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Fabrication and characterization of graphene oxide nanoparticles incorporated in poly (vinyl alcohol) electro-spun nanofibers and its vapor-phase crosslinking

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Abstract: Electrospun nanofibrous membranes have gained great focused in medical research due to its simplicity, diversity and biodegradability. The challenge to researchers is to make more effective and sustainable by incorporating pristine materials to address adverse health issues of society. In this work, considering the unique characteristics of Graphene and its derivatives, well-dispersed Graphene Oxide (GO) were prepared using Modified Hummer's method. Further, the mixture of solutions, Poly (Vinyl Alcohol) PVA with synthesized GO nano-particles, was successively fabricated into nanofibrous membranes by electrospinning technique. Further, the electrospun membranes were cross-linked through vapours of Glutaraldehyde (GA) in controlled environment to make membranes hydrophobic in nature. In addition, the characterization of synthesized GO and electrospun nanofibers were done using SEM, XRD and FTIR. The results show that GO incorporation decreases the average diameter of nanofibers from 422±133nm to 274.1±93.23nm, whereas crosslinking of nanofibers at various hours (12 to 48h) tends to increase the average diameter from 368.4±130.1nm to 671.41±293nm. In addition to that the 12h crosslinked nanofibers membrane shows better antibacterial activity than without crosslinked PVA/GO membrane against E.Coli after 24h of incubation. This primarily work provides a basis for further studies of this novel nanofibrous material.

Keywords: Graphene oxide, polymer nanofibers and crosslinking.

INTRODUCTION

Nanotechnology, the study of materials having at least one dimension in range of 1-100nm, at that scale materials exhibit a very high surface area to volume ratio, resulting improved physical and chemical properties of materials as compared to other bulk compounds (Tripathi *et al.,* 2018). The incorporation of nanomaterials in polymer solutions have become area of focus by of materials scientists due to in a result get the great improvement in yields and overall properties of material (Ghobadi *et al.,* 2015). The nanofillers may involve zero dimension nanoparticles (Chen *et al.,* 2010), one dimension nanotubes (Sui *et al.,* 2009) and two dimension layered materials (Quan *et al.,* 2009). Graphene and its derivatives have very constructive effect due to its superior mechanical, electrical and thermal characteristics along with extremely high specific surface area which makes it as best candidate as nanofillers resulting its applications in many areas such as micro and nano-electronics devices (Kim *et al.,* 2015), electrochemical sensors (Wang *et al.,* 2014), anti-corrosion coatings (Kyhl *et al.,* 2015) and flame-retardant high-performance nanocomposites (Yu *et al.,* 2015). Recent advances in materials science have allowed the use of Graphene in fields of biological and medical sciences.

The major requirements for nanocomposites are the homogenous distribution and interface integrity of nanofillers. Well dispersed Graphene and its derivatives, in polymer matrix, produce highly oriented microstructure; that enhance the nanocomposites properties. Polymer-based composites are usually made through extrusion techniques or by melt compounding but through these methods Graphene cannot be well disperse in polymer network(Steurer *et al.,* 2009), probably due to unsuitability with polymer matrix and large surface area of nanofillers' (Graphene and its derivatives)(Kim *et al.,* 2011). Further, The extremely thin sheets of Graphene made it hard for molten polymer to cover it through both sides, along with that the air bubbles removal get trapped in its sheets during compounding (Wang *et al.,* 2013).

Recently, Polymer Nanofibers, are of great interest due to its large number of applications employing different polymer-based composites.(Calamak *et al.,* 2017) Electrospinning is most common, simple technique for production of nanofibers of desired diameter using various nanofillers (Ceretti *et al.,* 2017). Moreover, the practice of high electric field during spinning improves the polymer matrix and its interaction with nanofiller, thus the coupling of filler/matrix is improved at interface in molecular state (Park, 2011).

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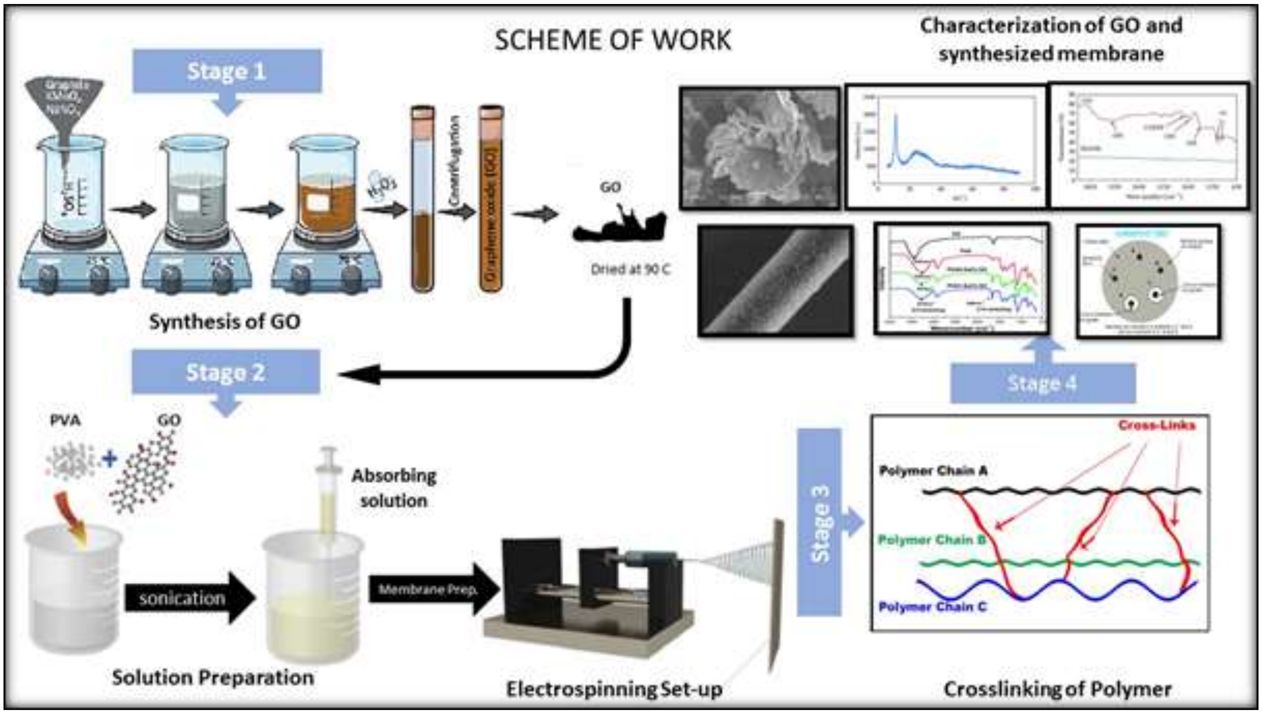

Fig. 1: Scheme of work 1) GO Synthesis 2) Solution Preparation 3) Vapor Phase crosslinking 4) Characterization

The most reliable bio-degradable precursors for the preparation of bio-compatible materials is Poly (vinyl alcohol) (PVA)(Sawada *et al.*, 2012). It shows great performance in various applications like enzyme immobilizing and transparent electrode membranes (Ramalingam *et al.*, 2014). Further, the incorporation of Graphene and its derivatives, having higher reinforcement abilities, in PVA's structure will yield polymer nanofibrous membrane with significant properties (Scaffaro *et al.*, 2017).

Table 1: Parameters for XRD Analysis

S. no	Parameters	Value
1.	Radiation	Cu Kα
2.	Voltage	40Kv
3.	2θ	5 to 55
4.	Scanning Speed	1^o/min

PVA can be fabricated into electrospun nanofibers using its solution(Alwan *et al.*, 2016). However, the resulting membrane gets dissolved instantly when immersed in water making it limited for only wet applications. This nanofibrous membrane can be made water insoluble by cross-linking (Ahmad *et al.*, 2012). The methods adopted for crosslinking of PVA are heat, radiation or chemical agents (Bolto *et al.*, 2009). Glutaraldehyde (GA) is considered as most effective agent used for cross-linking purpose (Destaye *et al.*, 2013a). In present work we have proposed the PVA/GO fibrous nanocomposite produced using electrospinning process (Fig. 1). Initially, the Graphene Oxide were synthesized using Modified Hummers' method, followed by the preparation of solutions of polymer (PVA) with 1 wt % concentrations of GO which were electro-spun, resulting membrane which were crosslinked using vapours of Glutaraldehyde. The comprehensive study of interior morphology of nanofibrous composite and synthesized graphene oxide were studied using Scanning Electron Microscope (SEM), ,XRD and FTIR. The anti-bacterial property of membranes was also studied against E. coli.

MATERIALS AND METHODS

Materials

Graphite Flakes (Merck-Schuchardt, Germany), Sodium Nitrate ($NaNO_{3,}$ (Merck-Schuchardt, Germany), PVA (average molecular weight 72,000 98% purity, Merck-schuchardt, Art. 821038), Potassium Permagnete ($KMnO_{4,}$Rankem), Hydrochloric Acid (HCL,37%, Rankem), H_2O_2 (Scharlas), H_2SO_4 (ACS)and Glutaraldehyde (GA, 25% aqueous solution, DAEJUNG) were used without any purification. DI-water were used for preparation of all aqueous solution.

Synthesis of Graphene Oxide

The Modified Hummer's method was adopted for synthesis of GO(Arthi G and Bd, 2015). Briefly, graphite flakes (1.5g), $NaNO_3$ (1.5g) and H_2SO_4 (69 mL) were mixed and stirred in an ice-water bath. Next, 9g $KMnO_4$ was added slowly. The mixture was stirred for an hour at room temperature followed by the addition of (100mL) DI water stirred for 30 min at 90^oC. Further, the 300 mL of water, with 30% H_2O_2 (10mL) was added. Finally, the resultant solution was washed with water and filtered for several times until the pH become 7, dried the filtrate at 98^o C on water-bath produced the GO powder.

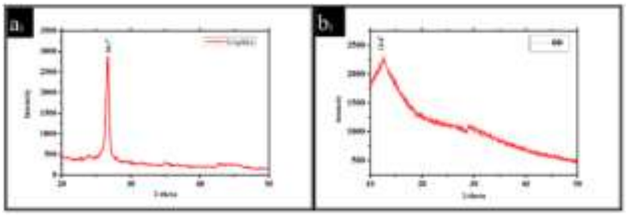

Fig. 2: XRD Spectra of a) Pure Graphite b) Graphene Oxide

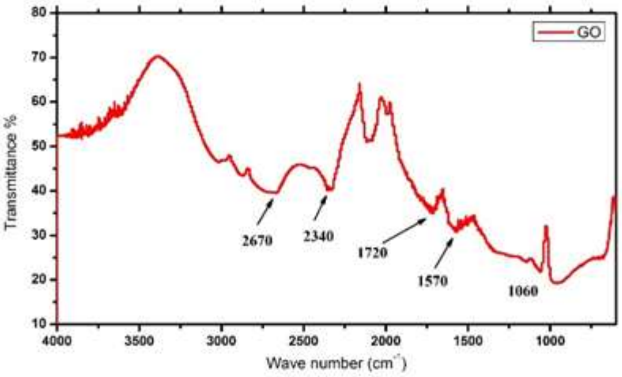

Fig. 3: FT-IR of Graphene Oxide

Suspension Preparation

The three different electro-spinning suspensions were prepared. The dried GO was dispersed in DI with 1 wt % under sonication and Preparation of 10 wt % PVA aqueous solution through stirring at 90^o C. Later, both prepared solutions were mixed to form stable GO/PVA suspension with ratio 4:1.

Electrospinning

The prepared suspension was converted in to nanofibers membrane using lab scale electrospun setup with fixed parameters to carry out Electrospinning process. The Tip-collector distance were kept 15cm, potential difference (DC voltage) of 18kV, with the flow rate of 1 mL/h. The electro-spun mats were collected on aluminium foil and then peeled off for further characterization.

Vapor-phase cross-linking of as-spun Membranes

The hydrophilic nature of PVA and its electrospun nanofibers make it difficult to use them in many applications; to make them of Hydrophobic nature, cross-linking of electrospun mat was carried out in sealed desiccator using GA vapours. Using 2M GA concentration, 50mL GA/HCl solution (140:1) was prepared and placed in sealed desiccator. The as-spun nanofibrous membrane were hanged in vapours of prepared solution of GA:HCl for various hours (12h, 24h and 48h).

Characterization Techniques

Surface Morphology

The surface morphology of GO as well as PVA/GO nanofibrous membranes was studied using SEM (Model: JEOL: JSM-6380L) at voltage of 10 to 15kV, under high vacuum. The morphological characteristics of synthesised of GO and its incorporation in electro-spun nanofibrous were observed at various magnification.

XRD Analysis

The XRD analysis of Graphene oxide was carried out using XRD (Model: Bruker-X8) at operating conditions shown in table below:

Fourier transform infrared Spectroscopy (FTIR)

FT-IR spectra of the synthesized GO and electro-spun PVA/GO nanofibrous crosslinked membranes were recorded using a Thermal Scientific Nicolet IR 200 spectrometer equipped with an attenuated total reflectance mode. The samples were scanned in the range of 4000–400 cm^{-1} with the resolution of 4cm^{-1} and 64 repeated scans.

Anti-microbial Study of membranes

The antimicrobial study of GO loaded nanofibrous membrane and 12h crosslinked of PVA/GO membrane was observed against *Escherichia coli* on Luria−Bertani (LB) agar nutrient medium. All materials were sterilized by UV-light before performing test. The antimicrobial activity was observed around the nanofibrous mat having diameter size of 12mm on the surface of already inoculated bacterial culture plate after 24 hours of incubation at 37^{o}C.

RESULTS

Characterization of Graphene Oxide

XRD Analysis

The XRD spectra obtain for Graphite and as synthesized GO shown in Fig. 2. In fig.2 (a) the peak of pure graphite $2\theta= 26.7^o$, can be observed and the disappearance of graphite peak in fig. (b) and sharp peak at $2\theta= 12.1^o$ confirms the complete oxidation of graphite.

FT-IR Analysis

The FTIR spectrum of GO is shown in Fig. 3, the presence of two peaks observed, at 1570 cm^{-1} and 1060 cm^{-1} are the attribute of stretching vibration of C=C and C=O that represent the carboxylic acid and carbonyl groups presence on the edges of graphene oxide. The peak at 1720 cm^{-1} corresponding to the stretching and bending vibration of OH groups of water molecules adsorbed on graphene oxide. However, the absorption peaks of 2340 cm^{-1} to 2670 cm $^{-1}$ are representing the symmetric and anti-symmetric stretching vibrations of C-H_2.

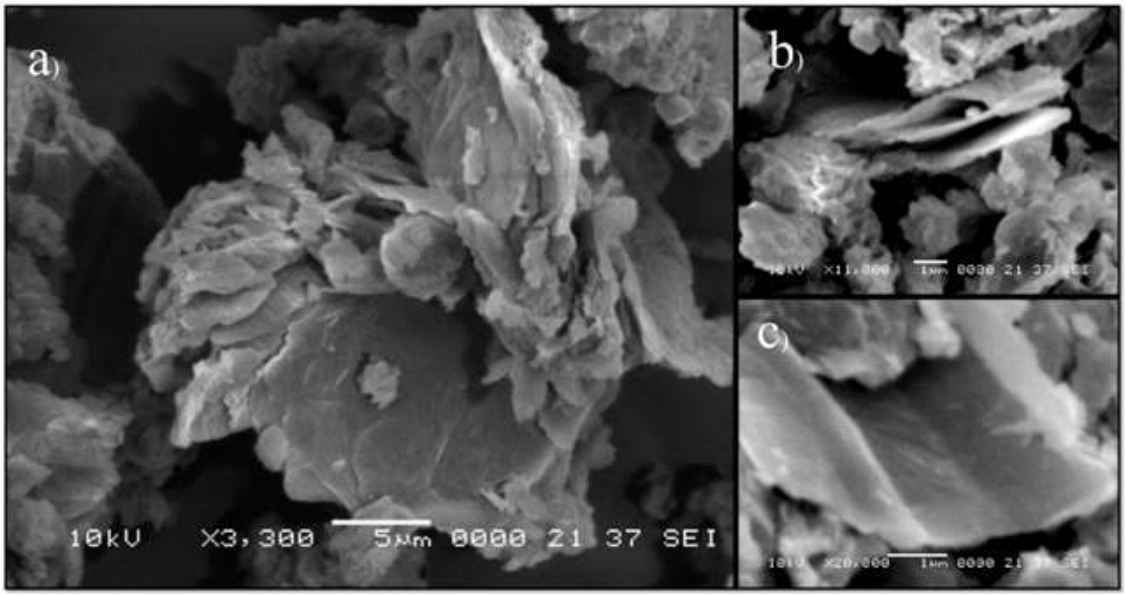

Fig. 4: a), b) and c) SEM of Graphene Oxide at different scales

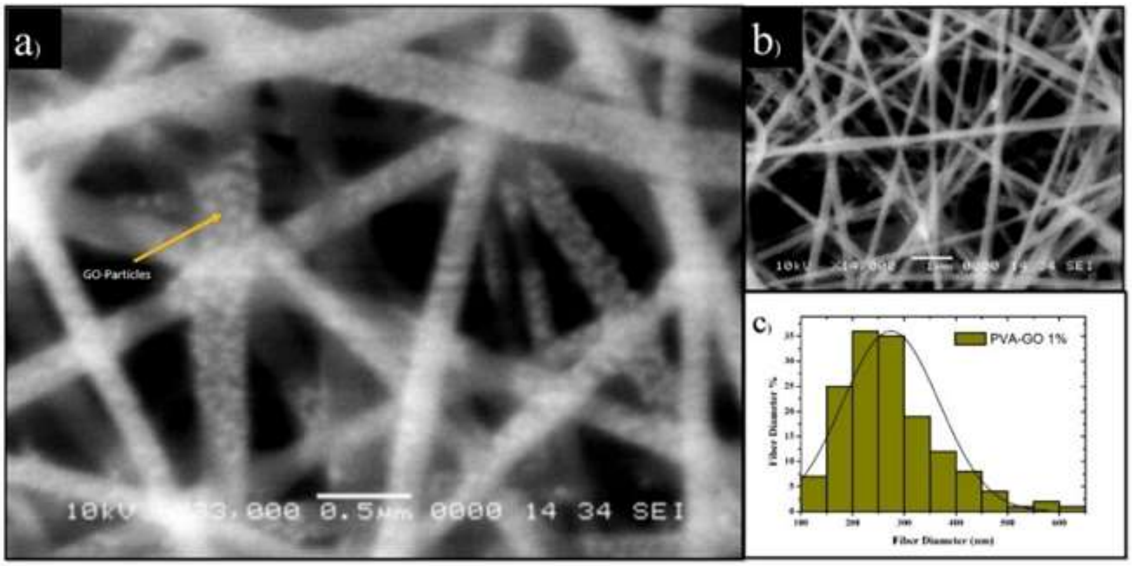

Fig. 5: a), b) SEM analysis of PVA electrospun nanofibers 1-% wt GO and c) Diameter study of Nanofibers

SEM Analysis (Surface Morphology)

The surface morphology of as synthesized GO was studied at different magnification as shown in fig. 4. It could be observed that GO has layered structure, with ultrathin homogeneous films. These films are continuously folded, and the edges of individual sheets are distinguished in the image. Exfoliation of sheets could also be observed from images.

Characterization of Electrospun Nanofibers Membrane

SEM Analysis

The fig. 5 shows the surface morphology of electrospun PVA nanofibers that confirms the incorporation of GO particles in nanofibers. The filler content can be observed from fig. 5 a) and the fibre morphologies are almost identical with pristine polymer samples, as shown in Fig. 5b). The improved surfaces morphological conditions can be obtained by well-dispersing GO within PVA solution media or by employing the organic solvent. Few other factors that affect the morphology and diameter of nanofibers are the filler quantity and the fluctuations of parameters during electrospinning process.

STATISTICAL ANALYSIS

Statistical Analysis of fibres were carried out using MS EXCEL to calculate average diameters and standard deviations. Diameter was calculated from SEM images using ImageJ software. Here Fig. 5c) represents the average diameter of nanofiber is 274.16±93.23nm.

FT-IR Analysis Electrospun Nanofibers membranes

The FTIR spectra of spun membranes is shown in a) and b) spectra of fig. 6. The peaks between 900-1150 cm^{-1} mentioned to be determining peak for C-O or -OH group. (see in Region I, II, III and IV in Fig. 6) shows prominent peaks of both membranes. Peaks of GO NPs could be matched from GO FT-IR as studied through Fig. 3.

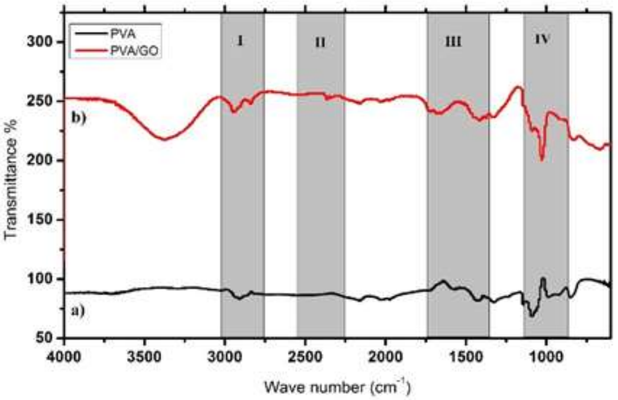

Fig. 6: FT-IR spectra of a) As-spun membrane of PVA b) as-spun membrane of PVA loaded with 1 wt % GO NPs

Characterization of Vapor Phase Cross-linked membranes using GA.

The as-electrospun nanofibrous membranes cross-linked through Vapours of GA at 12h, 24h and 48h has following characteristics:

SEM Analysis

The Fig. 7 a) and b) show the crosslinking and incorporation of GO nanoparticles in as spun nanofibers.

The variation in morphology of crosslinked PVA nanofibrous membrane by exposure GA (2M conc.) vapours of at 12h, 24h and 48h can be observed from fFig. 8 (b, c and d) respectively and Fig. 8 (f, g and h) representing the significant change in diameter of nanofibers at mentioned hours.

FTIR Analysis

As shown in Fig. 9, the crosslinking of PVA nanofibrous membranes were also confirmed using FTIR, The three major bands observed in FTIR spectra that have changed upon crosslinking by exposure to GA (2M conc.) vapor. The first large band shows the stretching of hydroxyl (-OH) group resulting from intramolecular hydrogen bonds (region I in Fig. 9) between 3000-3650 cm^{-1}. The C=O stretching observed at between 1500-1750 cm^{-1} shows the unreacted end of aldehyde group and due to presence of GO NPs in nanofibrous membranes (region II of Fig. 9). The gradual board peak at 1000-1150 cm^{-1}, resulted due to increase in crosslinking time associated with O-C-O vibration of acetal group (region III of fig 9).

Antimicrobial study

The antibacterial activity of fabricated mat tested against E.coli, gram negative bacteria where PVA/GO crosslinked membrane have shown higher resistance as compared to without cross linked PVA/GO sample as shown in Fig. 10 after 24 hours of incubation. It was observed that PVA/GO crosslinked membrane have shown higher resistance (14mm) as compared to without cross linked PVA/GO sample (12mm) as shown in Fig. 10 after 24 hours of incubation.

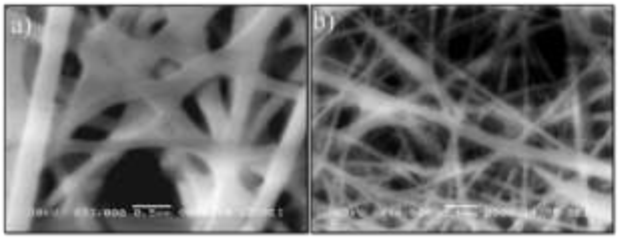

Fig. 7: SEM of a) and b) SEM micrograph of Vapour phase crosslinked PVA nanofibrous membrane incorporated with GO

DISCUSSION

Nanomaterial offers a very unique physic-chemicals properties that makes it most promising for verities of

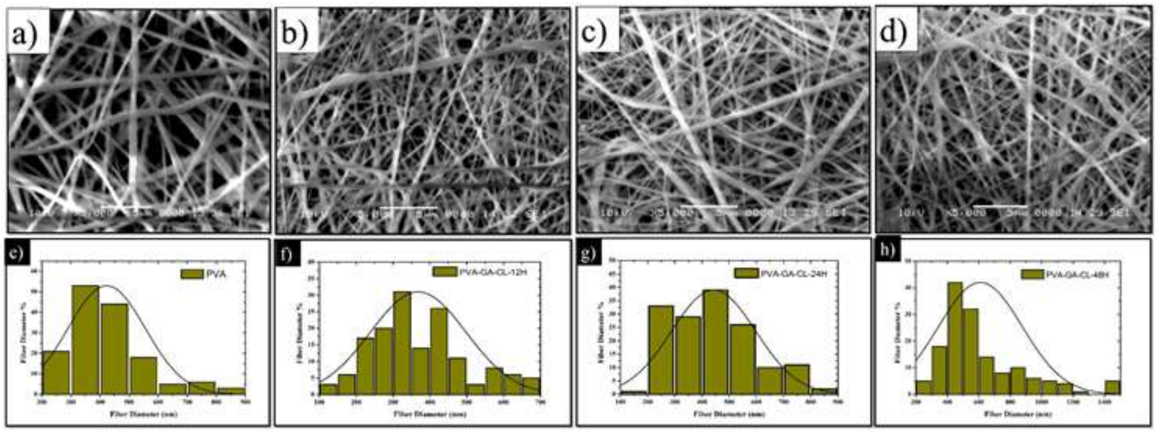

Fig. 8: Surface Morphology and Diameter study of PVA (a, e), 12h CL (b, f), 24h CL (c, e) and 48h CL (d, h)

applications (Tripathi *et al.*, 2018, Ghobadi *et al.*, 2015). Recently, Graphene and its derivatives based polymeric nanofibers, are of great interest due to its large number of applications employing different polymer-based composites in fields of biological and medical sciences (Calamak *et al.,* 2017). Electrospinning is very simple and easy technique used for synthesis of nanofibers of desired diameter (Ceretti *et al.*, 2017). PVA is most reliable bio-degradable precursors for the preparation of bio-compatible materials (Sawada *et al.,* 2012). PVA can be fabricated into electrospun nanofibers using its solution (Alwan *et al.*, 2016). However, the resulting membrane gets readily dissolved when immersed in water making it limited for only wet applications. This nanofibrous membrane can be made water insoluble by cross-linking (Ahmad *et al.,* 2012). In present work we have fabricated the PVA/GO fibrous nanocomposite using electrospinning process. Where initially, the Graphene Oxide were synthesized using Modified Hummers' method, followed by the preparation of solutions of polymer (PVA) with 1 wt % concentrations of GO which were electro-spun, further membrane were cross linked using vapours of glutaraldehyde.

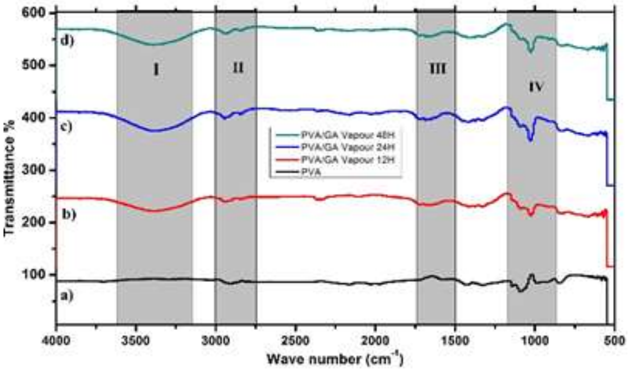

Fig. 9: FTIR a) PVA bare b) PVA-GA 48h, c) PVA-GA 24h d) PVA-GA 12h

The XRD spectra shows the peak of pure graphite at 2θ= 26.7° and sharp peak at 2θ= 12.1° confirms the complete oxidation of graphite after chemical oxidation and exfoliation, Similar peak were previously reported by (Wang *et al.*, 2008) and (Monteagudo *et al.*, 2019) that confirming the oxidation of graphite**.** In the FTIR spectra the presence of oxygen-containing groups confirms the synthesis of GO (Guo *et al.*, 2009). Hence, hydrophilic nature of GO is due to the formation of hydrogen bonds between graphite and water molecules. (Liu *et al.*, 2017) The SEM images show the GO has layered structure, with ultrathin folded film. The surface morphology of electrospun PVA nanofibers loaded with GO particles as shown in Fig. 5. By the addition of GO in PVA nanofibers, slight change in size were observed. It is previously reported that change in viscosity of solution effects on nanofibers diameter (Bhutto *et al.,* 2016). The brought little shuffles in peaks of pure polymer (PVA) membranes in FTIR analysis are also confirming the presence of GO nanoparticles in electrospun nanofibers membrane (fig. 6). The variation in morphology of crosslinked PVA nanofibrous membrane by exposure of GA (2M conc.) vapours of at 12h, 24h and 48h (Fig. 8) representing the significant change in diameter of nanofibers at mentioned hours. In the light of above results, it is noted that the exposure time has direct effect on the diameter of nanofibers. Previously many researcher have been used the GA solution for crosslinking of other nanomaterials (Jiang *et al.*, 2018) and PVA nanofibers (Fazel *et al.*, 2016) and achieved the same results .The crosslinking mechanism of GA based on the chemical bounding of aldehyde group of GA with hydroxyl group of PVA, that act as catalyst (Tang *et al.,* 2010). The formation of hydroxyl group which results from hydrogen bonds and decreasing intensity indicates the involvement of more -OH group in acetal bridge formation (Mansur *et al.*, 2008). Similar peaks pattern of PVA nanofibrous mate cross linked with GA as shown in results (fig. 9) were also reported by Destaye *et al.*, 2013 so our results are in good agreement with literature.

Fig. 10: Anti-microbial Study of nano-fibrous membranes a) PVA/GO membrane and b) PVA/GO-GA crosslinked membrane

In antimicrobial testing cross linked membrane shows significant antibacterial activity as compare to without cross linked PVA/GO nanofibrous membrane. This might be due to change in average diameter size because crosslink membrane possesses larger diameter as compared to without cross-linked membrane of PVA/GO. Similarly Bingan Lu, et al have reported the antibacterial activity of chitosan–PVA nanofibers containing graphene against E.coli (Lu *et al.*, 2012). However Destaye *et al.*, 2013b reported the antibacterial activity of PVA nanofibrous crossed linked with GA mat loaded with Ag nanoparticles against E.coli. Ag nanoparticles loaded PVA nanofibrous crossed linked with GA mat (13.77 mm in length) showed 19.3 mm clear zone of inhibition whereas no zone of inhibition was observed against without loaded sample of GA vaporous crossed linked PVA nanofibrous mat (control). In the light of above result it is suggested that our samples have shown significance antibacterial activity and this nanofibrous material could be used for further applications such as delivery of other antimicrobial agent, wound dressing, catalysis, air and water applications etc.

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CONCLUSION

We have succesfully fabricated and characterized the Poly (Vinyl Alcohol) Electro-spun nanofibers mate loaded with graphene oxide nanoparticles and further cross liked with vapours of GA. It was observed during electro spinning process under control parameters PVA nanofibers loaded with GO nanoparticles showed smooth morphology with continues fibres structure. It is further concluded that the vapour exposure time of GA has direct effect on the average diameter size of nanofibers, and it was observed that the exposure time of GA is directly proportional to the average diameter size of nanofibers. In addition, cross linked membrane shows significant antibacterial activity as compare to without cross linked PVA/GO nanofibrous membrane. The present work provides a basis for further studies of this novel nanofibrous material for further applications such as delivery of other antimicrobial agent, wound dressing, catalysis, air and water applications etc.

REFERENCES

Ahmad AL, Yusuf NM and Ooi BS (2012). Preparation and modification of poly (vinyl) alcohol membrane: Effect of crosslinking time towards its morphology. *Desalination,* **287**(1): 35-40.

Alwan TJ, Toma ZA, Kudhier MA and Ziadan KM (2016). Preparation and characterization of the PVA nanofibers produced by electrospinning. *Madridge J. Nano. Tec. Sci.,* **1**(1): 1-3.

Arthi G PB and Bd L (2015). A simple approach to stepwise synthesis of graphene oxide nanomaterial. *J. Nanomedicine Nanotechnol.,* **06**(1): 1-4.

Bhutto MA, Wu T, Sun B, EI-Hamshary H, Al-Deyab SS, Mo X (2016). Fabrication and characterization of vitamin B5 loaded poly (l -lactide-co-caprolactone)/silk fiber aligned electrospun nanofibers for schwann cell proliferation. *Colloids Surf. B Biointerfaces,* **144**: 108-117.

Bolto B, Tran T, Hoang M and Xie Z (2009). Crosslinked poly(vinyl alcohol) membranes. *Prog. Polym. Sci.,* **34**(9): 969-981.

Calamak S, Shahbazi R, Eroglu I, Gultekinoglu M and Ulubayram K (2017). An overview of nanofiber-based antibacterial drug design. *Expert Opin. Drug Discov.* **12**(4): 391-406.

Ceretti E, Ginestra PS, Ghazinejad M, Fiorentino A and Madou M (2017). Electrospinning and characterization of polymer-graphene powder scaffolds. *CIRP Ann.,* **66**(1): 233-236.

Chen X, Wei S, Gunesoglu C, Zhu J, Southworth CS, Sun L, Karki AB, Young DP and Guo Z (2010). Electrospun magnetic fibrillar polystyrene nanocomposites reinforced with nickel nanoparticles. *Macromol. Chem. Phys.,* **211**(16): 1775-1783.

Destaye AG, Lin CK and Lee CK (2013a). Glutaraldehyde vapor cross-linked nanofibrous PVA mat with in situ formed silver nanoparticles. *ACS Appl. Mater. Interfaces*, **5**(11): 4745-4752.

Destaye AG, Lin CK and Lee CK (2013b). Glutaraldehyde vapor cross-linked nanofibrous pva mat with in situ formed silver nanoparticles. *ACS Appl. Mater. Interfaces,* **5**(11): 4745-4752.

Fazel R, Torabi SF, Naseri-Nosar P, Ghasempur S, Ranaei-Siadat SO and Khajeh K (2016). Electrospun polyvinyl alcohol/bovine serum albumin biocomposite membranes for horseradish peroxidase immobilization. *Enzyme Microb. Technol.,* 93-94: 1-10.

Ghobadi S, Sadighikia S, Papila M, Cebeci FC and Gursel SA (2015). Graphene-reinforced poly (vinyl alcohol) electrospun fibers as building blocks for high performance nanocomposites. *RSC Adv.,* **5**(103): 85009-85018.

Guo HL, Wang XF, Qian QY, Wang FB and Xia XH (2009). A Green Approach to the Synthesis of Graphene Nanosheets. *ACS Nano.,* **3**(9): 2653-2659.

Jiang S, Ma BC, Huang W, Kaltbeitzel A, Kizisavas G, Crespy D, Zhang KAI and Landfester K (2018). Visible light active nanofibrous membrane for antibacterial wound dressing. *Nanoscale Horiz.,* **3**(4): 439-446.

Kim H, Kobayashi S, Abdur Rahim MA, Zhang MJ, Khusainova A, Hillmyer MA, Abdala AA and Macosko CW (2011). Graphene/polyethylene nanocomposites: Effect of polyethylene functionalization and blending methods. *Polymer,* **52**(8): 1837-1846.

Kim S, Zhao P, Aikawa S, Einarsson E, Chiashi S and Maruyama S (2015). Highly stable and tunable n-type graphene field-effect transistors with poly (vinyl alcohol) Films. *ACS Appl. Mater. Interfaces*, **7**(18): 9702-9708.

Kyhl L, Nielsen SF, Cabo AG, Cassidy A, Miwa JA and Hornekær L (2015). Graphene as an anti-corrosion coating layer. *Faraday Discuss*, **180**: 495-509.

Liu R, Gong T, Zhang K and Lee C (2017). Graphene oxide papers with high water adsorption capacity for air dehumidification. *Sci. Rep.*, **7**(1): 9761.

Lu B, Li T, Zhao H, Li X, Gao C, Zhang S and Xie E (2012). Graphene-based composite materials beneficial to wound healing. *Nanoscale*, **4**(9): 2978.

Mansur HS, Sadahira CM, Souza AN, Mansur AAP, (2008). FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde. *Mater. Sci. Eng. C.*, **28**(4): 539-548.

Monteagudo JM, Durán A, San Martín I, Carrillo P, 2019. Effect of sodium persulfate as electron acceptor on antipyrine degradation by solar TiO2 or TiO2/rGO photocatalysis. *Chem. Eng. J.*, **364**: 257-268.

Park JS (2011). Electrospinning and its applications. *Adv. Nat. Sci. Nanosci. Nanotechnol.*, **1**(4): 043002.

Quan H, Zhang B, Zhao Q, Yuen RKK and Li RKY (2009). Facile preparation and thermal degradation studies of graphite nanoplatelets (GNPs) filled thermoplastic polyurethane (TPU) nanocomposites. Compos. *Part Appl. Sci. Manuf.*, **40**(9): 1506-1513.

Ramalingam KJ, Dhineshbabu NR, Srither SR, Saravanakumar B, Yuvakkumar R and Rajendran V (2014). Electrical measurement of PVA/graphene nanofibers for transparent electrode applications. *Synth. Met.*, **191**: 113-119.

Sawada K, Sakai S and Taya M (2012). Enhanced productivity of electrospun polyvinyl alcohol nanofibrous mats using aqueous N,N-dimethylformamide solution and their application to lipase-immobilizing membrane-shaped catalysts. *J. Biosci. Bioeng.*, **114**(2): 204-208.

Scaffaro R, Maio A, Lopresti F and Botta L (2017). Nanocarbons in electrospun polymeric nanomats for tissue engineering: A Review. *Polymers*, **9**(2): 76.

Steurer P, Wissert R, Thomann R and Mülhaupt R (2009). Functionalized graphenes and thermoplastic nanocomposites based upon expanded graphite oxide. *Macromol. Rapid Commun.*, **30**(4-5): 316-327.

Sui XM, Giordani S, Prato M and Wagner HD (2009). Effect of carbon nanotube surface modification on dispersion and structural properties of electrospun fibers. *Appl. Phys. Lett.*, **95**(23): 233113.

Tang C, Saquing CD, Harding JR and Khan SA (2010). In situ cross-linking of electrospun poly (vinyl alcohol) nanofibers. *Macromolecules*, **43**(2): 630-637.

Tripathi RM, Pudake RN, Shrivastav BR, Shrivastav A, (2018). Antibacterial activity of poly (vinyl alcohol) biogenic silver nanocomposite film for food packaging material. *Adv. Nat. Sci. Nanosci. Nanotechnol.*, **9**(2): 025020.

Wang C, Li Y, Ding G, Xie X and Jiang M (2013). Preparation and characterization of graphene oxide/poly (vinyl alcohol) composite nanofibers via electrospinning. *J. Appl. Polym. Sci.*, **127**(4): 3026-3032.

Wang G, Yang J, Park J, Gou X, Wang B, Liu H, Yao J, (2008). Facile synthesis and characterization of graphene nanosheets. *J. Phys. Chem. C.*, **112(22)**: 8192-8195.

Wang J, Zhao X, Li J, Kuang X, Fan Y, Wei G, Su Z, (2014). Electrostatic assembly of peptide nanofiber-biomimetic silver nanowires onto graphene for electrochemical sensors. *ACS Macro Lett.*, **3**(6): 529-533.

Yu B, Shi, Y, Yuan B, Qiu S, Xing W, Hu W, Song L, Lo S and Hu Y (2015). Enhanced thermal and flame retardant properties of flame-retardant-wrapped graphene/epoxy resin nanocomposites. *J. Mater. Chem. A.*, **3**(15): 8034-8044.