

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH



MATERIALS ENGINEERING

**Departments of Polymers and petrochemical
Industries**

RESEARCH ABOUT

**Studding the physical properties of non-woven polymeric
nanofibers for separation of the oil stains from water.**

Supervisor

Assist .Prof .Dr. Salih Abbas Habeeb

PREPARING STUDENTS

Mohammed Salam Ktab

Ali Jawad Kadhim

Dedication

To

**Dear parents, my God protect them and all the members of
my family**

**I extend my sincere thanks, great gratitude and deep
appreciation to**

The supervisor, Assist .Prof .Dr. Salih Abbas Habeeb

**With my patience for the time, effort and direction you gave
me, I also**

Extend my sincere thanks to my

Honorable teachers

And to all friends

**Moreover, to everyone who contributed to receiving me,
even a letter, in my school life?**

Thanks

**As we take our final steps in University life, we must offer the
Highest names of thanks, gratitude, appreciation and
Love to those who paved the way for us to know and know our best
teachers**

Especially of them by mentioning

(Assist .Prof .Dr. Salih Abbas Habeeb)

Who supervised the writing of this?

**Research and he did not skimp on any
Advice, direction and guidance throughout the researching period.**

**Also, I extend my thanks and
Appreciation to everyone who gave me advice and scientific advice,
and drew my attention to an idea or information**

Mohammed Salam Ktab

Ali Jawad Kadhim

2021

2022

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Abstract

In this study, both polyvinyl chloride (PVC) and polyacrylonitrile (PAN) were dissolved in dimethyl formaldehyde (DMF) with 8 wt. % concentrations at (25 :75 , 50:50, and 75:25) % PVC: PAN . For the investigation of the homogeneity and compatibility of mixture polymer solutions, examined by rheological properties such as viscosity, shear stress, shear rate, and calculation of the flow behavior index. While , for investigation of the stability and high density of nanofibers without beads used field-emission scanning electron microscopy (FE-SEM) , Fourier transform Near-infrared spectroscopy (FT-NIR) , X-Ray Diffraction (XRD), thermogravimetric analysis (TGA) , and differential scanning calorimetry (DSC) . The results show that, blending of PAN with PVC lead to improving of the electrospun ability of PVC with more stability and improvement of thermal stability of PVC and changing the behavior of the nanofibers from hydrophobicity to hydrophilic. Furthermore, the low interaction between the chains of polymers and the crystallinity (%) and crystalline size (nm) of blend nanofibers as slightly decreased compared to the pure polymers. According to all testes, the 25 % PVC: 75 % PAN was the best blending ratio, which gave a more stable nanofiber produced at low concentrations.

Chapter one

1.1. Introduction.

Each polymer has special properties or advantages that differ from the other polymer properties, for improving the performance of the polymer and enabling it to obtain new properties. It can be blended with another polymer to obtain a blending that combines the new properties with the properties of the original polymer [1, 2] . The importance of blending polymers has increased in recent times to improve the performance or reduce the products cost of polymers due to the increase in engineering and medical applications [3]. Viscosity is an important parameter that directly affects the productivity and uniformity of nanofibers produced from polymeric mixtures using the electrospinning technique, which has a low surface area, if the viscosity is high [4, 5].

Therefore, the value of the electric applied voltage must be sufficient to exceed the surface tension of the polymeric solution and form a jet of fibers [5, 6]. In addition, the properties of the fibers produced from polymeric mixtures such as the morphological properties represented by the diameter of the fibers and the formation of beads with the fibers deposited on the collector are related to the properties of the solvent and the concentration of the polymer[8]. Polyvinyl chloride is one of the polymers that possesses high mechanical properties due to in addition of this polymer is a stiffener [9] and poor hydrophilicity[10] , therefore, Alazab Alnaqbi et al., blended polystyrene and polyvinyl chloride to obtain more felsitic properties [11]. Moreover, it is blended with a lot of polymers such as ethylene vinyl acetate (EVA), polyvinylidene fluoride (PVDF), and chlorinated Polyvinyl chloride (CPVC) to improve the performance of PVC membrane for many engineering applications [12, 13]. On the other hand, solvents play an important role in controlling the surface tension, conductivity, and dielectric constant and make polymeric solutions suitable for electrospinning [14]. Many researchers have used a mixture of solvents such as tetrahydrofuran (THF) and dimethylformamide (DMF) for dissolving high concentrations

of polymer PVC mixtures in different ratios, for example Ovidiu Chiscan et al., used THF: DMF 4:1 v/ v[15], and Zhong et al., used THF: DMF 7:3 w/w[7]. THF solvent has a low boiling point, which leads to rapid evaporation of the solvent and an increase in the solidification rate of the fibers, which leads to unstable jet [16,17], while DMF has high boiling point [14] also, the diameters of nanofibers decreases with increasing boiling point and solvent density [18]. The production of nanofibers from polymers with low concentrations leads to the production of unstable fibers accompanied by the formation of beads on the surface of the fibers because of the decrease in the surface tension of the solution and the breaking of the liquid into droplets instead of pulling it into uniform fibers [19]. Therefore, the blending of the PVC with PAN is essential because PAN nanofibers are more hydrophilic than PVC nanofibers, and PAN solution produces continuous fibers when the applied voltage force exceeds the surface tension force of the solution [20, 21].

1.2. AIM.

In this study, both polyvinyl chloride and polyacrylonitrile were dissolved in dimethyl formaldehyde with 8 wt. % concentrations at different blending ratios, in addition to studying the effect of polyacrylonitrile ratios on the rheological, morphological, crystalline, and thermal properties of nanofibers.

Chapter Two: Theoretical Part

2.1 Polyvinyl chloride

(Polyvinyl chloride, in literal translations, polyvinyl chloride (abbreviated PVC) is a very widely used plastic material, which is one of the most valuable products of the chemical industry, and polyvinyl chloride is one of the joining polymers of which very large quantities are made through a free radical mechanism. Worldwide, more than 50% of manufactured polyvinyl chloride is used in construction as a construction material because it is cheap and easy to install. In recent years, polyvinyl chloride has replaced many construction materials in many areas, although there are concerns about the impact of polyvinyl chloride on the environment and human health. As this polymer is unstable towards light and heat, and this leads to wide changes in the structure due to the removal of HCl, and this also affects its physical, chemical and mechanical properties. Polyvinyl chloride is prepared from vinyl chloride monomer, which is a very important compound in industry. Annual global production of vinyl chloride is about 17 million tons in 1985 and over 26 million tons in 1995, with more than 64% of it produced in Europe and the USA. About 95% of the world's production of vinyl chloride is used to produce polyvinyl chloride. Polyvinyl chloride was discovered accidentally in the nineteenth century, first in 1835 by the world Regnault and the second in 1872 by the world Baumann. In both discoveries, the polymer appeared as a white solid substance inside vinyl chloride bottles that were left exposed to sunlight. At the beginning of the twentieth century, the Russian scientist Ostromisleusky tried to use polyvinyl chloride in commercial products, but the difficulties he faced in treating it were great, and sometimes he obtained a brittle polymer. In 1926, Simon developed a method for treating polyvinyl chloride by mixing it with various additives, and the result was a more flexible and easy-to-manufacture material, and this method made it a widely used material in all aspects of life. When P.V.C burns, it produces a poisonous gas, HCE, which becomes fatal if a person inhales it frequently [22] .

2.1.1. Properties of polyvinyl chloride

The mechanical and physical properties of PVC depend on its composition and production methods for this compound. The chemical properties of homogeneous PVC are determined by the basic chemical structure of the polymer molecule, but it is certain that some chemical properties (thermal stability) are affected by the presence of irregularities in the structure such as side chains and unsaturation. Polyvinyl chloride has a large molecular weight. At normal temperatures, a large number of organic compounds have no effect on it. The compounds that attack it are chlorine aromatic hydrocarbons and some esters. Soft and

tough polyvinyl chloride properties: Soft PVC Soft PVC Volumetric 1.2 -1.6 1.4-1.6
Compressive strength Kgf/cm² 87.5 100 Cutting elongation 105 - 210 25 Specific heat
cal/cm 0.4 0.25 Linear expansion coefficient. 1 5 Maximum application temperature 104-
80 °C 65-70 Water absorption in 24 hours 0.25 0.1-0.4 [22].

2.2. Polyacrylonitrile (PAN)

Also known as Creslan 61, is a semi-synthetic organic polymer resin, having the linear formula (C₃H₃N)_n. Although it is thermoplastic, it does not melt under normal conditions. Degrades before melting. It melts above 300°C if heating rates are 50°C or higher. Almost all PAN resins are copolymers made from mixtures of monomers with acrylonitrile as the main monomer. It is a versatile polymer used to produce a large variety of products including ultrafiltration membranes, hollow fibers for reverse osmosis, fibers for textiles and PAN oxidized fibers. PAN fiber is a chemical precursor to high quality carbon fiber [23. PAN carbon monoxide thermally oxidizes in air at 230°C to form oxidized PAN fibres, then chars above 1000°C in an inert atmosphere to make carbon fibers found in a variety of everyday high-tech and general applications such as civil and military aircraft, primary and secondary structures, and missiles solid-fuel rocket engines, pressure vessels, fishing rods, tennis rackets, badminton rackets and high-tech bikes . It is a repeating unit component in several important polymers, such as styrene-acrylonitrile (SAN) plastics and acrylonitrile-butadiene styrene (ABS) plastics [24,25] .

2.2.1. PAN Material Characteristics

Acrylic fabric - the most durable among materials for artistic purposes. It is well tolerated under direct sunlight and rain. PAN - is a high-quality synthetic fiber raw material for the production of which is petroleum derivatives, namely polyacrylonitrile solutions. On the market, such tissues are called acrylic, orlon, nitron, and many other names [26,27]. PAN - material composition and appearance resembles wool, so acrylic is often called artificial wool. PAN - warm, soft, lightweight and flexible yarn, which will not damage the mole. It should be noted, describing the PAN material, that this is a quality acrylic, which is able to hold its shape under the influence of mechanical and chemical disinfection fluctuations of nature. It is almost not subject to fading and discoloration; it is easy to paint, so the products are obtained bright and saturated colors. Glass transition temperature is around 95 °C and fusion temperature is at 322 °C. PAN is soluble in polar solvents, such as dimethylformamide, dimethylacetamide, ethylene and propylene carbonates, and in aqueous solutions of sodium thiocyanate, zinc chloride or nitric acid.[28]. Solubility parameters: 26.09 MPa^{1/2} (25 °C) are 25.6 to 31.5 J^{1/2} cm^{-3/2}. Dielectric constants: 5.5 (1 kHz, 25 °C), 4.2 (1 MHz, 25 °C). Can behave as branched as well as linear polymer. Polyacrylonitrile finds use as a porous supporting polymer for adsorbents for a variety of

applications including ion exchange for cleaning up nuclear wastes. The PAN in this case is dissolved in a polar solvent such as DMSO along with the desired adsorbent and a surfactant and then dropped into water where it is crashed out and forms beads suitable for column use [29] .

2.3. Dimethylformamide (DMF)

is an organic compound with the formula $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$. Commonly abbreviated as DMF (although this initialism is sometimes used for dimethylfuran, or dimethyl fumarate), this colourless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Dimethylformamide is odorless, but technical-grade or degraded samples often have a fishy smell due to impurity of dimethylamine. Dimethylamine degradation impurities can be removed by sparging samples with an inert gas such as argon or by sonicating the samples under reduced pressure. As its name indicates, it is structurally related to formamide. DMF is a polar (hydrophilic) aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as $\text{S}_{\text{N}}2$ reactions [30,31].

2.3.1 Structure and properties

As for most amides, the spectroscopic evidence indicates partial double bond character for the C-N and C-O bonds. Thus, the infrared spectrum shows a C=O stretching frequency at only 1675 cm^{-1} , whereas a ketone would absorb near 1700 cm^{-1} . [32] . DMF is a classic example of a fluxional molecule.

The ambient temperature ^1H NMR spectrum shows two methyl signals, indicative of hindered rotation about the (O)C-N bond. [32] At temperatures near $100 \text{ }^\circ\text{C}$, the 500 MHz NMR spectrum of this compound shows only one signal for the methyl groups. DMF is miscible with water. [8] The vapour pressure at $20 \text{ }^\circ\text{C}$ is 3.5 hPa. A Henry's law constant of $7.47 \times 10^{-5} \text{ hPa m}^3 \text{ mol}^{-1}$ can be deduced from an experimentally determined equilibrium constant at $25 \text{ }^\circ\text{C}$ [33]. The partition coefficient $\log P_{\text{OW}}$ is measured to -0.85 . [11] Since the density of DMF (0.95 g cm^{-3} at $20 \text{ }^\circ\text{C}$ [8]) is similar to that of water, significant flotation or stratification in surface waters in case of accidental losses is not expected.

2.3.2. Reactions of Dimethylformamide

Strong acids and bases, especially at elevated temperatures, hydrolyze DMF. With sodium hydroxide, DMF converts to formate and dimethylamine. DMF undergoes decarbonylation near its boiling point to give dimethylamine. Distillation is therefore conducted under reduced pressure at lower temperatures. In one of its main uses in organic synthesis, DMF was a reagent in the Vilsmeier–Haack reaction, which is used to formylate aromatic compounds. [33] The process involves initial conversion of DMF to

a chloroiminium ion, $[(\text{CH}_3)_2\text{N}=\text{CH}(\text{Cl})]^+$, known as a Vilsmeier reagent, which attacks arenes. Organolithium compounds and Grignard reagents react with DMF to give aldehydes after hydrolysis in a reaction named after Bouveault.^[16]

Dimethylformamide forms 1:1 adducts with a variety of Lewis acids such as the soft acid I_2 , and the hard acid phenol. It is classified as a hard Lewis base and its ECW model base parameters are $E_B = 2.19$ and $C_B = 1.31$. Its relative donor strength toward a series of acids, versus other Lewis bases, can be illustrated by C-B plots [33].

2.3.3. Applications of DMF

The primary use of DMF is as a solvent with low evaporation rate. DMF is used in the production of acrylic fibers and plastics. It is also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings.^[8]

- It is used as a reagent in the Bouveault aldehyde synthesis and in the Vilsmeier-Haack reaction, another useful method of forming aldehydes.
- It is a common solvent in the Heck reaction.
- It is also a common catalyst used in the synthesis of acyl halides, in particular the synthesis of acyl chlorides from carboxylic acids using oxalyl or thionyl chloride. The catalytic mechanism entails reversible formation of an imidoyl chloride (also known as the 'Vilsmeier reagent'):
- DMF penetrates most plastics and makes them swell. Because of this property DMF is suitable for solid phase peptide synthesis and as a component of paint strippers.
- DMF is used as a solvent to recover olefins such as 1,3-butadiene via extractive distillation.
- It is also used in the manufacturing of solvent dyes as an important raw material. It is consumed during reaction.
- Pure acetylene gas cannot be compressed and stored without the danger of explosion. Industrial acetylene is safely compressed in the presence of dimethylformamide, which forms a safe, concentrated solution. The casing is also filled with agamassan, which renders it safe to transport and use.

As a cheap and common reagent, DMF has many uses in a research laboratory.

- DMF is effective at separating and suspending carbon nanotubes, and is recommended by the NIST for use in near infrared spectroscopy of such. DMF can be utilized as a standard

in proton NMR spectroscopy allowing for a quantitative determination of an unknown compound.

- In the synthesis of organometallic compounds, it is used as a source of carbon monoxide ligands.
- DMF is a common solvent used in electrospinning.
- DMF is commonly used in the solvothermal synthesis of Metal–Organic Frameworks.
- DMF-*d*₇ in the presence of a catalytic amount of KO^t-Bu under microwave heating is a reagent for deuteration of polyaromatic hydrocarbons [34].

2.4. Electrospinning

Is a fiber production method that uses electric force to draw charged threads of polymer solutions or polymer melts up to fiber diameters in the order of some hundred nanometers? Electrospinning shares characteristics of both electrospraying and conventional solution dry spinning of fibers.[35] The process does not require the use of coagulation chemistry or high temperatures to produce solid threads from solution. This makes the process particularly suited to the production of fibers using large and complex molecules. Electrospinning from molten precursors is also practiced; this method ensures that no solvent can be carried over into the final product. When a sufficiently high voltage is applied to a liquid droplet, the body of the liquid becomes charged, and electrostatic repulsion counteracts the surface tension and the droplet is stretched; at a critical point a stream of liquid erupts from the surface. This point of eruption is known as the Taylor cone. If the molecular cohesion of the liquid is sufficiently high, stream breakup does not occur (if it does, droplets are electrosprayed) and a charged liquid jet is formed [36,37].

As the jet dries in flight, the mode of current flow changes from ohmic to convective as the charge migrates to the surface of the fiber. The jet is then elongated by a whipping process caused by electrostatic repulsion initiated at small bends in the fiber, until it is finally deposited on the grounded collector. The elongation and thinning of the fiber resulting from this bending instability leads to the formation of uniform fibers with nanometer-scale diameters [37].

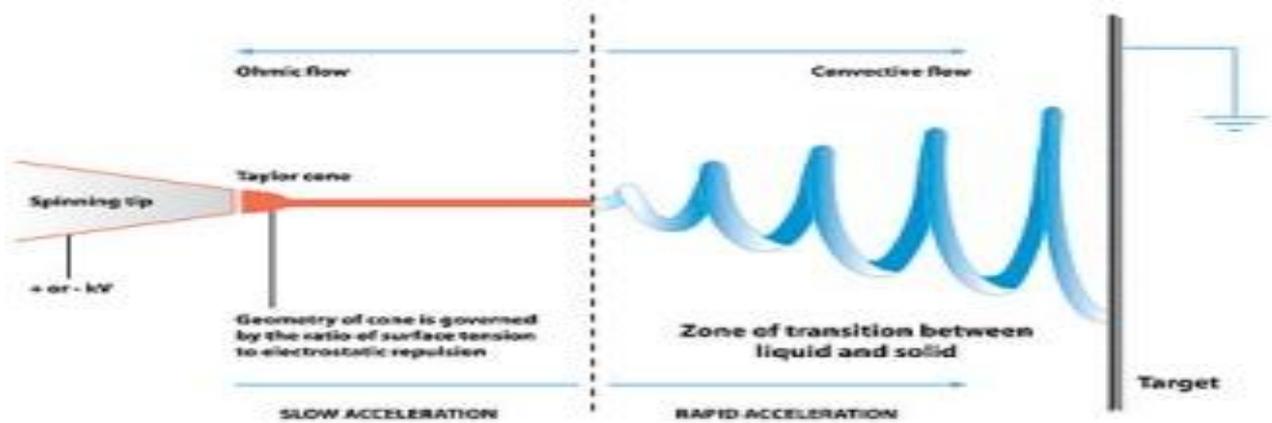


Fig.1 Elongated the Taylor cone for producing the nanofibers by electrospinning

The standard laboratory setup for electrospinning consists of a spinneret (typically a hypodermic syringe needle) connected to a high-voltage (5 to 50 kV) direct current power supply, a syringe pump, and a grounded collector. A polymer solution, sol-gel, particulate suspension or melt is loaded into the syringe and this liquid is extruded from the needle tip at a constant rate by a syringe pump.^[6] Alternatively, the droplet at the tip of the spinneret can be replenished by feeding from a header tank providing a constant feed pressure. This constant pressure type feed works better for lower viscosity feedstocks [38,39].

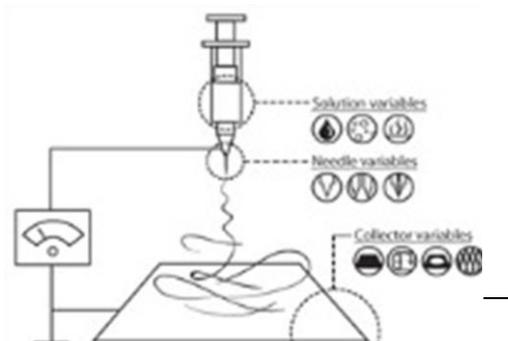


Fig.2 Apparent devise of electrospinning

Chapter Three: Experimental Part

3.1. Materials

The Sigma-Aldrich –Germany supplied commercial PAN powder with a molecular weight of 150 000 g /mol . N,N dimethylformamide (DMF, 99.7%) was purchased from ALPHA CHEMIKA-India. Poly (vinyl chloride) with chemical formula $(\text{CH}_2\text{CHCl})_n$ and average molecular weight ~233,000 was Supplied by Sigma-Aldrich –Germany .

3.2 Preparation Solutions and Method

Dissolving polyacrylonitrile and polyvinyl chloride powders with dimethyl formaldehyde solution at a concentration 8 wt.% for each polymer using a magnetic stirrer and a temperature not exceeding 40 C and until homogeneity of the solution occurs for 45 minutes in PAN : DMF solution, while continues mixing the PVC: DMF solution under a temperature of 60 C until the homogeneous solution. Blending of PVC: PAN solutions with different ratios (100 % PAN, 25 % PVC, 50 % PVC, 75 % PVC, and 100 % PVC). Homogeneous solutions are prepared according to the above blending ratios for the electrospinning technique to produce nanofibers , where the solution is pumped at a flow rate 0.5 mL/ h by MS-2200-Daiwha syringe infusion pump , the applying voltage , rotational speed of the collector , and the distance between the needle and the collector were 20 Kv, 600 rpm and 20 cm respectively.

3.3 Characterizations

The morphology (size, shape, and diameter) of the PVC: PAN nanofiber was evaluated using field-emission scanning electron microscopy (FE-SEM) (MIRA3, TESCAN-FRANCE). Using the Digitizer image analysis software application , the average diameter with standard deviation (SD) was estimated, and the frequency histograms of the diameter distribution of the nanofibers were plotted using QI Macros (SPC Software for Excel, Six Sigma Software). Mountans9 software used to estimate the texture direction for PVC: PAN

nanofibers. The viscosity of the solutions was measured by using (Brookfield DV-III Ultra Rheometer) in cP units with a shear rate range of (0.00-200) s⁻¹. A contact angle system was used to test the wettability of the nanofiber samples by using “SL200B Optical Dynamic / Static Contact Angle Meter. Fourier transform Near-infrared spectroscopy (Spectrum Two NTM FT-NIR, PerkinElmer, Inc.-USA) was used to characterize the electrospun within the sample range of 400–4,000 cm⁻¹. The crystal structures of the samples were investigated by the X-Ray Diffraction (Philips PAN alytical –X’Pert High Score Plus) at room temperature, and used the [X-Ray Tube: Cu (K α = 1.54060 Å), Generator Settings: 30 mA, at 40 kV, and $2\theta = 9.9250^\circ - 80.0750^\circ$, Step Size ($^\circ 2\theta$): 0.0500.]. The thermal analysis as DSC-TGA of electrospun nanofibers used SDT Q600 V20.9 Build 20 thermal gravimetric Universal V4.5A, TA Instruments, New Castle, DE, USA.

Chapter Four

4. Results and Discussion

4.1. Rheological Properties

Ionic conductivity is one of the important properties of the polymer, which directly relates to viscosity, and polymeric solutions with low viscosity produce high ionic conductivity due to the presence of more voids in the polymer matrix. Therefore, all viscoelastic materials depend on the deformation schedule. The study of flow technique and deformation characteristics is known as the study of rheological properties represented by the relationship of shear viscosity with the shear rate of mixing polymer solution (PVC: PAN) in different ratios. Figure 3 shows a decrease in shear viscosity with an increase in shear rate as a result of the inhomogeneity of PVC on PAN where it represents a large deformation at (75-90% PVC) [22] while a little deformation of the viscosity is observed when the ratio (25 % PVC) at low shear rate (6-96 S-1). On the other hand, the deformation or decrease in viscosity is stable at high shear rates (126-200 S-1). The ratio (25 % PVC) represents the best mixing ratio between polyvinyl chloride and polyacrylonitrile, discussed by Namsaeng et al [40].

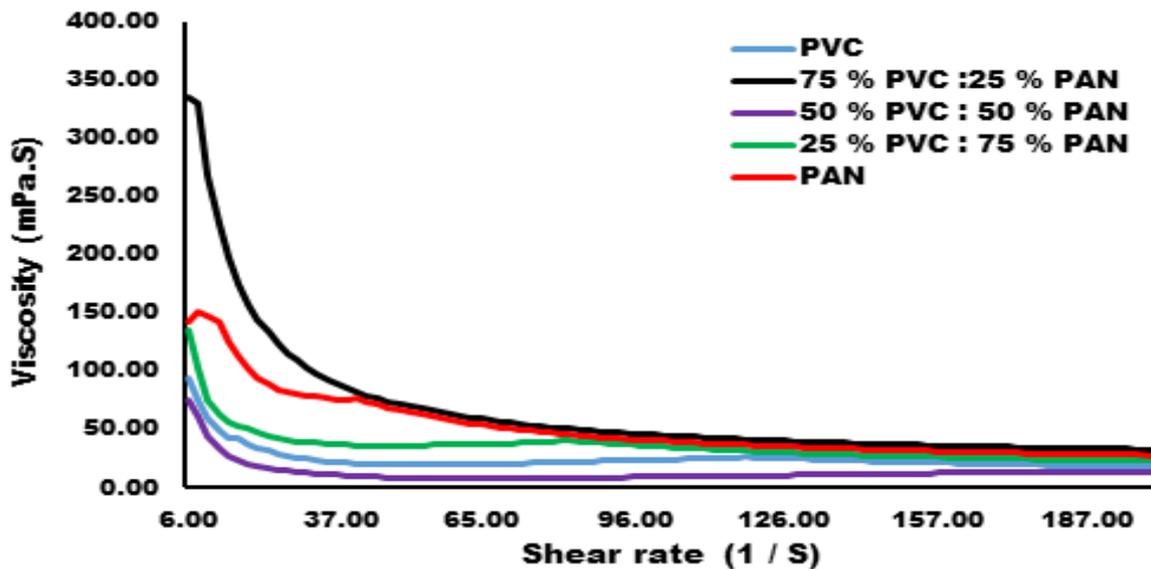


Fig.3 represented the relation between the shear viscosity (mPa.S) and shear rates (S^{-1}) of different PVC: PAN blending ratio solutions

Figure 3 and Table 1 represent the relationship of shear stress with the shear rate for PVC blends, where the shear stress increases with the increase in shear rate, indicating that the

behavior of PVC blends is non-Newtonian, and the behavior of the shear stress-shear rate curves follows the power law system. The power law Index (n) and the consistency coefficient (K) can be calculated according to the following equations [41]:

$$\delta = K\gamma^n \quad (1)$$

$$\text{Log}\delta = \text{Log} K + n \text{Log}\gamma \quad (2)$$

Where (δ) shear stress, shear rate (γ) and flow behavior index (n) represent the slope and (log K) represents the consistency coefficient. All values of the flow index (n) were lower than unity, which indicates a more pseudoelastic behavior of PVC blends, and the decrease in (n) values means that the mixtures were more homogeneous and contain cross-links. PVC blend at 25 % PVC represents the best homogeneity between PVC and PAN, while the increase in the values of (R²) correlation coefficient indicates an improvement in the homogeneity of PVC blends [41].

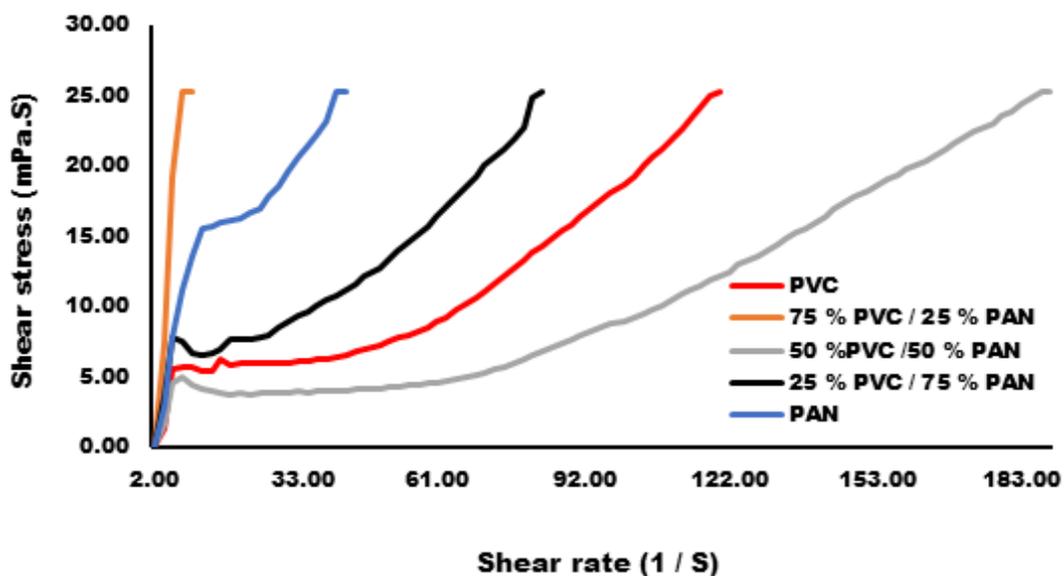


Fig.4 shows the shear stress- shear rates curves for different PVC: PAN blending ratio solutions

Table 1 represents the results of logarithmic fitting equations for PVC blending.

PVC : PAN Solutions concentrations (wt.%)	Log K	n	Fitting equation	R ²
0.0	3.38	0.988	y = 0.988 x + 3.38	0.998
25	0.3467	0.4897	y = 0.4897 x + 0.3467	0.8887
50	0.3673	0.6957	y = 0.6957 x - 0.3673	0.7397
75	0.3307	0.6704	y = 0.6704 x + 0.3307	0.8166
100	0.0774	0.6347	y = 0.6347 x - 0.0774	0.7886

n: flow behavior index, log K: Logarithmic of consistency coefficient, and R² = Correlation coefficients

4.2 .Water Contact Angle

PAN is one of the important and commercially available polymers due to its ability to absorb water and is thermally stable, while PVC has a low water absorption capacity, so PVC has been mixed with PAN to improve the performance of PVC nanofibers [14]. Figure 5 shows the decrease in the water contact angle from $110.33 \pm 6.49^\circ$ to $33.588 \pm 1.176^\circ$ when the PVC % decreases from 100 % to 25%, and thus the behavior of the nanofibers changes from hydrophobicity to hydrophilic, which indicates that PAN nanofibers had a good hydrophilicity, discussed by Yang and Liu [42].

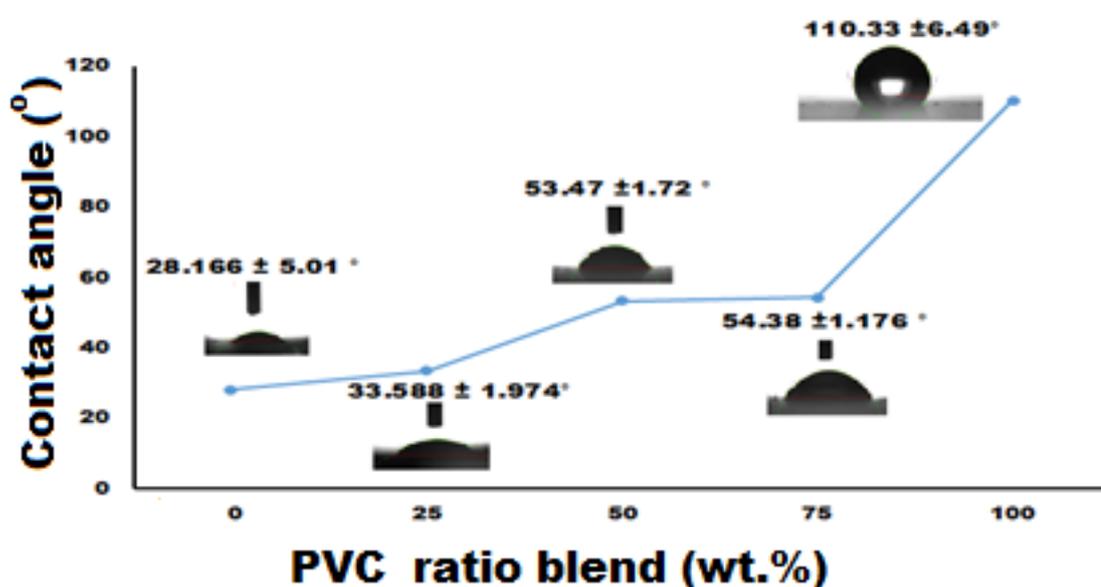


Fig.5 Shows the changing of the water contact angles on the surface of PVC: PAN nanofibers dependent of increased the PVC wt. %.

4.3 Morphological Properties

One of the important factors affecting on the morphological properties of nanofibers produced from the blending of PVC with PAN is the type of solvent used such as DMF, which has a good relative vitality, high polarity, and high dielectric constant, these properties lead to formation a low fiber diameter and low beads formation. Moreover, the high density of nanofibers deposited on the collector [9, 43], compared with the diameters of the nanofibers produced from PVC: PAN blends by using a mixture of solvents as (THF: DMF), where the diameters were at twice the size from 407 to 567 nm [40]. In this study, only DMF solvent was used to dissolve PVC and PAN at different ratios. Figure 6 and Table 2 showed the effecting of PAN on morphological properties such as the size, number of beads formation, stability, and density of the nanofibers. In addition to, the decrease in the average diameter (AD) with

standard deviation (Stdv) and range of nanofibers diameters (from 138.1 ± 72.89 to 59.12 ± 32.10 nm) and (from $47.62 - 357.143$ to $11.90-142.85$ nm) respectively. When increased, the PVC ratio (%) of pure PAN to 50% PVC and then the diameter increases with an increase in the size and number of beads formed. On the other hand, decreasing in the density and stability of the nanofibers when the PVC ratio (%) increases (from 75 to 100 %), which is an indication of the heterogeneity of polymeric mixtures in the presence of PVC for more than 75%. These results indicated for production a low nanofiber diameter by bending the PVC with PAN, discussed by Alnaqbi et al [2].

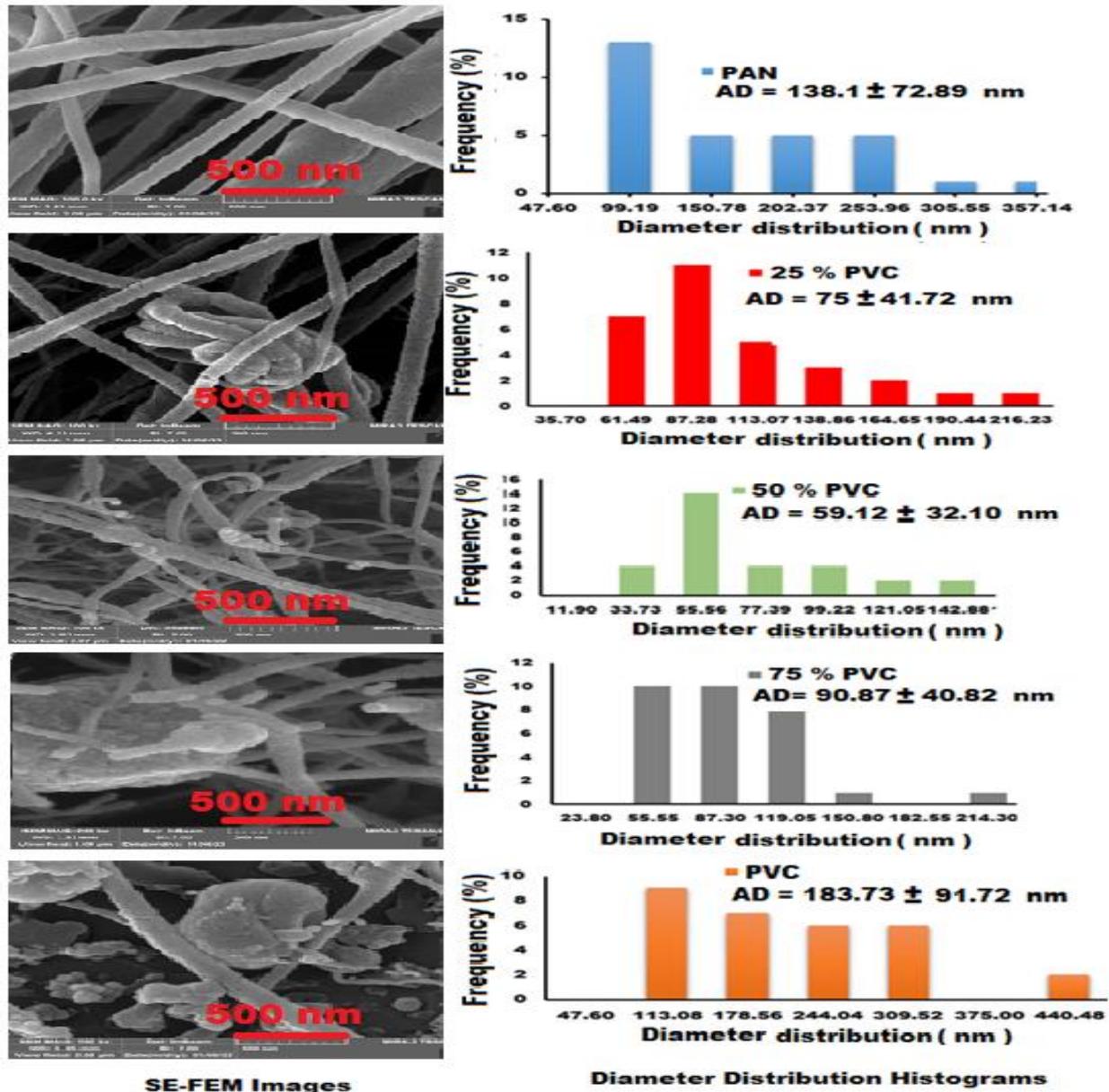


Fig.6 shows the micro-FE-SEM images and diameter distribution histograms for pure and PVC: PAN nanofibers

Table 2 shows the results of average diameter (AD) with standard deviation, ranges, and morphological properties of pure and blended nanofibers.

PVC : PAN Ratio (%)	AD (nm)	Ranges (nm)	Nanofibers Morphology
0.0	138.1±72.89	47.62 – 357.143	High density of nanofibers , low beads
25	75±41.72	23.809 – 214.28	High density of nanofibers , low beads
50	59.12±32.10	11.90-142.85	Good density of nanofibers , high beads
75	90.87±40.82	35.71 – 190.47	Low density of nanofibers, high beads and aggregations
100	183.73±91.72	47.62-440.48	Low density of nanofibers , high beads

AD= average diameter

4.4. Fourier transform Near-infrared Analysis

FT-NIR spectroscopy is used to detect the interactions between polymer chains, especially when the polymeric blends are homogeneous and compatible. Figure 7 represents the FT-NIR spectroscopy of the nanofibers of PAN, PVC, and 25% PVC: 75% PAN. Where the spectroscopy of pure PAN indicates a strong absorption peak at 2244 cm⁻¹ which represented stretching vibration of (C≡N). In addition of , found the a strong absorption peak at 2933 and 3418 cm⁻¹ which indicated to C-H alkane and O-H alcohol respectively , while the 1237,1452,1667, and 1738 cm⁻¹ indicated to vibration bands[44,45] . Pure PVC nanofiber FT-NIR spectrum were characterized by strong peak at 1430 , 2851 cm⁻¹ for vibration band of deformation of CH₂ , CH stretching vibration, and stretching C-H of CH₂ respectively . Also, found the stretching C-Cl at 618 and 689 cm⁻¹, while the absorption peak at 1540 indicated for C-N amide II band. Moreover, the peaks 2330, 2358, 1730, 3300, and 3368 - 3797 cm⁻¹ represented the C=C conjugated and C≡C, C=O stretch, (N-H) amines, and (O-H) alcohol respectively [46,47]. The FT-IR spectrum of 25 % PVC: 75 % PAN nanofibers was shifted of some absorption peaks of pure PAN and PVC nanofibers , the strong peak at 2244 for C=N nitrile group of PAN was shifted from blending polymers to 2348, while the absorption peak at 618 and 689 of PVC were shifted to 665 for blend polymers . Furthermore, the some functional groups as (O-H) alcohol and (N-H) amine were found in blending of nanofibers, the results indication for molecular interactions between polymers [9].

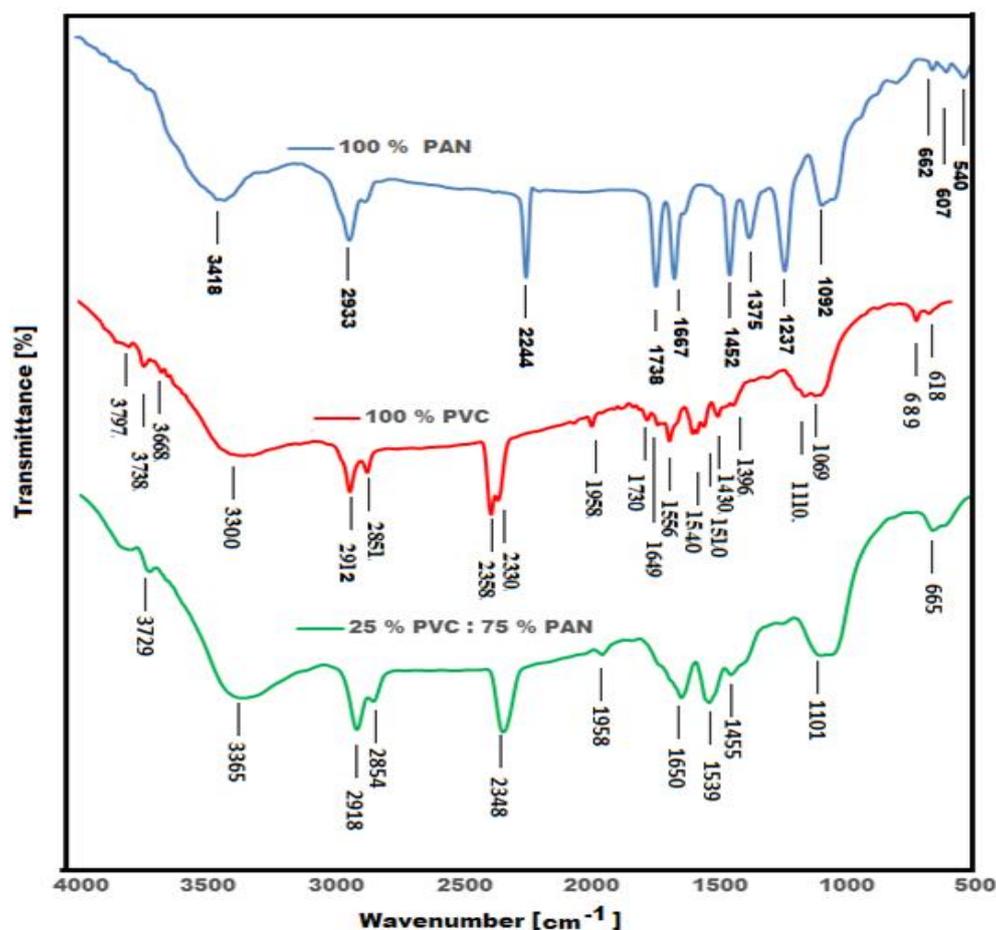


Fig.7 Shows the FT-R-IR spectra for pure PAN, Pure PVC, and 25 % PVC: 75 % PAN nanofibers.

4.5. X-Ray Diffraction analysis

Figure 8 shows the XRD spectra of pure PAN, pure PVC, 25 % PVC: 75 % PAN nanofibers. The XRD analysis of many calculated structural parameters such as crystallinity (%), crystalline size (nm), FWHM, reflection Intensity, interplanar distance (nm), and Peak position (2θ) are summarized in Table 3 according to different peaks. The XRD peaks at $2\theta=18.32^\circ$ and $2\theta=24.101^\circ$ were found in the PVC [48]. It was noted that the value of 2θ at $17.8^\circ, 19.32^\circ, 21.16^\circ, 21.43^\circ, 25^\circ,$ and 26.2° corresponds to pure PAN respectively [49]. While the peaks at $17.4^\circ, 20^\circ, 20.985^\circ,$ and 21.112° correspond to 25 % PVC: 75 % PAN blend. It was noted that both PNA and PVC had an amorphous behavior and there are a poor interaction between their molecule's at blending [2]. On the other hand, d-spacing was found to be slightly increased at blending of polymers, which indicated that low interaction between the PAN and PVC chains, in addition of the slightly decreasing in crystallinity (%), crystalline size (nm) at 25 % PVC: 75 % PAN blend.

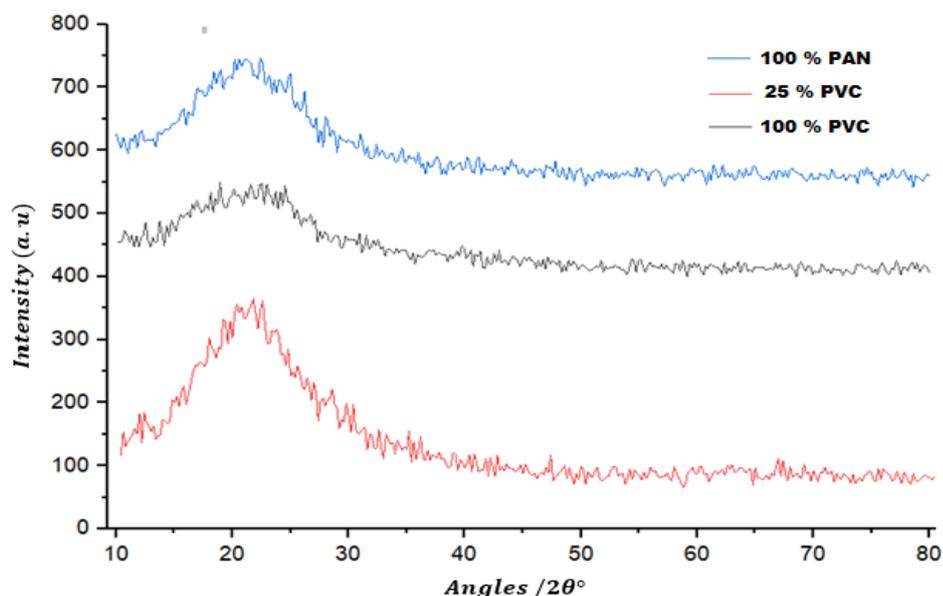


Fig.8 XRD spectra of pure PAN, pure PVC, 25 % PVC: 75 % PAN nanofibers.

Table 3 Results of XRD analysis of many calculated structural parameters such as Crystallinity (%), Crystalline size (nm), FWHM, Reflection Intensity, d-spacing (d), and Peak position (2θ) of pure PAN, pure PVC, 25 % PVC:75 % PAN nanofibers .

samples	2θ	d(nm)	Rel. Int. (%)	FWHM	Crystalline size (nm)	Crystallinity(%) in (100) Rel. Int.
Pure PAN	17.788	0.49822	34.8	0.962	8	61.2
	19.324	0.45896	50	1.065	7	
	21.16	0.41952	100	1.883	4	
	21.432	0.41425	43.3	0.824	9	
	25	0.35589	46.5	1.127	7	
Pure PVC	26.2	0.33985	11.7	0.399	21	63.44
	18.32	0.48388	80.5	0.416	19	
	24.101	0.36896	100	0.576	14	
25 % PVC : 75 % PAN	17.4	0.50924	36.1	1.426	5	60.00
	20	0.44359	84.8	1.252	6	
	20.985	0.42298	84.6	1.299	6	
	21.112	0.42046	100	1.382	5	

Rel. Int. = Reflection Intensity, d= d-spacing, 2θ = Peak position

4.6. Thermal analysis

The thermal properties as thermogravimetric analysis (TGA) of pure PAN, pure PVC, and their blends were summarized in Figure 9. The thermal degradation contentions stable until 328.94 C , then the degradation with mass lost about 32.94 % at 600 C, while the pure PVC with low thermal stability with high mass lost 97.57 % . Moreover, the increasing of mass lost % increased ratio of PVC in the blends (42.57, 49.1, and 96.2 %) when the PVC ratio increased from 25% to 75 % respectively. These results indicated that PVC is thermoplastic with low

thermal stability [50], while PAN has more thermal stability [51]. On the other hand, Figure 10 showed the differential scanning calorimetry (DSC) curves for pure PAN, pure PVC, and their blends. The results of DSC analysis prove that the pure PAN was more thermal stability when the sample exposed to heating rate 10 °C/ min with range of heating up to 600 °C, the degradation temperature (Td) was 328.72 °C, followed the 25 % PVC blend with 262.8 °C. We found that the thermal stability increased with increasing the PAN ratio [52].

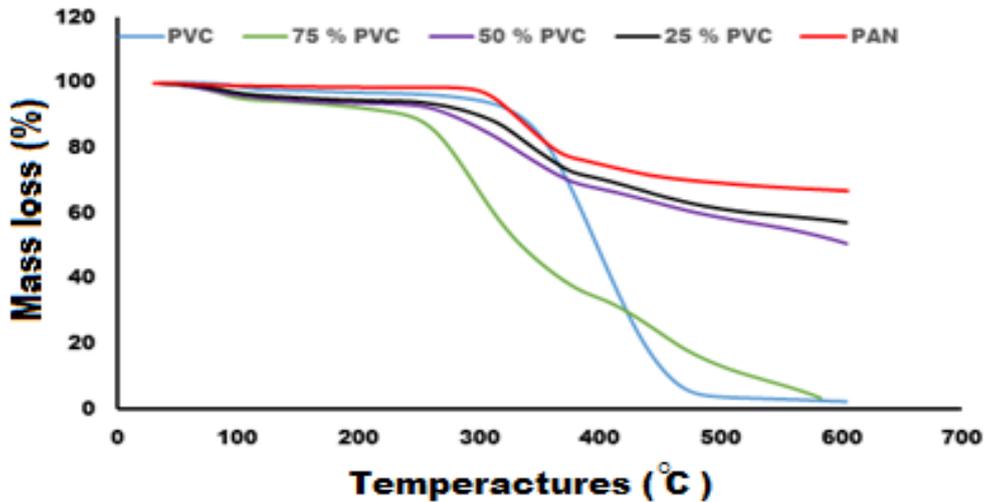


Fig. 9 Shows the TGA analysis curves for pure PAN, Pure PVC, and many blending nanofibers.

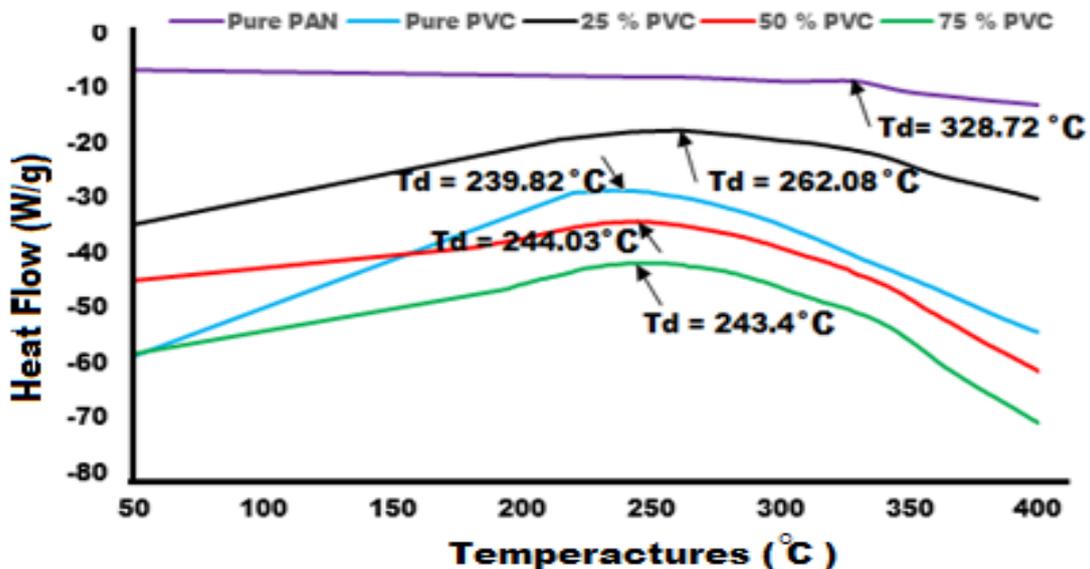


Fig. 10 Shows the DSC analysis curves for pure PAN, Pure PVC, and many blending nanofibers.

Conclusion

PVC is a thermoplastic material with low thermal stability, stiffness, and brittle. These properties limit the application of the polymer compared with PAN, which has good thermal stability and good polarity. The results of the rheological properties proved that PVC: PAN blends showed incompatibility and homogeneity at high ratios of PVC, indicating that the behavior of PVC blends was non-Newtonian. Morphological properties proved that an increase in the ratio of PAN leads to an increase in the density of nanofibers with improved stability and a decline in the formation of beads; also, the diameters of the nanofibers of the blends were less than the diameters of the nanofibers of pure polymers. On the other hand, PVC increases the water contact angle, while PAN improves the thermal stability. The results of FT-IR and XRD-analysis proved the bonding between PVC and PAN chains was weak, but there is good homogeneity at low ratios of PVC. Moreover, the crystalline properties such as crystallinity (%) and crystalline size of the blends are lower than in pure polymers.

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