INVESTIGATION OF MORPHOLOGY AND CHARACTERIZATION OF ELECTROSPUN PVA/PANI/FE_3O_4 NANOFIBER COMPOSITE MATERIALS

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ABSTRACT. Polymers nanocomposites containing inorganic fillers like metal particles dispersed in thepolymer matrix are of great interest for the optical and dielectric application. Polymer/inorganic composites such as polyaniline/magnetite nanocomposites (PAni/Fe_3O_4) can be manipulated through various treatments in fabricating desire material such as nanofibers textile for many applications. The modified magnetite (Fe_3O_4) nanoparticles were successfully synthesized and incorporated into polyaniline at different weight ratio and blended with polyvinyl alcohol (PVA) to achieve a spinning solution, further PAni/Fe_3O_4 nanofiber composites solution were used for fabrication of nanofiber textile by an electrospinning method, and the composites nanofiber textile materials were investigated. The crystalline phase structure of PAni/PVA andPAni/Fe_3O_4 composites nanofibers textile was determined by XRD, shows the existence of peaks at 2θ = 24.13º and 35.63º for PAni and Fe_3O_4 nanoparticles respectively. The FTIR analysis indicated a slightdecrease in the intensity and broadening of the absorption bands at 3462 $cm^{-1}$and 3431 cm^{-1}, are due to vibration stretching –NH group. The disappearance of the peakfor PAni/Fe_3O_4 composites nanofibers textile sample containing 25 wt% of Fe_3O_4 nanoparticles clearly indicated the interaction of nanoparticles with nitrogen, hydrogen, carbon, and oxygen atoms in the PAni and PVA chain. FESEM analysis of the composites nanofibers textile shows clearly no accumulation of nanoparticles on the surface of polymeric composites nanofibers. This implies that the growth of nanoparticles on the surface of polymeric composites hassuccessfully been prevented.

KEYWORDS: PAni; PVA; PAni/PVA nanofiber; Electrospinning technique

1 INTRODUCTION

Electrospinning is a favourable method for producing continuous polymer nanofibers textile material with diameters ranging from micro to nano-scale. The textile generated by conventional methods such as spinning from melt or solution is in the range of 500 nm to 5 µm such are favourable for many applications such as microwave absorption, filtration, cell separation and wearable sensing applications where a high surface area is needed. During electrospinning, an external electric field is imposed on the polymer solution or melt, the composites solution, spinning parameters and conditions will greatly affect the textile formation. The diameters and morphology of the nanofibers will depend on parameters such as the polymer type, polymer chain conformation, viscosity and concentration of a solution, conductivity, polarity and surface tension of the solvent. Spinning conditions such as applied electric field strength, tip to collector distance and the follow rate also need to be optimized for efficient nanofiber formation; the detailed regarding electrospinning has been discussed in the current work.

Electrospinning of continuous nanofibers textile of conducting polymers (such as PAni composites) via aqueous solutions has previously been considered impossible due to the repulsive forces between the ionogenic groups as well as their ability to form specific intra- and intermolecular interactions. Recently, a nanofiber textile material was electrospun from ionogenic polymers by utilizing mixed solutions of ionogenic polymer and non-ionogenic polymer(Santibenchakul *et al*., 2015; Salimbeygi *et al*., 2015).Blending with non-ionogenic polymers improves the electrospinnability of PAni Composites, as well as the physical and mechanical properties of the PAni/Fe_3O_4 nanofiber textile composites. Suitable non-ionogenic partners for electrospinning of PAni/Fe_3O_4 nanocomposites include polylactide (PLA), poly (vinyl alcohol) (PVA), poly (vinyl pyrrolidone) (PVP), and poly (ethylene oxide) (PEO) (Salimbeygi *et al*., 2013).The different non-ionogenic polymers were blended with the

PAni derivatives followed by electrospinning into bi-component nanofibers, in order to determine physical properties which indicate surface modification of (PAni/Fe_3O_4 nanocomposites) bi-component combination. Polyvinyl alcohol (PVA) is a suitable platform for blending of PAni/Fe_3O_4 nanocomposites due to its high heat resistance, dimensional stability, thermoplasticity and low toxicity(Ramana *et al*., 2015). The reactive malefic anhydride groups enable polymer modification(Medeiros *et al*., 2010). The author of this research is aims to nanofiber with different level of Fe3O4 nanoparticles as well as different electrospinning parameters.

2 MATERIAL AND METHODS

The entire chemical were used without further purification, include iron chloride ($FeCl_3$) (Sigma Aldrich), ferrous chloride ($FeCl_2$) (Sigma Aldrich), ammonium hydroxide (NH_4OH) (Sigma Aldrich), N-phenyl-1,4-phenylenediamine (Sigma Aldrich), succinic anhydride (Sigma Aldrich), Diethyl ether, and dichloromethane CH_2Cl_2 (Sigma Aldrich). Aniline ($C_6H_5NH_2$ R & M chemicals) ammonium peroxidisulfate $(NH_4)_2S_2O_8$ (Sigma Aldrich), polyvinyl alcohol (Mw 89-90) (Sigma Aldrich),dimethyl sulfoxide (DMSO) (Sigma Aldrich), Sulphuric acid H_2SO_4 (Sigma Aldrich), phospghoric acid (H_3PO_4) and hydrochloric acid (HCl) (Sigma Aldrich 37%) were used in the production of Fe_3O_4, PAni/Fe_3O_4 nanocomposites and PVA/PAni/Fe_3O_4 composites nanofibers textile respectively.

3 PREPARATION OF ELECTROSPINNING SOLUTION

Some quantity of PVA was dissolved in deionized water under constant stirring process for a period of 4h at 80^0C to an obtained aqueous solution of PVA. In an effort to prepared spinning solution, some quantity of prepared PAni/Fe_3O_4 nanocomposites prepared (Saliza &Takai *et al.,* 2018; Mustafa *et al.,* 2018) was dispersed in 15 ml of dimethyl sulfoxide (DMSO) under magnetic stirrer for 1h at room temperature, to obtained homogeneous solution of PAni/Fe_3O_4 nanocomposites in DMSO. Then the solution of PAni/Fe_3O_4 nanocomposites was blended in the PVA solution to obtained PAni/Fe_3O_4 nanofiber textile composites solution.

4 ELECTROSPINNING TECHNIQUES

During electrospinning techniques, traditional electrospinning apparatus was used to fabricate PAni/Fe_3O_4 composites nanofibers textile 5 ml solution of PAni/Fe_3O_4 composites nanofiber textile were loaded on the syringe and pumped using syringe pump through the tube into the needle of the electrospinning machine, which was connected to a high DC voltage power supply. The function of using the syringe pump is to make smooth flow of the polymer at constant and controllable manner. The grounded counter electrode was attached to the rotating collector. The distance from the end tip of the nozzle to the rotating collector is known as spinning distance. The electrospun nanofibers would be collected using a rotating collector, which was wrapped with an aluminium foil. The entire electrospun nanofiber mat obtained was dried under vacuum in order to remove residual solvent. Figure 1, shows the schematic diagram of the single nozzle electrospinning process.

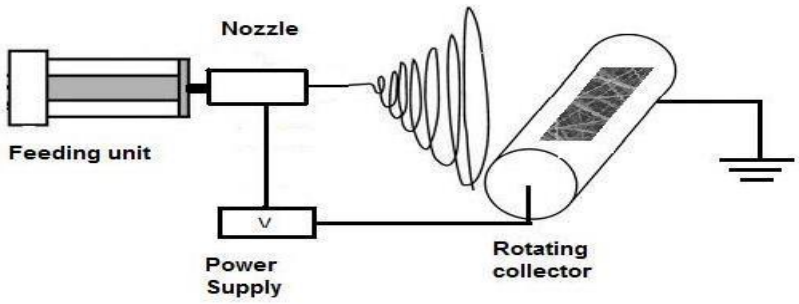


Figure 1: Schematic diagram of electrospinning techniques

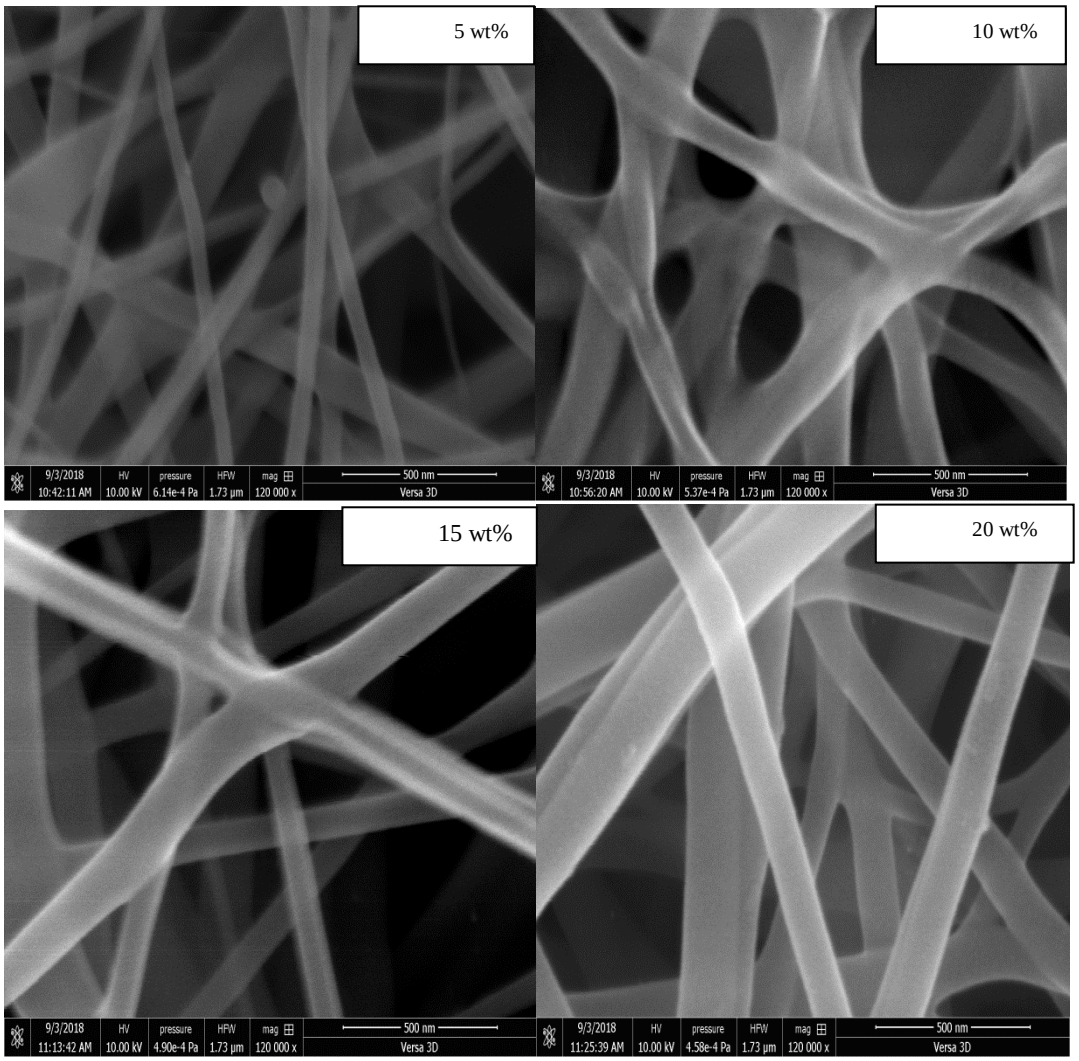
5 CHARACTERIZATION

The phase structure of the prepared PVA/PAni/Fe_3O_4 composites nanofibers textile were investigated by mean of XRD, Bruker D8 FOCUS) with Cu Kα, λ radiation wavelength. The morphologies and internal structure of PVA/PAni/Fe_3O_4 composites nanofibers textile were studied by Field Emission Scanning Electron Microscope (FESEM, XL-30). The chemical bonding PVA/PAni/Fe_3O_4 composites nanofibers textile material were study using FTIR.

6 SURFACE MORPHOLOGY ANALYSIS OF PVA/PANI/FE_3O_4 NANOFIBERS TEXTILE COMPOSITES

FESEM analysis of PAni/Fe_3O_4 composites nanofibers textile spinning with 5 ml electrospinning solution, 12kV applied volt and 8 cm tip to collector distance was performed so as to identify the distribution of Fe_3O_4 contained within the polymeric nanofibrous composites. Figure 2 showed the morphologies of PVAPAni/Fe_3O_4 composites nanofibers textile materials with a different level of Fe_3O_4 nanoparticles.

The results clearly state that Fe_3O_4nanoparticleshave been distributed uniformly in the polymeric nanofibers textile composites (Shen *et al*., 2012). Interestingly, Fe_3O_4nanoparticles didn`t accumulate on the surface of polymeric composites nanofibers, this implies that the growth of nanoparticles on the surface of the composites has successfully been prevented.



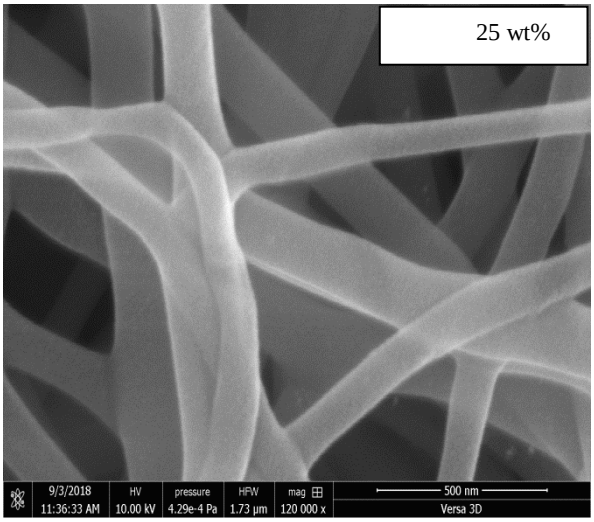


Figure 2: FESEM image of PAni/Fe_3O_4 composites nanofibers textile with different content of Fe_3O_4 nanoparticles spinning with 5 ml (12 kV, 0.15 m/h and 8 cm)

7 STRUCTURAL ANALYSIS OF PVA/PANI/FE_3O_4COMPOSITES NANOFIBERSTEXTILE

The XRD pattern of the PVA/PAni/Fe_3O_4 composites nanofibers textile at the different quantity of Fe_3O_4 nanoparticles (5, 10, 15, 20, 25 wt %) reveals its amorphous nature as shown in Figure 3. This can be attributed to the presence of a higher amount of PAni and PVA in the composites, the result obtained in this research are in agreement with what was obtained by other groups (Chiscan *et al*., 2011; Yu *et al*., 2004).

Besides, all PAni/Fe_3O_4 composites nanofibers textile show the existence of PVA peaks at 2θ = 23.2^o and the presence of Fe_3O_4 also determined by the characteristic peaks at 2θ = 32.94^o, 35.63^o, 43.33^o, 57.39^o, 58.15^o, 62.23^o, 63.93^o and71.9^o (Sarmah & Kumar, 2013;Shalini *et al,* 2003 ; Sun *et al.,* 2004;Yang *et al*., 2015). Hence, it can be suggested that addition of the magnetic materials (Fe_3O_4 nanoparticles) do not affect the chemical structure of PAni/Fe_3O_4 composites nanofibers textile because of all PAni/Fe_3O_4 composites nanofibers textile material show almost identical peaks for FTIR, and XRD spectra.

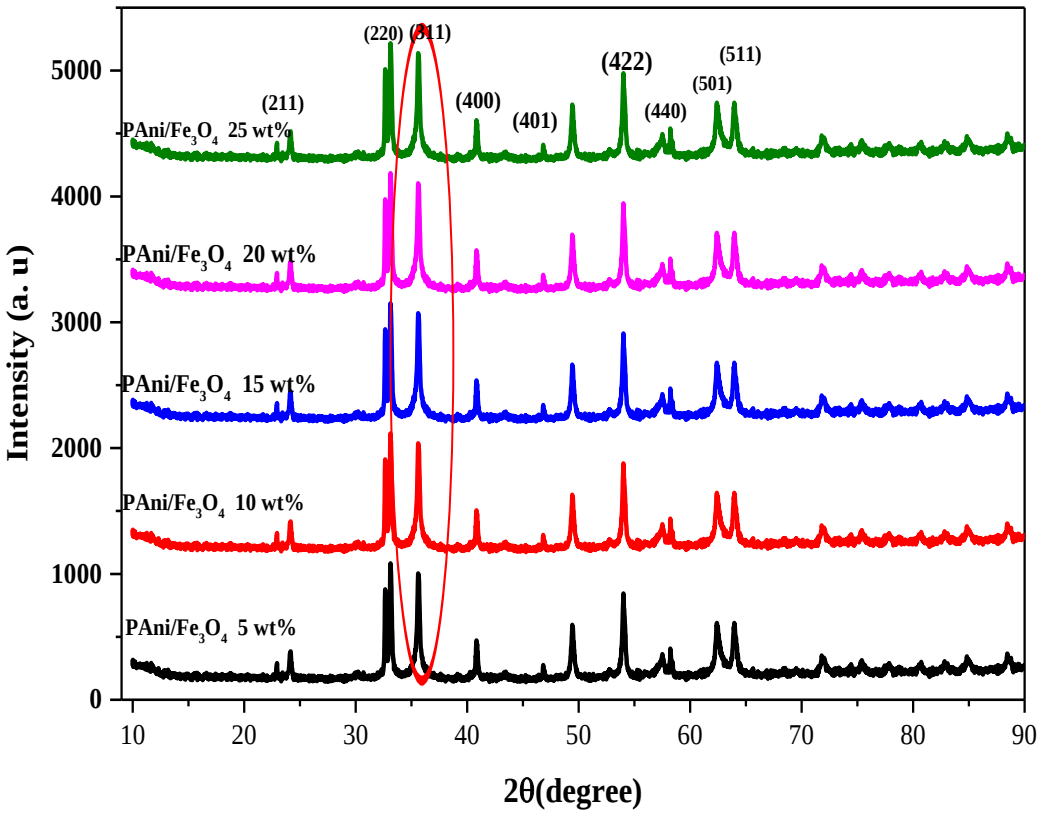


Figure 3: XRD plot of 5 ml solution of PAni/Fe_3O_4 composites nanofibers textile prepared at 0.15 ml/h, 8 cm tips to collector distance with different content Fe_3O_4 nanoparticles

8 CHEMICAL BONDING ANALYSIS FOR PVA/PANI/FE_3O_4 NANOFIBERS TEXTILE COMPOSITES

In order to further understand the chemical bonding analysis of the PVA/PAni/Fe_3O_4 composites nanofibers textile, the FTIR spectral analysis was performed to determine the molecular structure of the composites nanofibers textile electrospun with 5 ml 12kV, 8cm and 0.15 ml/h shown in Figure 4. However, the IR spectra of PAni/Fe_3O_4 composites nanofibers textile indicating higher possibility of interaction between these polymers and metals nanoparticles, the composites nanofibers textile reveal through the FTIR analysis indicate slight decrease in the intensity and broadening of the absorption bands at 3462 cm^{-1}, 3431 cm^{-1}, 3372 cm^{-1} and 3275 cm^{-1} are due to vibration stretching –NH group, sudden disappearance of peak in the PAni/Fe_3O_4 composites nanofibers textile sample containing 25 wt% of Fe_3O_4 nanoparticles clearly indicate the interaction of nanoparticles with N, H, C, and O atoms in the PAni and PVA chain (Medeiros *et al*., 2008; Lim & Choi, 2017).

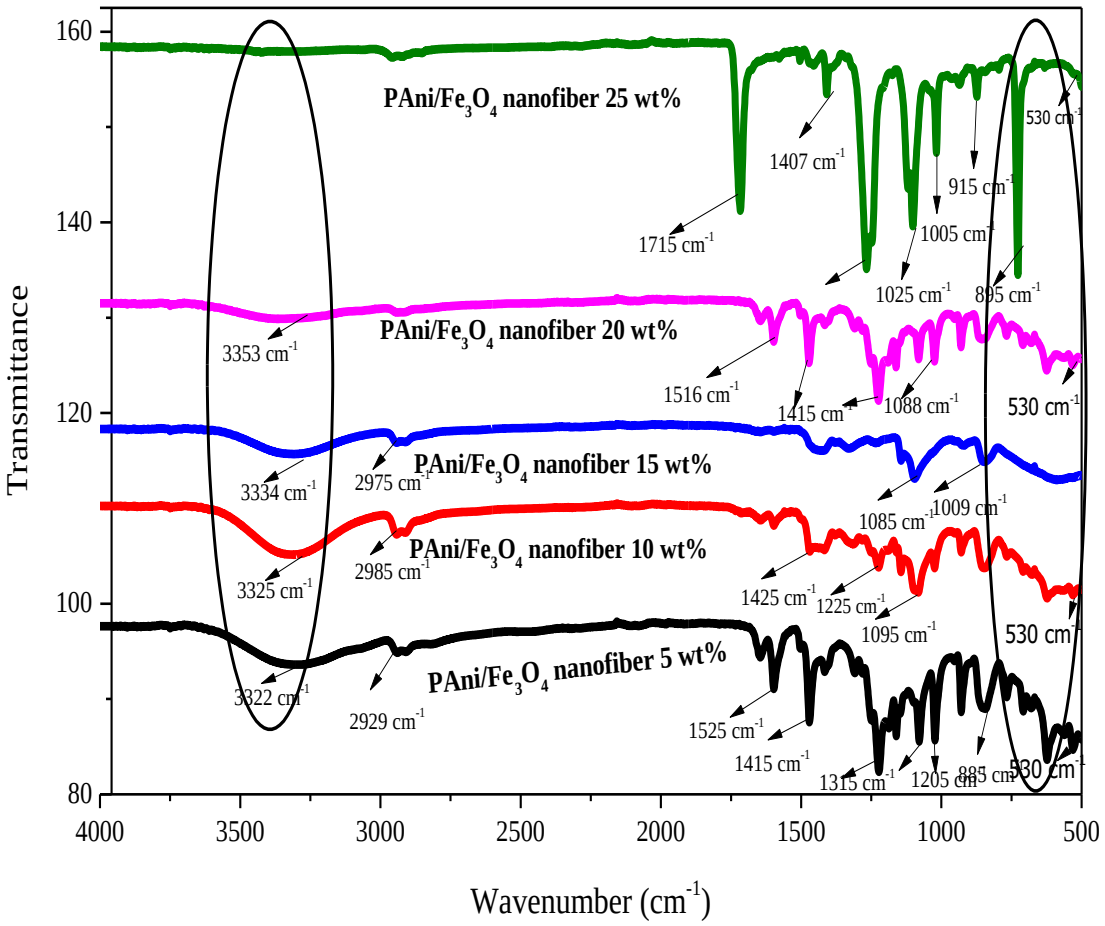


Figure 4: FTIR spectra of PAni/Fe_3O_4 composites nanofibers textile spinning at 12 kV, 0.15 ml/h and 5 ml

However, the FTIR spectra of the synthesized Fe_3O_4 nanoparticles before incorporating into the PAni and PVA was described by .Showed a band at 3350 and 3409 cm^{-1} which are assigned to the O-H stretching vibration of water molecules, this provides an interface for bonds interaction between –NH in the PAni and OH^- in the PVA (Wang *et al*., 2016).

Further, decrease in the intensity and broadening of bonds at 1672 cm^{-1}, 1634 cm^{-1}, 1521 cm^{-1} suggest the decoupling between C-H and O-H bonds, due to bond formation of Fe_3O_4 nanoparticles with O and H atoms and disappearance of bonds in the PAni/Fe_3O_4 composites nanofibers textile sample containing 15 and 20 wt% of Fe_3O_4 nanoparticles observed at 1483 cm^{-1} also indicates the chemical conjugation of Fe_3O_4 nanoparticles with molecules of PAni and PVA chains (Shiwei*et al*., 2018). The change in the intensity of the bonds occurs at 1490 cm^{-1}, 1447 cm^{-1}, 1062 cm^{-1}, 1031 cm^{-1}, 893 cm^{-1}, 784 cm^{-1} and 693 cm^{-1} are also suggest the interaction between the host PAni matrix incorporate Fe_3O_4 nanoparticles, some peaks were also observed at lowest wavenumber 510 cm^{-1}, 593 cm^{-1} indicated the presence of Fe_3O_4 nanoparticles are present in PAni/Fe_3O_4 composites nanofibers textile (Sun *et al*., 2014).

9 CONCLUSION

The morphology of the PVA nanofibers posses the homogenous and smooth surface with larger diameter, but addition of PVA into PAni, slightly decrease the nanofiber diameter, incorporating PAni to PVA, the net charge density of the solution might have increased favouring the formation of nanofibers with smaller diameter, has been observed using image-j analysis, the diameter decrease with increase in PAni solution. Higher net charge density results in higher stretching of the nanofibers, thus reduce the diameter of PAni/PVA composites nanofibers textile. The X-ray diffraction patterns for PVA/PAni/PVA composites nanofibers textile show amorphous behaviour which represents the characteristic of doped of PAni in the matrix. For XRD analysis of PAni/Fe_3O_4composites nanofibers

textile shows the existence of PVA, PAni and Fe_3O_4 nanoparticles at 2θ = 23.2°, 24.13° and 35.63° in the prepared PAni/Fe_3O_4 composites nanofibers textile. The structural transformation of PVA, PAni/PVA and PAni/Fe_3O_4 composites nanofibers textile spinning at different parameters such as flow rate, applied voltage and tip to collector distance was investigated using FTIR.

The FTIR analysis was performed to determine the molecular structure of PAni/Fe_3O_4composites nanofiber textile spun with 5 ml 12 kV, 8 cm and 0.15 ml/h. It was observed that in the FTIR spectra of PAni/Fe_3O_4composites nanofibers textile there is higher interaction between these polymers and metals nanoparticles. The nanofibers textile composites reveal through the FTIR analysis slight decrease in the intensity and broadening of the absorption bands at 3462 cm^{-1}, 3431 cm^{-1}, 3372 cm^{-1} and 3275 cm^{-1} are due to vibration stretching –NH group, sudden disappearance of peak in the PAni/Fe_3O_4 composites nanofibers textile sample containing 25 wt% of Fe_3O_4 nanoparticles clearly indicate the interaction of nanoparticles with N, H, C, and O atoms in the PAni and PVA chain.

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