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Synthesis, Electrospinning and Characterization of Schiff Base Polyvinylmethylketone and 2-Amino, 4,6-Dihydroxylpyrimidine

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Abstract

The Polyvinylmethylketone (polymer) was synthesized with 2-amino-4,6-dihydroxylpyrimidine (ligand) via a Schiff base condensation reaction to form a synthesized polymer and electrospun into a nanofibers. The characterization of the polyvinylmethylketone synthesized with 2-amino-4,6-dihydroxylpyrimidine electrospun nanofibers (APPMKNFs) was done using fourier transform infrared (FTIR). The peaks at 1696 cm^{-1} and 3139 cm^{-1} on the polymer and on the ligand respectively as the starting materials, these peaks however disappeared to form a new band at 1613 cm^{-1} indicative of the presence of imine functional group on the synthesized polymer. Elemental micro analysis (CHNS) on polymer shows the presence of functional groups of carbon and hydrogen with the absence of nitrogen before the synthesis and the presence of nitrogen after the synthesis with the ligand. The best optimum condition for the morphology using scanning electron microscope (SEM) for APPMKNFs was 20% (w/v) with diameter 127-200 nm. The surface area of APPMKNFs, material was measured, using the BET method and the results was 114.2 m^2/g.

Keywords: Synthesis; Polyvinylmethylketone; 2-amino-4,6-dihydroxylpyrimidine; Electrospinning nanofibers

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Introduction

The chemistry of 2-Amino-4,6-dihydroxylpyrimidine synthesized with polyvinylmethylketone has generated intensive scientific interest due to their aminated properties [1-3]. The pyrimidines as a class are known to possess extraordinary biological properties that are generally distinguished qualitatively by their applications in pesticides, herbicides, bactericides, and medicine intermediates [4,5]. Bidentate schiff bases are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry. Schiff bases of 2-amino-4,6-dihydroxypyrimidine and polyvinylmethylketone [4-6] plays a vital role in designing ketones related to synthetic and natural oxygen carriers [6-9].

Many bidentate Schiff bases of amines with different ketones have been prepared and studied intensively [10-12]. However less attention has been focused on bidentate Schiff bases derived from amines and different aldehydes / ketones. A search of literature reveals that no work has been done on polyvinylmethylketone synthesized with 2-amino, 4,6-dihydroxylpyrimidine via the Schiff bases reaction and electrospun into a nanofibers. Electrospinning is a process whereby fibres are generated by the application of electrostatic forces to a jetting polymer solution. The incorporation of nanofillers into electrospun fibers enhances the fiber properties relevant to a number of applications, particularly mechanically reinforced composites [13-15]. Electrospinning is allowed for the creation of nanofibres (fibres with a diameter well in the realm of nano dimensions), that can be collected to form a non-woven fabric [16-21].

The aim of this work is to synthesize polyvinylmethylketone with 2-amino-4,6-dihydroxylpyrimidine, electrospun into a nanofiber and characterize using Fourier transform infrared (FT-IR) spectra, CHNS Microanalysis, Scanning Electron Microscopy (SEM) and Brunauer, Emmett, Teller (BET).

Materials and Methods

0.33 g of 2-amino-4,6-dihydroxylpyrimidine (ligand) was weighed in 15 mL of prepared 0.02 M NaOH solution to dissolve the ligand, and was reflux for 2 hrs at 70°C after complete dissolution. 0.035 g of polyvinylmethylketone (polymer) was dissolved in 10 mL of DMSO in a beaker and was added drop wise into the reflux ligand with continuous stirring for 12 hrs at 70°C via a Schiff base condensation reaction as shown in **Scheme 1.1**. On cooling, the solution was slowly poured, while stirring vigorously into a 250 ml beaker containing ethanol to precipitate the synthesized polymer, which was filtered under vacuum suction, washed extensively with diethyl ether and dried in a desiccator. The different weight of synthesized polymer were dissolved in N,N'-dimethyl formamide (DMF), Tetrahydrofuran (THF) and also electrospun into a nanofibers as shown in **Table 1.1.**

Electrospinining parameters

Many parameters can influence the transformation of polymer solutions into nanofibres through electrospinning. These parameters include the following:

The solution concentration of polymer solution is a very important technique during fibre formation via electrospinning.

At lower polymeric concentrations, due to the effect of the applied voltage and surface tension of the polymeric solution, the charged jet fragments into discrete droplets before reaching the collector [22,23]. At an increased polymeric concentration, as the viscosity increases the chain entanglement between polymeric chains improves and nanofibres are formed.

The molecular weight is important in the solution parameter that affects the morphology of the electrospun nanofibers, when the molecular weight solution is too low, this tends to form beads rather than fibres, and a high molecular weight solution produces fibres with larger average diameters [24].

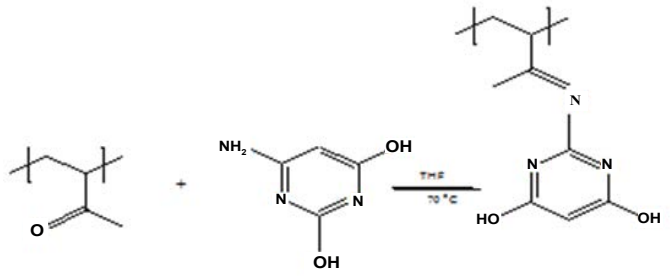
The choice of solvent is important for polymer to solubilize and be transformed into nanofibres during electrospinning. When selecting a solvent, the solubility of the polymer in the solvent and the boiling point of the solvent as indicative of its volatility are important. Volatile solvents are preferred as they facilitate dehydration of the nanofibres, the capillary tip to the collector surface owing to their lower boiling point and hence rapid evaporation rate [23,25].

Table 1.0 below shows some of the solvent parameters needed for electrospinning. Several solutions of various concentrations of the synthesized polymer, with the composition of the electrospinning solutions were prepared for Electrospinning [10] as detailed in **Table 1.1**.

Magnetic stirrer was inserted as well as a weighted quantity of polymer into the flask and the flask was fitted with a stopper to avoid evaporation of the solvent and the stirring steps were done to get approximately 10 mL of the solution.

Under magnetic stirring and at room temperature, the powder dissolved in three hours for the lowest concentrations to 24 hrs for the highest ones. After total dissolution, the mixture was homogeneous and transparent [11]. It was then transferred into a syringe as shown in **Figure 1.1**.

The electrospinning setup above utilized in this study consists of a 20 mL polypropylene syringes, and were utilized to load the electrospinning solution [26-28]. An electrically grounded, detachable, flat metal screen that is adjustable to a desired height as shown in **Figure 1.1** and flat metal screen was used to collect electrospun nanofibers.



Scheme 1.1 shows the polyvinylmethylketone (polymer) Synthesized with 2-amino-4,6-dihydroxylpyrimidine at 70°C to form the synthesized polymer with functional groups, such as the hydroxyl (OH) and the imine (NH).

Table 1.1 Shows the different concentrations of APPMKNFs used for electrospinning.

Wt of polymer	5%	7.5%	10%	15%	20%
Solvent	DMF/THF	DMF/THF	DMF/THF	DMF/THF	DMF/THF
Ratio	3:7	3:7	3:7	3:7	3:7
Flow rate	0.5 ml/h	0.5 ml/h	0.5 ml/h	0.5 ml/h	0.5 ml/h
Distance	13 cm	13 cm	13 cm	13 cm	13 cm
Voltage	12 Kv	12 Kv	12 Kv	12 Kv	12 Kv

FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectra of 2-amino-4,6-dihydroxylpyrimidine, synthesized with polyvinylmethylketone were obtained using a PerkinElmer Spectrum 100 FT-IR spectrometer with an AutoIMAGE Systems.

CHNS micro analysis

A vario Elemental ELIII Micro cube elemental analyzer was used for CHNS elemental analysis.

Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was used to determine the surface morphology of the 2-amino-4,6-dihydroxylpyrimidine, synthesized with polyvinylmethylketone dusted onto a carbon sticker, then coated with gold using a sputter coater (Balzers Union, FL-9496) for 30 min. Images were recorded using

Table 1.0 Shows the solvent properties and the resulting fibers.

Solvent	Boiling point (°C)	Other properties	Fibre morphologies	References
DCM	39.8	Low electric constant and high surface tension	Beaded large diameter	[26]
Chloroform	61.2	High intrinsic viscosity Beaded at very low polymer concentration	Beaded with low concentration	[27]
Methanol	64.7	High dielectric constant Small fiber diameter with in concentration	Increase methanol concentration until 50% then increase fiber diameter	[28]
THF	66	High dipole moment, good conductivity ribbon-like, high pore density	Smooth and beaded	[28]
Ethyl acetate	77.1	High surface tension	Smooth and beaded	[26]

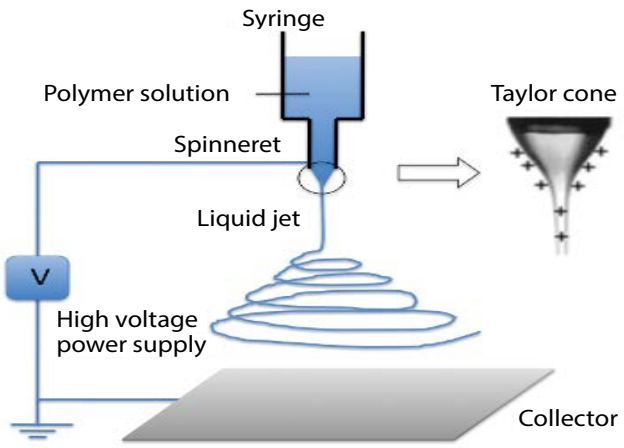


Figure 1.1 Schematic diagram of a typical electrospinning system.

INCAPentaFETx3 (Vega Tescan) SEM fitted with an Oxford ISIS EDS.

Brunauer, emmett, teller (BET) analysis

Brunauer, Emmett, Teller (BET) analysis involves carbon dioxide adsorption isotherms which were measured at 77K, using Micrometrics ASAP 2020 surface area and porosity analyzer. Prior to each measurement, the samples were degassed for a minimum of two weeks to ensure complete removal of adsorbed impurities. Degassing was performed at 70°C for the liner polymers and at 150°C for cross linked polymers.

Thermogravimetric analysis

Approximately 4.5 mg of the grounded APPMKNFs polymer was placed in an open aluminum pan. The sample was heated at a heating rate of 10°C / min 1 from 30-500°C temperature range under nitrogen atmosphere (flow rate=20 mL min^{-1}) using a Diamond TG=DTA (Perkin-Elmer).

Results and Discussion

The FTIR results of the polyvinylmethylketone (spectrum A) synthesized with 2-amino-4,6-dihydroxylpyrimidine (spectrum B) via a Schiff base condensation reaction to form the synthesized polymer (spectrum C) is presented in **Figure 1.2**.

In the polymer spectrum (A) in **Figure 1.2**, the characteristic band at 1696 cm^{-1} corresponded to the stretching vibration of the C=O groups. The broadband of the ligand, spectrum (B) ranging from 3139.24 cm^{-1} and 333.64 cm^{-1} correspond to the combination of the stretching vibration bands of both OH and NH groups. The polymer and the ligand spectra present new set of bands found at 1613, 1200 and 2921 cm^{-1}. The band at 1613 cm^{-1} can be assigned to the C=N stretching vibrations of the imine group, confirming the formation of Schiff bases between the spectrum (A) and spectrum (B). The bands at 1200 and 2928 cm^{-1} were assigned to the stretching vibrations of the C-N and C-H bonds.

CHNS microanalysis of APPMKNFs

The results of the CHNS microanalysis are listed in **Table 1.2** for the polymer and the synthesized polymer (APPMKNFs). It was evident that, the nitrogen content in the polymer was absent, and the nitrogen present after synthesis of the polymer with 2, amino-4,6dihydroxylpyrimidine is shown in the **Table 1.2**.

Scanning electron microscopy (SEM)

The SEM images of the electrospun nanofibers shows the different concentrations of APPMKNFs used for electrospinning as shown in **Table 1.1**. For the solution less than 10% (w/v) for **Figures 1.3A and 1.3B**, a droplet spray occurred and a continuous jet of polymer particles was formed. The jet from low viscosity solutions breaks up into droplets due to the lower amount of polymer in the solvent. At solution concentration of (10% and 15%) w/v APPMKNFs, the presence of beads in **Figures 1.4C and 1.4D** were observed, but the beads were completely disappeared and the formation of fibers were observed when the concentration of the solution was increased to 20%(w/v) APPMKNFs. It is believed that, the relatively high viscosity of the solution, made the morphology of the fiber to improve. The best optimum condition for the morphology used for APPMKNFs was 20% (w/v) with diameter 127-200 nm.

Thermogravimetric analysis is a powerful analytical tool to investigate the thermal stability of a material, or to investigate its behaviour in different atmosphere (e.g., inert or oxidizing). It is suitable for use with all types of solid materials, including organic or inorganic materials **(Figures 1.5-1.8)**. TGA curves of APPMKNFs degradation began at 270°C and ended at 500°C. The increase in thermal stability was attributed to the number of hydroxyl groups present in the APPMKNFs.

The x-ray diffraction of unfunctionalized and functionalized APPMKNFs was scanned in the range 5.0-90°. The diffraction and associated graph depict the 2θ value for each peak, relative

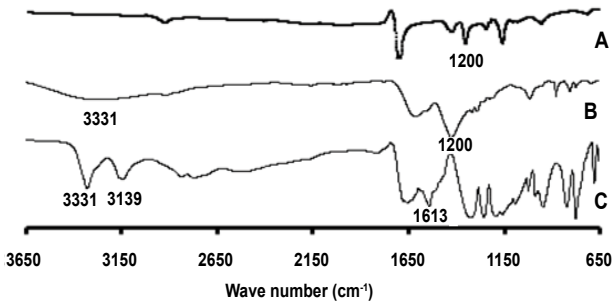


Figure 1.2 FTIR absorption spectra of polyvinylmethylketone, 2-amino-4,6 dihydroxylpyrimidine and the functionalized polymer nanofibres (APPMKNFs).

Table 1.2 CHNS Microanalysis.

APPMKNFs	C (%)	H (%)	N (%)
Unfunctionalized polymer	90.91	6.45	
Functionalized polymer	54.42	6.81	38.49

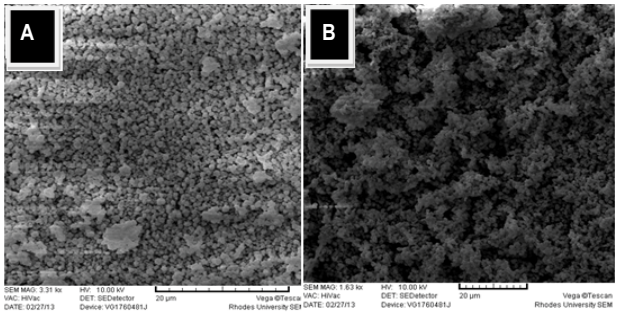


Figure 1.3 SEM images (scale bar=20 µm) showing the morphology (particles) of electrospun nanofibers from APPMKNFs at concentration of (A) 5 % w/v (B) 7.5 % w/v (voltage of 12 Kv and at a constant spinning distance of 13 cm).

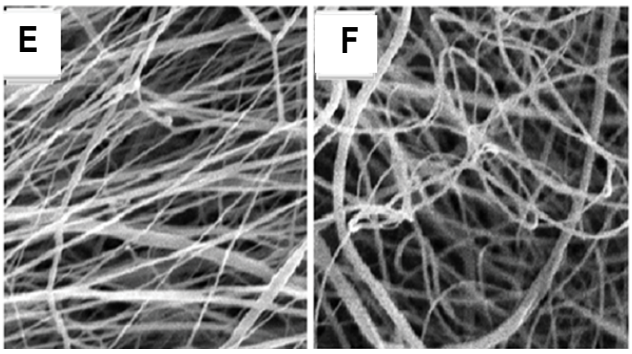


Figure 1.4 (a) SEM images (scale bar=20 µm) showing the morphology of (beeded) electrospun nanofibers from APPMKNFs at concentration of (C) 10 % w/v (D) 15 % w/v voltage of 12 Kv and at a constant spinning distance of 13 cm).

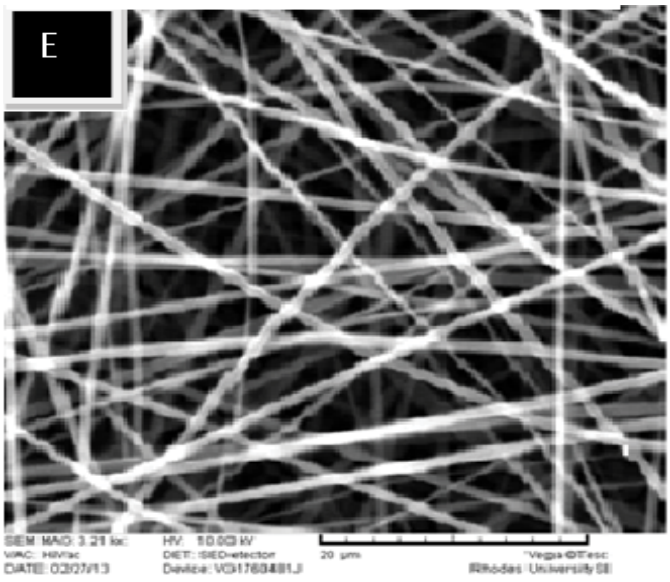


Figure 1.5 (b) SEM images (scale bar=20 µm) showing the morphology of (beed free) electrospun nanofibers from APPMKNFs at concentration of (E) 20 % w/v. (voltage of 12 Kv and at a constant spinning distance of 13 cm).

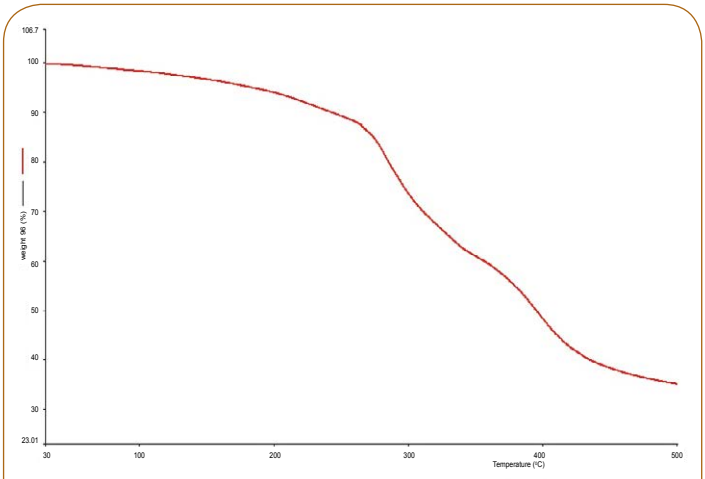


Figure 1.6 Thermogravimetric analysis of APPMKNFs polymers.

intensity and interplanar spacing (d-values). The diffraction of unfunctionalized APPMKNFs had the maxima at 2θ=21000 at a-u intensity axis. The diffraction of functionalized reflections with maxima at 2θ=6000 at a-u intensity axis. The diffraction of reflections with maxima at 2θ (40.5)=5090 at a-u intensity axis. The x-ray diffraction pattern of both the functionalized and functionalized APPMKNFs with their major peaks of relative intensity greater than 10%.

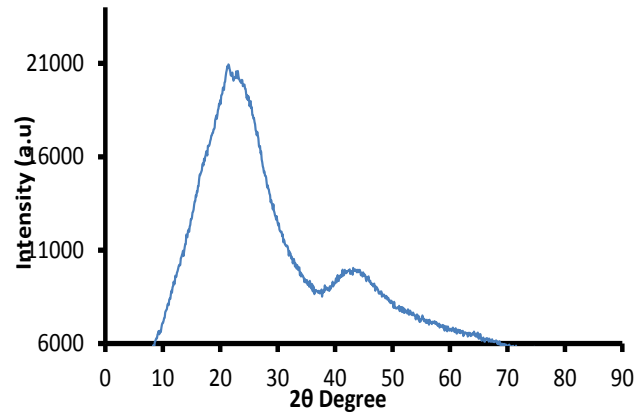


Figure 1.7 XRD before functionalization of APPMKNFs.

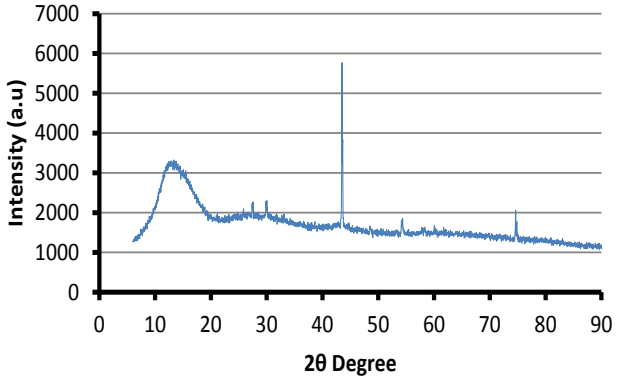


Figure 1.8 X-Ray Diffraction (XRD) for the functionalized APPMKNFs.

Table 1.3 BET single point surface area measurements for APPMKNFs, sorbent materials.

Materials	APPMKNFs
m^2/g	114.2 m^2/g

BET surface area

The specific surface area of the sorbent defines its efficiency for adsorption. The surface area of synthesized electrospun nanofibers (APPMKNFs), material was measured, using the BET method and the results are presented in **Table 1.3.**

Conclusion

In the present study, polyvinylmethylketone synthesized 2-amino-4,6-dihydroxylpyrimidine via a Schiff base condensation were investigated using the following instruments, fourier transform infrared (FTIR) analysis, scanning electron microscopy (SEM), Brunauer, Emmett, Teller (BET) Analysis, Thermogravimetric (TGA), and x-ray diffraction (XRD). These result shows that APPMKNFs is well synthesized using the above instruments for characterization and also presents APPMKNFs will be an efficient and low cost effective alternative for the removal of anions from solutions due to the functional groups present on the synthesized polymer.

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