Electrospinning, Functionalization and Quaternization of Polyvinylbenzylchloride (PVBC) Electrospun Nanofibers

Abstract
The polyvinylbenzylchloride (PVBC) was electrospun into nanofibers in a 1:1 (v/v) ratio of N,N-Dimethylformamide (DMF), Tetrahydrofuran solvent mixture, the surface was functionalized using ethylenediamine and finally quaternized PVBC using three different alkyl groups (CH₃, C₂H₅, and C₃H₇). Fourier transform infrared (FTIR) analysis was used to characterize the functional groups present. The band assigned to 670 cm⁻¹ (C-Cl) disappeared completely to form a new band at 1562 cm⁻¹ indicating the presence of NH group on the fibers. Energy dispersive x-ray spectrometer (EDX) for PVBC shows the presence of a broad peak for Cl on the unfunctionalized fiber and this peak disappears to form a sharp peak of nitrogen from the amine in ethylenediamine (EDA) of the fibers. X-ray diffraction (XRD) analysis of the fibers reveals the sharp peak on 40 (2θ) degree axis on the surface of the functionalized fibers. It was also observed that, Brunauer, Emmett, Teller (BET) surface area of the sorbent materials (PVBC) changed after the functionalization with amine.

Keywords: Polyvinylbenzylchloride (PVBC); Ethylenediamine (EDA); Alkyl groups (CH₃, C₂H₅, and C₃H₇)

Introduction
Electrospinning is the most versatile of all the methods for making nanofibers. The method could be applied to virtually every soluble or fusible polymer and the polymer solutions can be modified with additives prior to or after electro spinning for special purposes [1,2]. Though the electrospinning technique can be scaled up for commercial production, its productivity has been a challenge [2]. There have therefore been many attempts to improve on the productivity of the process. Improved and more efficient versions of electro spinning have recently evolved but they all operate on the basic principles of the techniques. The different versions can be categorized under mono nozzle, multi nozzle and needleless electro spinning.

The mono nozzle is the simplest type of electrospinning setup in which only one nozzle/needle discharges the polymer solution. Mono nozzle electrospinning is simple and does not require a lot of capital investment. Its major limitation is the low productivity.

In the multi nozzle electro spinning, the polymer solution is fed into an array of nozzles or needles which are either static or moving [3,4]. Uniform and bead-free nanofibers are formed only when all the electrospinning parameters are optimized. However, it is difficult to check case-by-case whether all the parameters are optimized prior to electrospinning. Optimization of the electrospinning parameters could be checked during electrospinning using the stability and shape of the Taylor cone or the pattern of nanofiber deposition.

The surface of the electrospun nanofibre can be functionalized with a ligand in order to create reactive sites that are specific to the desired binding molecules or analyte of interest [5] and also, to enhance their absorption properties (chemical sensors and biosensors) and also extend their shelf life [6]. The modern trends in the functionalization of nanofibers such as treatment by blending, coating, radiation with electromagnetic wave, electron beam, iron beam and corona or plasma treatment have also been found useful for the synthesis of electrospun nanofibers [7].

Corresponding author: Moronkola BA
kemimoronkola@yahoo.com
Department of Chemistry, Rhodes University, PO Box 94, Grahamstown, South Africa.
Tel: +8130296678

In this case Electrospin polyvinylbenzylchloride into nanofibers, post functionalized with ethylenediamine and then quaternized, using three different alkyl groups to produce different nanofibers and characterization of the sorbent materials.

Materials and Methods

Materials polyvinylbenzylchloride (PVBC), N,N-Dimethylformamide (DMF), Tetrahydrofuran (THF), ethylenediamine (EDA), were purchased from Sigma Aldrich (Johannesburg, South Africa) and used as obtained. All the chemicals were of analytical grade.

Electrospinning of polyvinylbenzylchloride (PVBC)

The different concentrations of PVBC from 20, 25, 30, 35, 40 and 45 wt% solutions were prepared in a 1:1 (v/v) ratio of DMF:THF solvent mixture. The mixtures were stirred at room temperature overnight until a homogeneous solution was formed. It was then transferred into a syringe. The syringe was connected to an electrospinning set-up consisting of a high voltage supply and an aluminum collecting plate. The flow rate of the polymer solution was controlled using a programmable syringe pump. The solution was electrospun at a positive voltage of 15 kV, the tip-to-collector distance was 15 cm and the flow rate was 0.2 mL/h and all these conditions gave a nanofiber. All procedures were carried out at room temperature.

Post functionalization of polyvinylbenzylchloride (PVBC) nanofibers

2.15 g of PVBC nanofiber presented in Figure 1.4 (E) was cut out in circular portions of (1.5 cm) of the nanofiber sheet soaked in 8.0 g of ethylenediamine (EDA) in 15 mL of ethanol and shaken on a mechanical shaker for five days (Figure 1.0) and the reaction in the vessel was allowed to proceed at 80-100°C for 36 hrs for the amination reaction. After the reaction, the modified fibers were removed from the solution and the fibers washed with methanol, Soxhlet extracted with methanol, and then air dried.

Quatenization of polyvinylbenzylchloride (PVBC)

2.0 g each of the post functionalized polyvinylbenzylchloride were prepared in different 100 mL reaction vessel. A 50 mL of ethylenediamine was introduced into the 100 mL vessel containing 7.0 g of methyl iodide in 4.0 g of lutidine and ethanol was added into 100 mL reaction vessel with a stirrer and was shaken on a mechanical shaker at 50°C to 60°C for 24 hrs. The quaternized fibre was filtered under vacuum and, washed extensively with water. The iodine was removed by washing the quaternized fibers with 100 mL of 0.1 M FeCl₃ in 6 M HCl, followed by using a hot 100 mL of 0.05 M Na₂S₂O₃ solution and finally 50 mL of conc. HCl was used to protonate the sites and the fiber was dried in a desiccator for 24 hrs (same procedure was used for ethyl and propyl).

FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectra of PVBC, functionalized PVBC and quaternized PVBC were obtained using a Perkin-Elmer Spectrum 100FT-IR spectrometer with an AutoIMAGE System.

Scanning electron microscopy (SEM)

To determine the surface morphology of the PVBC, EDA and quaternized of PVBC, ground particles of each polymer were taken and dusted onto a carbon sticker, then coated with gold using a sputter coater (Balzers Union, FL-9496) for 30 min. Images were recorded using INCApentaFET3 (VegaTescan) SEM fitted with an Oxford ISIS EDS.

Energy dispersive X-ray spectrometer (EDS)

The EDS is coupled to a Scanning Electron Microscope (SEM). The obvious advantage of EDS elemental analysis over conventional chemical analysis is that, elemental composition of selected phase can be analysed in a bulk sample. In order to get more structural information and understanding on the adsorption mechanism of the unfunctionalized and the functionalized PVBC, an energy dispersive x-ray spectrometer (EDS) was used to investigate the elemental composition of the fibers. The EDS detects X-rays from the sample when excited by the highly focused, high-energy, primary electron beam, penetrating into the sample.

X-ray diffraction analysis (XRD)

This technique is used to identify mineral phase of a sample and its particle size. Operating conditions of X-ray diffraction analysis

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. The BET theory [8] explains the physical adsorption of gas molecules on solid surfaces and provides the basis for measurement of the specific surface area of a material. The basic concept of the theory is an expansion of Langmuir theory, which deals with monolayer molecular adsorption and a multilayer adsorption built on the hypothesis that, gas molecules are adsorbed on solid layers and that, there is no interaction between each adsorption layer [9].

Results and Discussion
Characterization studies
FTIR studies of unfunctionalized and functionalized PVBC: The characteristic peaks in the spectrum (A) of the PVBC can be assigned as follows: 670 cm$^{-1}$ (C-Cl), 2976 cm$^{-1}$ corresponds to the CH (CH$_3$, C$_2$H$_5$, and C$_3$H$_7$), while 1451 cm$^{-1}$ spectrum represents the CH bending vibration of the same CH group in the alkyl groups. After the functionalization, the spectrum shows some significant changes. The (C-Cl) at 670 cm$^{-1}$ disappeared completely to form a new band at peaks 1562 cm$^{-1}$ which can be assigned to N-H group of the amine group, while the peaks at between 1610 and 799 cm$^{-1}$ are due to C=O and C=N stretching groups. The presence of band at 3336 cm$^{-1}$ is due to bonded OH groups, which indicates the presence of water of crystallization. According to the FTIR spectra, the location where the chemical reaction took place during the preparation of PVBC may be proposed in Figure 1.1.

Scanning electron microscopy (SEM)
Electrospinning is a technique that utilizes the electric force to drive polymer fluid and to produce polymer nanofibers. The shear viscosity, electric conductivity and surface tension of the polymer solution are the most important properties affecting the formation of nanofibers [10]. The increase in polymer concentration could adversely affect the cohesiveness of the liquid, thus leading to reduction in the surface tension of the polymer in solution.

The SEM images of the 20 and 25% (w/v) electrospun nanofibers for (PVBC) PVBC in N,N'-dimethyl formamide (DMF), Tetrahydrofuran (THF) solution are shown in Figures 1.2a and 1.2b, a droplet spray occurred and a continuous jet of polymer particles was formed at Figure 1.2a. The jet from low viscosity solutions breaks up into droplets due to the lower amount 20% w/v of polymer. At solution concentration of 25, 30, (w/v) PVBC in Figures 1.2b and 1.3c the presence of beads was observed, but the beads were completely disappeared and the formation of bead free fibers were observed when the concentration of the solution was increased to 40 and 45% w/v. It is believed that, the relatively high viscosity (30, 40, 45% w/v), of the concentration solution, voltage and distance made the morphology of the fiber to improve from bead to bead free fibers. The best optimum condition for the morphology was observed with 45% (w/v) solution, with diameter ranging from 650-680 nm and this was subjected for post functionalization using ethylenediamine (EDA).

![Figure 1.1](image1) FTIR absorption spectra for the unfunctionalized polyvinylbenzylchloride (A), functionalized PVBC (B) and the quaternized PVBC (R'=CH$_3$, C$_2$H$_5$ and C$_3$H$_7$) (C, D and E) nanofibres.

![Figure 1.2](image2) SEM images (scale bar=20 µm) showing the morphology of fibers electrospun from PVBC solutions at concentration of (a) (particles) 20% w/v (b) (beaded) 25% w/v. (voltage of 15 Kv and at a constant spinning distance of 15 cm).

![Figure 1.3](image3) SEM images (scale bar=20 µm) showing the morphology of fibers electrospun from PVBC solutions at concentration of (c) (beaded) 30% w/v (d) (bead free) 35% w/v. (voltage of 15 Kv and at a constant spinning distance of 15 cm).

Figure 1.5g the morphology of the 45% w/v electrospun PVBC nanofibers was functionalized with EDA. The SEM images was presented in Figure 1.5h with a slight difference with a change in morphology during functionalization and the fibers were not damaged. The fiber diameter range was 665-769 nm. This shows a slight increase in the fiber diameter after the functionalization with EDA.
After the functionalize PVBC in EDA, as shown in Figure 1.5h, the functionalized fibers were quaternized using, methyl, ethyl and propyl iodide, in lutidine and ethanol to give the SEM morphology in Figures 1.6I, 1.6J and 1.7K.

**Energy dispersive X-ray spectrometer (EDS) used for PVBC**

The EDS is coupled to a Scanning Electron Microscope (SEM). The obvious advantage of EDS elemental analysis over conventional chemical analysis is that, elemental composition of selected phase can be analysed in a bulk sample. In order to get more structural information and understanding on the adsorption mechanism of the unfunctionalized and the functionalized PVBC, an energy dispersive x-ray spectrometer (EDS) was used to investigate the elemental composition of the fibers as shown in Figures 1.8 and 1.9. The EDS detects X-rays from the sample when excited by the highly focused, high-energy, primary electron beam, penetrating into the sample. Comparing EDS images of unfunctionalized and functionalized PVBC, Figure 1.8 shows the presence of Chlorine on the PVBC, the removal of chlorine in Figure 1.9 confirms that the fibers were functionalized with the presence of Nitrogen as clearly observed in the EDS spectra and this was in corroboration with FT-IR results.
X-ray defraction analysis (XRD)

Figure 2.0a shows the spectrum of the PVBC with a broad peak at 2 theta in 2θ degree axis is assigned to carbon before post functionalization with EDA. The sharp peak on Figure 2 theata at 40 in 2θ degree axis is assigned to the N in the NH₃⁺ groups on the surface of the functionalized PVBC [11] verifying that, the enhanced nitrogen content on the fiber surface was from the amine groups Figure 2.0b.

BET surface area

The specific surface area of the sorbent defines its efficiency for adsorption. The surface area of unfunctionalized and the functionalized PVBC nanofiber materials were measured, using the BET method and the results are presented in Table 1.

It was observed that, the surface area of the sorbent materials (PVBC) changed after the functionalization with EDA. It can be concluded that the surface area of the sorbent materials was reduced as shown in Table 2.

Conclusion

In this study, the electrospinning of PVBC into a nanofibers were prepared, through the modification of fiber surface, using multi nitrogen containing aminating reagents for PVBC and quaternizes with R’ = CH₃, C₂H₅ and C₃H₇, characterized using different instruments such as Fourier transform infrared (FTIR), Scanning Electron Microscopy, Energy Dispersive X-ray Spectrometer (EDS), X-ray Defraction Analysis (XRD) and Brunauer, Emmett, Teller (BET) Analysis. The low cost sorbent material will be effective and serve as an alternative material for the removal of anions from aqueous solutions due to the functional groups present on the quaternized PVBC.

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References


