 nm were purchased from Angstron Materials. These materials were used without any further modifications or purifications.

Methods

Different weight percentages (0, 2, 4, and 8 wt.%) of MWCNTs and graphene nanoplatelets were dispersed in DMF and sonicated for 30 minutes prior to the addition of PAN powder. The solution was held at 60°C and constantly stirred at 700 rpm for 12 hours to informally disperse the inclusions. Extra care was taken to make a homogeneous blend of PAN polymeric solution in order to facilitate electrospinning conveniently.

The prepared dispersions were transferred to a 10 ml plastic syringe connected to a capillary needle with an inside diameter of 0.5 mm. A platinum electrode inserted inside the syringe tip was attached to a high DC voltage supply. The applied voltage was 20–25 kV, while the distance between the capillary tube and the collector screen was maintained at 20–25 cm. The pump speed was kept constant at 1 ml/hour throughout the tests. The mass flow rate has direct relationship with the fiber diameter. If the mass flow rate is high the fiber diameter will be large, as well. The mass flow rate was fixed (1 ml/hour) after reviewing many research articles and our experiences. The collector screen is usually grounded, but in some cases, a negative potential is applied on it in order to develop a strong electrostatic field. Electrospun fibers were then collected on a grounded screen and dried in an oven at 60^{o}C for 6–8 hours to remove all residual solvents. Scanning electron microscopy (SEM) (JEOL Model JSM -6460LV) was used to investigate the morphology and surface characteristics of the fibers. Figure 2 shows SEM images of electrospun PAN nanocomposite fibers



(a) (b)

Figure 2. Selected SEM images of PAN fibers: (a) with 4 wt. % MWCNTs, and (b) with 8 wt. % graphene nanoplatelets

A Q1000 differential scanning calorimeter (TA Instruments) interfaced to a personal computer (PC) was used to measure the thermal properties of the nanocomposite fibers. The T_g and T_m values were investigated at a heating rate of 20°C/min with a nitrogen flow rate of 50 ml/min. The samples were sealed in a Tzero™ pan (TA Instruments), and measurements were taken in the temperature range of 25–350°C. A predetermined weight of each sample was used in this experiment. The DSC heat flow and temperature were calibrated with an indium standard. Thermal stability of the nanocomposite fibers was studied by using a Q500 thermogravimeter (TA Instruments). TGA was conducted on nanocomposite fiber samples from 25 to 850^{o}C with a nitrogen flow rate of 60 ml/min and a heating rate of 10°C/min. FTIR analysis was performed with a Bruker spectrometer. Infrared spectra were recorded in the wavenumber range of 500–4000 cm^{-1}.

RESULTS AND DISCUSSION

DSC Analysis

Table 1 provides the T_g values of PAN nanocomposite fibers as a function of MWCNTs and graphene inclusions. PAN is a semicrystalline polymer in which the T_g value primarily depends on the amorphous part of the PAN structure [14]. The T_g of pure PAN in bulk form is 85^{o}C. The increase in T_g in fibrous form (Figure 3) may be attributed to the presence of polar solvent (DMF) entrapments in the pores and voids, which could potentially cause dipole-dipole interactions with the nitrile groups present in the PAN structure. The T_g of PAN fibers was determined as 104.09°C. Alarifi et al. [3] studied the thermal properties of PAN electrospun fibers by DSC, and their results showed that the glass transition temperature (T_g) of PAN fibers is 104°C, which is close agreement with this study. In the presence of 2 and 4 wt. % of graphene in PAN fibers, T_g values increased to 105.07°C and 105.75°C, respectively, and then decreased to 102.82°C at 8 wt. % of graphene. Similarly, T_g values of PAN fibers increased to 105.08°C and 108.19°C with the additions of 2 and 4 wt. % of MWCNTs, respectively, and then decreased to 104.98°C at 8 wt. % MWCNTs. These results indicate that a percolation threshold exists at 4 wt. % of the filler materials. The reduction in T_g values of the PAN nanocomposites beyond 4 wt.% inclusions may be due to the presence of a high amount of filler materials, which restrict the mobility of the fibrous matrix and aggregation/clustering in PAN [19]. The excessive amount of filler materials present in the polymeric matrix may cause encumbrance in the chain segmental motion, thereby reducing the transition temperature of the polymer. Nanofillers act as nanobarriers in polymer chain mobility. The nano-confinement of the filler materials on the polymer chain hinders the segmental motions at the interface [20].

Table 1. T_g values of PAN nanocomposite fibers as function of MWCNTs and graphene inclusions

Weight Percentages of Inclusions (%)	Tg of PAN with MWCNTs (°C)	Tg of PAN with Graphene (°C)
0	104.09	104.09
2	105.08	105.07
4	108.19	105.75
8	104.98	102.82

The polymer degradation as measured by DSC appears as a distinct exotherm, as shown in Figures 3 to 6. No melting was observed with DSC, as indicated by the green lines. However, melting was observed with modulated DSC (modulate 1.5^{o}C/60 S), as indicated by the blue lines.

The DSC thermogram of the PAN fiber is different than that of bulk PAN. The bulk sample of PAN shows a sharp exothermal peak at 311.62°C (Figure 4), whereas the PAN fibers show a broad exothermal peak at 312.38°C (Figure 3). Broadening of the exothermic peak could be due to the cyclization process. The cyclization of nitrile groups is highly exothermic and leads to fragmentation of the chains owing to heat that builds up rapidly in the sample and does not dissipate rapidly [21]. It is difficult to completely eliminate DMF in the PAN fibers, even after drying them at 60oC for 8 hrs. The DMF molecules occluded with the PAN polymer, and as a result, the DSC thermogram of bulk PAN is different from that of pure PAN fibers. Heat that evolved from the PAN fibers is higher compared to the bulk sample. The characteristic of PAN that dominates its unique properties is the presence of nitrile groups at an intramolecular distance of only a few tenths of a nanometer [21]. The CN groups have a variety of ways in which to interact with their surroundings. The lone pair orbital situated at the nitrogen and oriented approximately 180o away from the CN bond to participate in nitrogen bonding with water or Brönsted acids and in electron-donor-acceptor formation with Lewis acids [21]. Therefore, molecular interaction between PAN and DMF are expected [21]. Intermolecular dipole-dipole interactions between PAN molecules are replaced by the interaction of PAN nitrile groups with the dipole of the solvent (e.g., DMF) [21]. The dipole of nitrile groups interacts with the dipole of polar DMF. Melting studies of PAN fibers demonstrate that the characteristic enthalpy changes associated with first-order transitions are in conformity with peaks observed in DSC thermograms (Figure 3).

Krigbaum and Tokita [22] demonstrated that the melting temperature of PAN is 317^{o}C using a number of experiments with PAN in DMF and γ- butyrolactone. The strong nitrile dipole interactions are the main reasons for the high melting temperature of PAN [23]. The single exothermic peak observed in all DSC thermograms can be attributed to the cyclization of PAN molecular chains [24]. It is well known that the cyclization reactions in PAN are based on the free radicals and initiated at high temperature [1]. Therefore, the single exothermic peak observed in PAN can be attributed to the overlapping of the free-radical cyclization and other exothermic reactions that can take place at high temperature [1, 25]. One study is a strong exothermic peak at around 300^{o}C, which shows the cross-linking of PAN chains by eliminating hydrogen cyanide (HCN) and/or the formation of naphtyridene rings along the chains [26]. Cyclization is a highly exothermic process and is accompanied by the evolution of a large amount of heat flow that can promote cyclization of the nitrile group in PAN [1]. The intermolecular oligomerization of nitrile groups leads to the cross-linking structure that is possibly more important than the intramolecular reaction leading to the ladder-like structure at high temperatures in PAN [24].

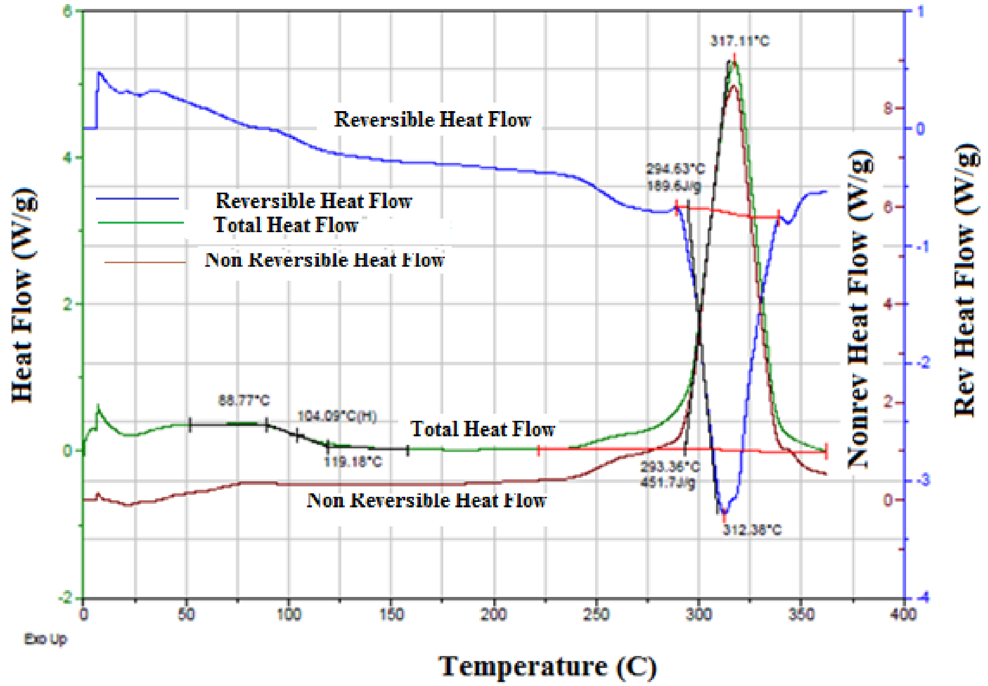


Figure 3. DSC thermograms of pure PAN fibers

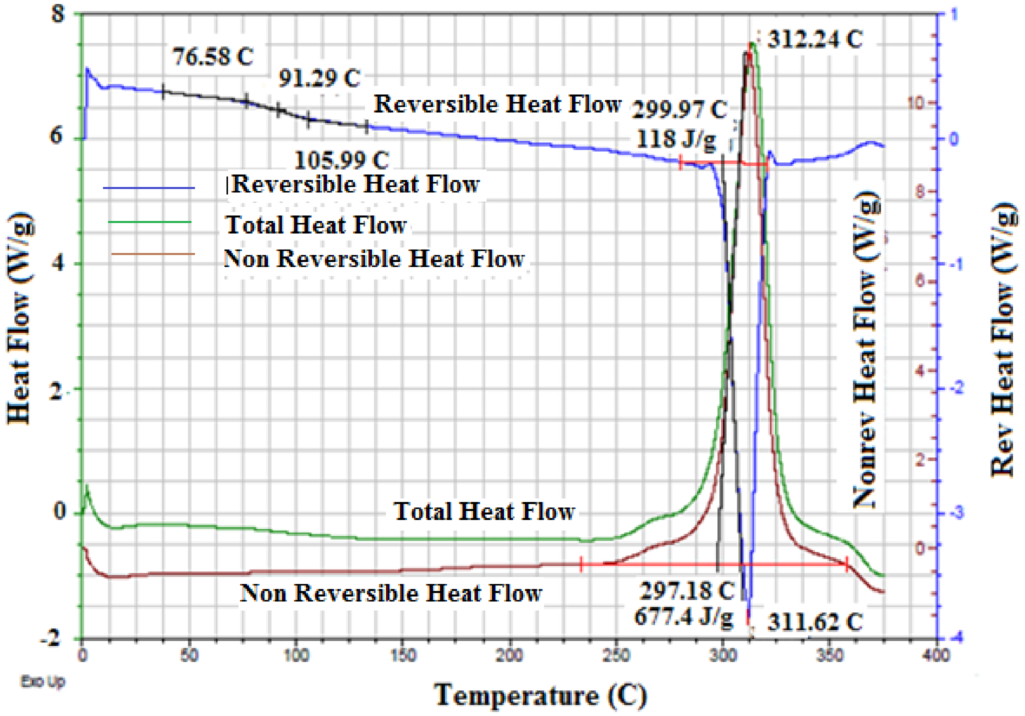


Figure 4. DSC thermograms of bulk PAN

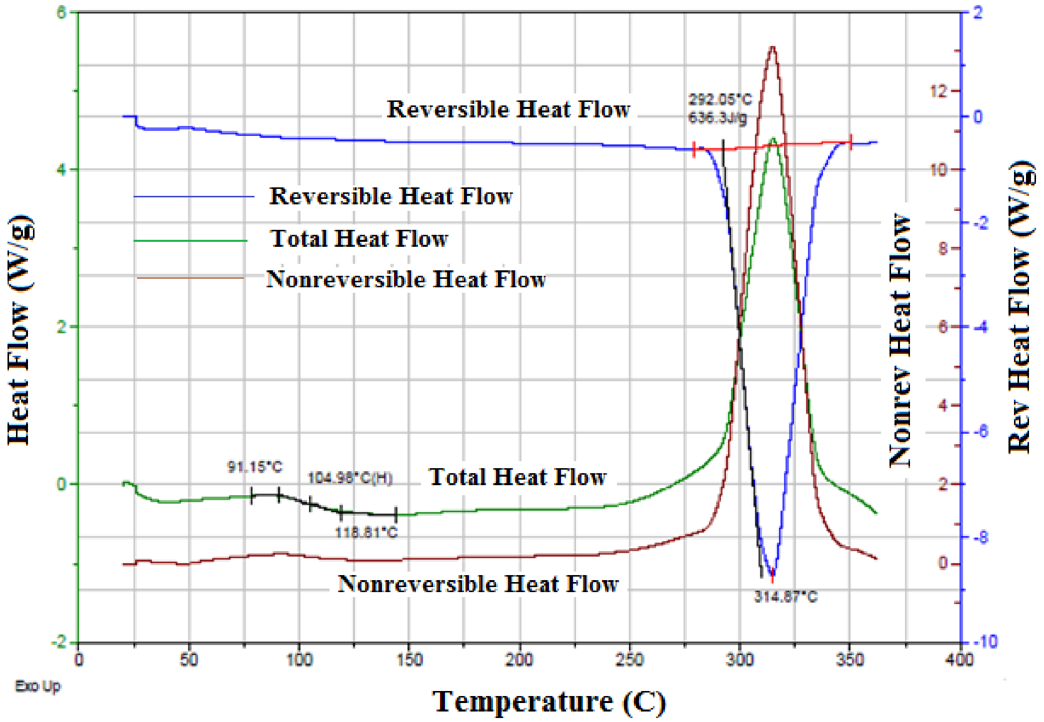


Figure 5. DSC thermograms of PAN nanocomposite fibers with 8 wt. % MWCNTs

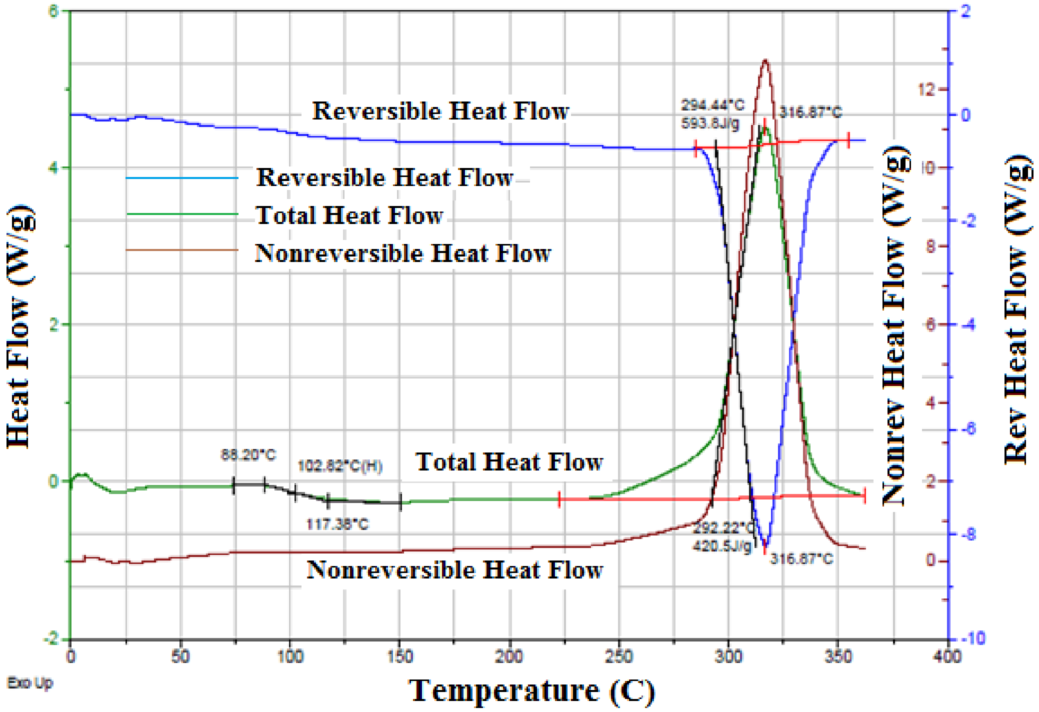


Figure 6. DSC thermograms of PAN nanocomposite fibers with 8 wt. % graphene nanoplatelets

Oligomerization of the nitrile group becomes dominant at temperatures above 200°C, where a radical mechanism most likely takes place [27]. The carbon-carbon bonds are the weakest bonds in a PAN polymer, and a homolytic main chain scission may be assumed as the consequential outcome of heat treatment [27]. The radicals formed then initiate the CN oligomerization [27].

From the DSC thermograms, it is clear that the melting temperature of pure PAN fiber is 312.38°C and the melting temperature of bulk PAN is 311.62°C. The increase in melting temperature is due to the interactions of DMF with the nitrile groups present in PAN. The melting temperature of nanocomposite fibers with 2 wt. % MWCNTs and graphene nanoplatelets increases slightly (e.g., 313.92°C for graphene nanoplatelets-based nanocomposite fibers and 314.26°C for MWCNT-based nanocomposite fibers). However, with 8 wt. % graphene nanoplatelets and MWCNTs, the melting temperature increased to 316.87°C and 314.87°C, respectively. The increased melting temperature may be because nanoparticles retard the mobility of polymer chains, and subsequently higher energy is required to move the polymer chains in the PAN structure [20]. DMF may also cause a plasticized effect on the PAN polymer and may be responsible for forming complexes with the PAN polymer [21]. DSC thermograms show the melting endotherm of the nanocomposite fibers, and the quantity of heat evolved is considerably more than the amount usually required for fusion [26]. The other factor that has a significant effect on melting is the compositional changes during the exothermic reaction [26]. PAN undergoes degradation before melting at 320–330°C [7]. The heat of degradation is added to the heat of fusion during endothermic reactions.

TGA Analysis

Thermogravimerty offers a quantifiable analysis of the amount of moisture and volatile compounds present in nanocomposite fibers, weight loss, and thermal breakdown. It also assists in determining the degradation mechanism. The samples used for TGA contained 3.237–5.5660 mg of nanocomposite fibers. A TGA study was employed to determine the weight loss patterns of the PAN fibers as a function of temperature. Measurements were started at room temperature (25°C) and ramped to 850°C at a heating rate of 10°C/min using a nitrogen purge of 60 mL/min in a platinum pan. Figure 7 shows the thermogravimetric curve of pure bulk PAN. Figures 8 and 9 show the thermogravimetric curves of nanocomposite fibers with different weight percentages of graphene nanoplatelets and MWCNTs.

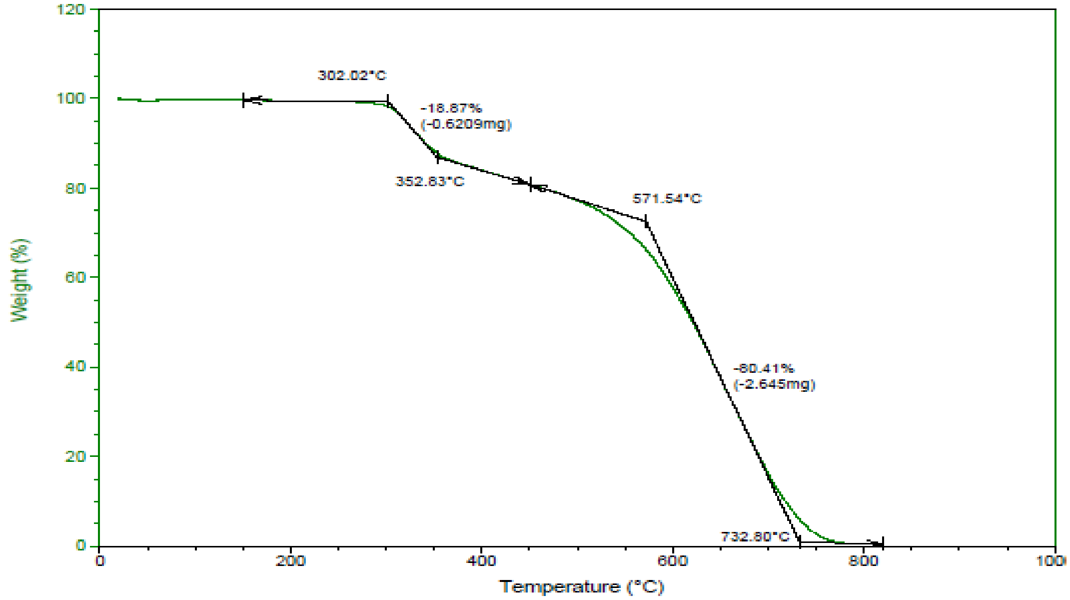
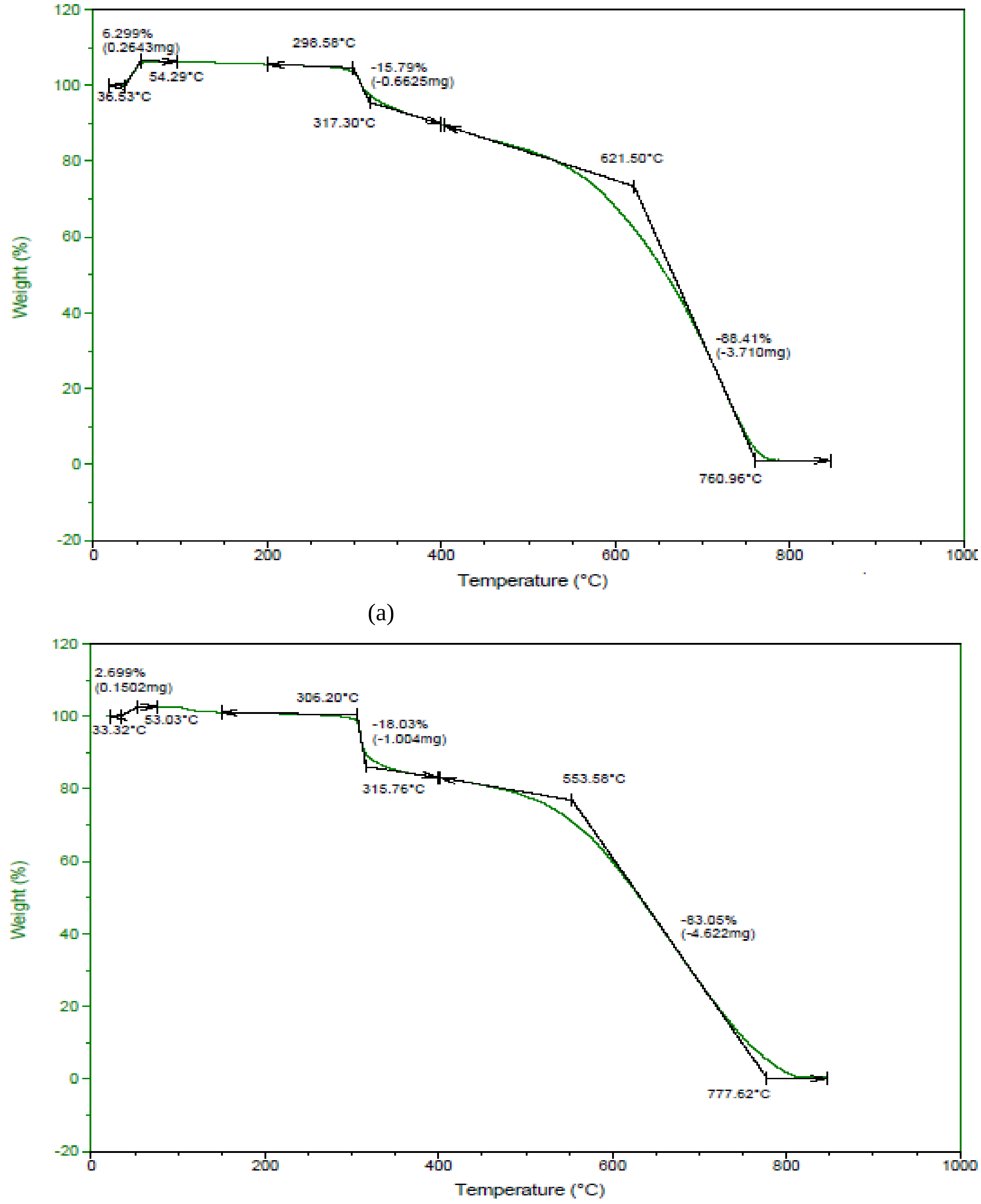


Figure 7. TGA curve of pure PAN bulk

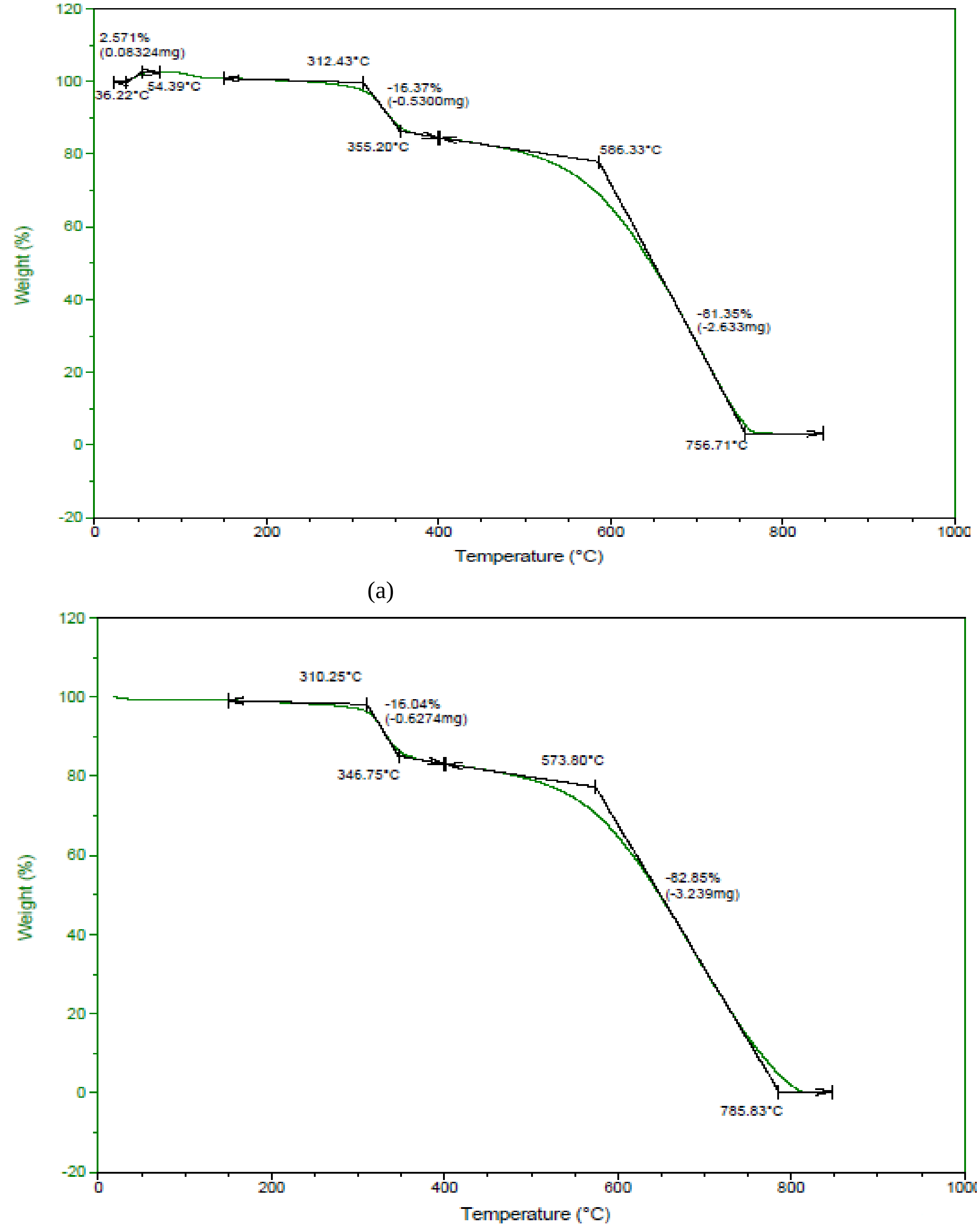


(a)

(b)

Figure 8. TGA curves of PAN: (a) with 2 wt. % graphene, and (b) with 8 wt. % graphene

The heating of PAN produces chemical reactions, such as cyclization, degradation, and cross-linking, so the mechanism of these processes depends on the heating rate, medium, mass of the polymer, and type and nature of the filler materials [28]. The TGA curves of pure PAN and PAN fibers with different weight percentages of graphene nanoplatelets and MWCNTs show a four-step weight loss. These curves show that the weight loss caused by pyrolytic reactions mainly occurred at around 302°C for pure PAN, 298.58°C for 2 wt. % graphene nanoplatelets, 312°C for 2 wt. % MWCNTs, 306°C for 8 wt. % graphene nanoplatelets, and 310°C for 8 wt. % MWCNTs.



(a)

(b)

Figure 9. TGA curves of PAN: (a) with 2 wt. % MWCNTs, and (b) with 8 wt. % MWCNTs

The cyclization reactions continued until the residual nitrile groups did not react with other functional groups, and the pyrolytic reactions of PAN fibers proceeded with minimum heating and shrinkage effects [29]. The cyclization of PAN proceeds before any mass loss, and the factor responsible for cyclization process is the formation of aromatic rings [6].

In the first stage, there was no weight loss. Combining DSC results with TGA results, it is clear that cyclization reactions take place in this step because the reaction does not cause any weight loss theoretically [25]. However, some weight gain was observed in 2, 4, and 8 wt. % graphene nanoplatelets samples and the 2 wt. % MWCNTs sample. This could be attributed to possible attachment of nitrogen with nitrile groups or graphene nanoplatelets/MWCNTs, since thermal decomposition was carried out in a nitrogen atmosphere. Weight loss does not begin until cyclization process is complete. The gases evolved during thermal degradation of PAN come from the cyclized products [6]. In the second stage of weight loss (TGA curves for all samples), weight loss is between 15.79% and 18.87% for a temperature range of 315.76–356.29^{o}C, indicating that a chemical reaction forms and volatile gases evolve [30]. This exothermic peak is due to the oligomerization of nitrile groups in PAN. The cyclization peak temperature was between 298.58 and 312°C, as can be seen in the DSC thermograms for all samples. A further decrease of weight loss was observed in the temperature range of 315.76– 621.50°C for all the samples, which may be attributed to the partial evaporation of anhydrous ammonia (NH_3) and HCN [25]. In the fourth stage in the temperature range of 710–785.83^{o}C, a monotonous decrease of weight loss was observed, with a total loss between 80% and 88%, indicating complete evaporation of polymer chain fragments from the PAN fibers.

The activation energy of PAN decomposition is 4.52 x 10^4 Kcal mole^{-1} [24]. The heat of decomposition is 213.2 cal per gram (892.42 J/g) of PAN [24]. The TGA analysis of nanocomposite fibers has shown that the degradation process of PAN is exothermic and accompanied by the evolution of gaseous products [24]. Table 2 provides the decomposition products of PAN at different percentages [24]. Based on the calculation, 5,000 kg of PAN can have decomposition products that consist mainly of solid residue of (3,350 kg) and volatile products (1,650 kg) [24]. The volatile products are composed of HCN, AN, methacrylonitrile, acetonitrile, and other oligomeric products. The weight proportion of HCN, AN, and acetonitrile is 229.2 kg, and the weight proportion of other oligomeric products is 1,420.8 kg [24].

Table 2. Decomposition products of PAN at different percentages

Decomposition Products of PAN	Percentage (W/W)
HCN, AN, methacrylonitrile, and acetonitrile	13.89
C- C (CN)-C = C – CN	7.84
C-C (CN)-C-C (CN)-C-C (CN)-C-C-(CN)	4.3
C-C (CN)-C=C (CN)	4.27
C-C (CN)-C-C (CN)-C-C (CN) = C	2.48

FTIR Analysis

The FTIR spectra of PAN with different weight percentages of MWCNTs and graphene nanoplatelets are shown in Figures 10 and 11, respectively. As can be seen, a peak is observed at 3,650 cm^{-1} due to OH stretching vibrations. The peak corresponding to 2,900 cm^{-1} can be attributed to aliphatic C-H vibrations. The intensities between 2,400 and 2,200 cm^{-1} for all samples of PAN having different weight percentages of MWCNTs and graphene nanoplatelets correspond to the C≡N band for saturated nitrile groups [1, 31]. Rahman et al. [32] demonstrated that PAN fibers showed prominent peaks at 2940 cm^{-1} , 2240 cm^{-1}, 1452 cm^{-1}, due to C-H stretching, C-N stretching and CH_2 bend, correspondingly. These intensities corresponding to 1,700–1,600 cm^{-1} are due to the cyclic C=O peak for methyl acrylate comonomer [31]. The peaks corresponding to 1,450 cm^{-1} in Figures 10 and 11 are due to C-H. There is no significant difference between Figures 10 and 11, mainly because both the MWCNTs and graphene nanoplatelets were physically dispersed in the PAN polymeric solution without making any covalent bonds with the polymer chain. However, if the nanofiller materials had developed chemical bonds (covalent bonds) with the host polymer, then the FTIR spectra would have shown peaks corresponding to those bonds. Figure 12 shows the FTIR spectra of PAN fibers after heat treatment (carbonization) at 850^{o}C in an argon atmosphere.

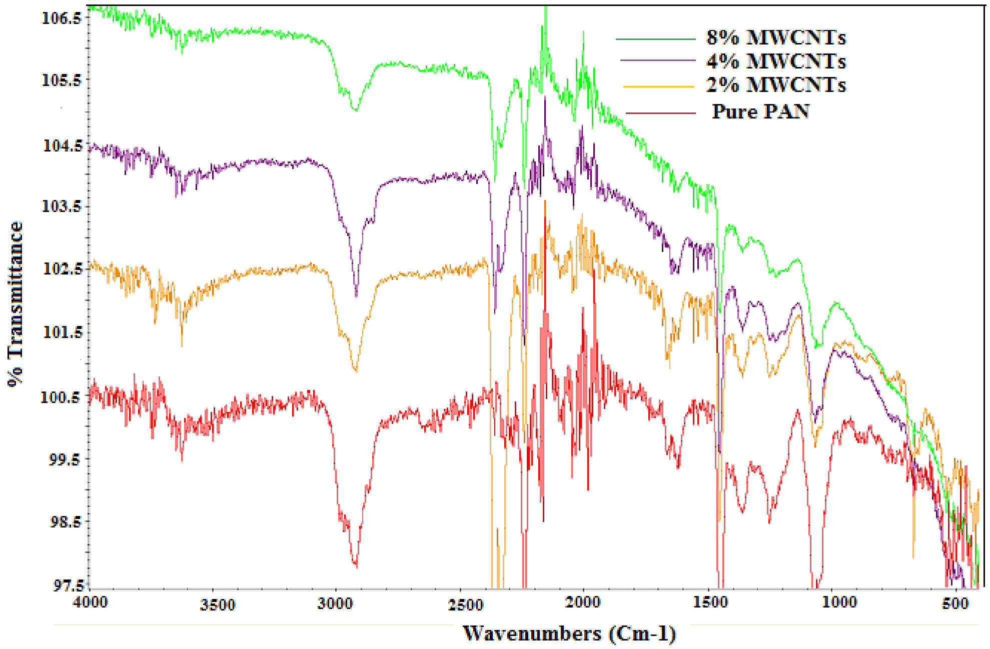


Figure 10. FTIR spectra of PAN with different wt% MWCNTs

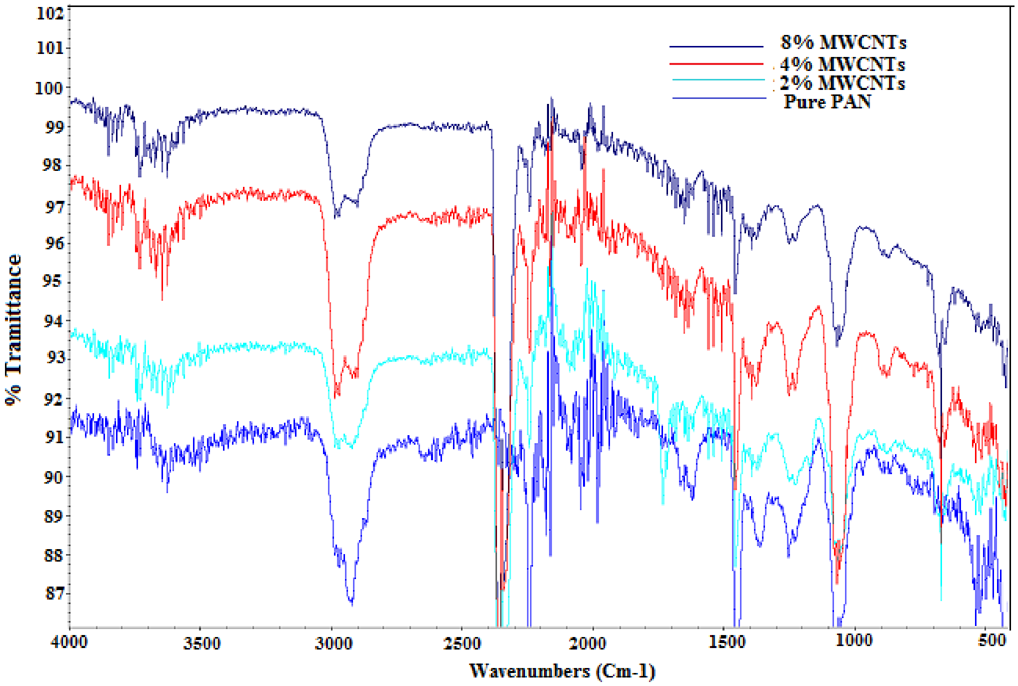


Figure 11. FTIR spectra of PAN with different wt% graphene nanoplatelets

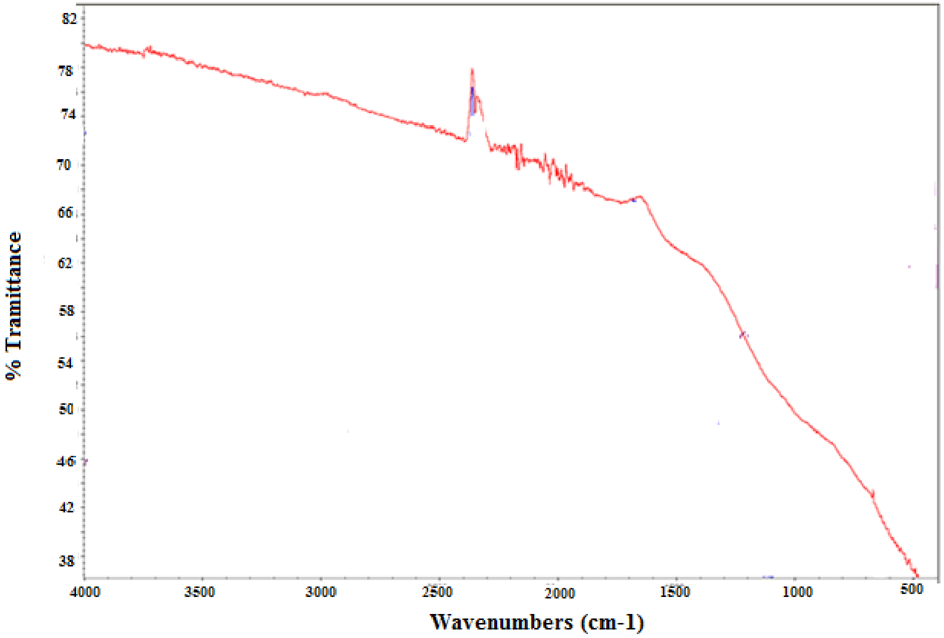


Figure 12. FTIR spectra of PAN after heat treatment at 850°C

As shown in Figure 12, a peak is observed at 2,250 cm^{-1} due to the presence of nitrile groups in the PAN electrospun fibers. Theoretically, after carbonization, all functional groups are eliminated, leaving behind a graphite structure [31]. PAN contains around 68% carbon by weight, and after carbonization at a higher temperature (2,000–3,000°C), it is transformed to around 99% carbon by weight. However, due to experimental limitations, the maximum temperature attained in this experiment was 850°C, which means that some compounds in addition to carbon in the PAN matrix and nitrile group still exist. The peak at 2,250 cm^{-1} confirms the existance of a nitrile group in the PAN fibers.

UNCERTANITY ANALYSIS

90 wt. % of DMF and 10 wt.% of polymer (PAN) was used in making PAN polymeric solution. The measurement scale carries an error +/- 0.01

weight of DMF = 22.5g, weight of PAN = 2.5 g
Uncertainty = 0.01/25 = 0.0004
% Uncertainty = 0.04

CONCLUDING REMARKS

Thermal behaviors of the electrospun PAN nanocomposite fibers with various weight percentages of graphene nanoplatelets and MWCNTs were investigated. The T_g values of the nanocomposite fibers with MWCNTs and graphene nanoplatelets increased until reaching 4 wt% of both inclusions, indicating a percolation threshold at 4 wt. %, and then drastically decreased at 8 wt. % of the inclusions. This downshift can be attributed to the constraint effects of graphene nanoplatelets and MWCNTs in the polymer structures, as well as agglomeration. The single exothermic peak observed in all samples was due to cyclization of PAN molecular chains under heat. The T_m values of nanocomposite fibers also increased as a function of inclusions in the polymer because nanoinclusions impede the mobility of PAN chains. A four-step weight-loss pattern was observed for all the samples represented in the TGA curves. In the first stage, (298.58–312°C), there was no weight loss; however, in the second stage (315.76–356.29°C), the weight loss took place between 15.79% and 18.87%, indicating a chemical reaction and evolution of volatile gases. The maximum weight loss was observed in the fourth stage (710–785.83^{o}C), where weight loss was between 80% and 88%, indicating clear thermal decomposition. The FTIR spectra of PAN with both MWCNTs and graphene nanoplatelets do not show any pronounced differences mainly because nanofiller materials were physically dispersed in the PAN solution.

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NOMENCLATURE

DSC	Differential Scanning Calorimetry
MWCNTs	Multiwall Carbon Nanotubes
PAN	Polyacrylonitrile
TGA	Thermogravimetric Analysis
NH_3	Ammonia Gas
CH_4	Methane Gas
CO	Carbon Monoxide
CO_2	Carbon Dioxide
H_2O	Water (Vapor)
FTIR	Fourier transform infrared spectroscopy
DMF	Dimethylformamide
HCN	Hydrogen Cyanide
AN	Ammonium Nitrate
Wt. %	Weight Percentage
SEM	Scanning electron microscopy

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