

Effect of Solvent System on the Morphology of PLA Electrospun Nanofibres

Shirishkumar Vhanbatte¹, Swapnil Deshmukh²

Associate Professor, Department of Textiles, DKTES Textile and Engineering Institute, Ichalkaranji, India¹

PG Student, Department of Textiles, DKTES Textile and Engineering Institute, Ichalkaranji, India²

ABSTRACT: Electrospinning is simple, versatile and most efficient technique used for the synthesis of electrospun nanofibrous nonwoven webs. The electrospun nanofibres made out of biocompatible polymers are widely used in biomedical applications because of their bio-acceptability and morphology. The electrospun nanofibres are having a diameter in the nanoscale range with porous structure and high surface to volume ratio. Poly lactic acid (PLA) is a synthetic aliphatic polyester. The PLA is biodegradable and biocompatible polymer. The present research work gives an idea regarding the synthesis of PLA nanofibres by using the electrospinning technique. The effect of single and binary solvent system on the morphological behavior and diameter of the PLA electrospun nanofibres has studied. The spinning dope with 5 and 10% concentrated PLA in selected solvent systems were prepared to produce nanofibres. These were evaluated for fineness, diameter distribution and crystallinity developed.

KEYWORDS: Dope parameter, electrospinning, effect of solvents, nanofibres, polylactic acid.

I. INTRODUCTION

Electrospinning is considered to be a simple, versatile¹ and cost-effective technique for generating continuous aligned nonwoven nanofibrous web from various polymeric solutions^{2,3}. The various precursor solutions of natural and synthetic polymers and their blends have been electrospun into nanofibres structures with diameter ranging from the nanometer to micrometer scale⁴. The electrospun nanofibres exhibits several remarkable properties such as small diameter, nanoscale pores, large surface area, high aspect ratio, unique physiochemical properties and flexibility^{5,6,7}. Electrospinning is technique that uses electrostatic force to produce nanofibrous nonwoven webs^{8,9}. The setup of electrospinning process has recently been well discussed. The three basic components of the electrospinning setup are high voltage supply, syringe pump and grounded collector⁷. There are several factors, which has influence on the morphology and diameter including process parameters and ambient conditions. The selection of appropriate solvent or solvent system is essential¹⁰ to optimize the electrospinning process for the production of homogeneous nanofibrous webs¹¹. Nowadays, electrospun nanofibres loaded with different kinds of drugs are used in the treatment of numerous several diseases. Electrospun membranes are applied to local drug delivery systems¹² or implants, cancer treatment and for wound healing purpose⁷.

Biodegradable polymers are engineered to undergo controlled degradation over time, which makes them uniquely useful for medical applications. The exploration of biodegradable polymers in life sciences and pharmaceuticals has grown rapidly. The biodegradability makes them suitable for many applications including drug encapsulation and delivery, sutures, tissue engineering, surgical plates and dental devices¹³. Poly lactic acid (PLA) is a linear, lipophilic, biodegradable polymer. Lactic acid, the monomer, is easily derived from renewable resources like corn starch or sugarcane using bio-synthesis method. The PLA nanoparticles have widely been studied as delivery systems for systemic and topical applications¹⁴, because of their biodegradability, biocompatibility and environment friendly characteristics¹⁵. The chlorinated and fluorinated solvents could dissolve PLA (amorphous PDLA or crystalline PLLA). For biomedical applications a low toxicity solvent system would be preferable when nanofibrous webs are produced to avoid any adverse reactions¹¹.

The objective of present work is to study effect of spinning dope concentration on morphology and development of nanofibrous web. Single and binary solvent systems were used and evaluated for morphology of web.

II. EXPERIMENTAL AND METHODS

Materials

Poly (lactic acid) was obtained from Sigma Aldrich. Chloroform (RCFL Ltd.) and Acetone (SRL Chemicals) were used as solvents.

Preparation of solution

5 and 10 % (w/v) concentrated PLA solutions were prepared using chloroform and acetone as solvents. 10 % solution was prepared by using single solvent system with chloroform, and 5% solution was prepared by using binary solvent system with chloroform and acetone at 60 : 40 volume ratio. In case of binary solvent system, initially PLA was dissolved in chloroform and solution was diluted using Acetone. For dissolution magnetic stirrer was used at 900 RPM speed. The temperature was maintained at about 10°C by using ice cubes in out container.

Electrospinning

The 5% and 10% PLA solutions were prepared by using single and binary solvent system as above and filled in the 6 ml syringe having capillary 1 mm diameter. The variable high voltage of 15 kV was applied to capillary. The flow rate of polymer solution was maintained at 1 mL/h. The rotating disc collector covered with aluminum foil was used for the deposition of the nanofibres. The distance between the capillary and aluminum foil covered disc collector was maintained at 10 cm.

Characterization

After the synthesis of the nanofibres to study the effect of solvent system on the morphology and mean diameter following characterizations were carried out.

Scanning electron microscope (SEM)

SEM (Zeiss Sigma - FESEM) is a type of electrospun microscope that produces images of sample by scanning the surface with focused beam of electrons. This method is also known as SEM analysis and SEM microscopy, and it is very effectively in nano and microanalysis. Electron microscopy is performed at higher magnifications, generates high resolution images and precisely measures very small features and objects. For the SEM analysis the sample surface should be conductive. Sputtering of specimen were carried out for 10 minutes to impart conductivity.

X-ray diffraction (XRD)

The X-ray diffraction (XRD) (Bruker D8 Advanced X-Ray Diffraction System) is a powerful method for the study of nano materials, with structural features of at least one dimension in the range of 1-100 nm. The wavelength of X-rays is on the atomic scale, therefore, XRD is a primary tool for probing structure of nano materials. XRD offers high accuracy in the measurement of atomic spacing and is the technique of choice for determining strain states in thin films. The intensities measured with XRD can provide quantitative, accurate information on the atomic arrangements at interfaces. The X-ray diffraction of PLA nanofibrous nonwoven webs is carried out by setting the scanning angle 10-90°. The normal scanning is carried out for the analysis. The scanning rate was maintained at 5°/minutes.

III. RESULT AND DISCUSSIONS

Prior to the preparation of spinning dope, molecular weight analysis of PLA and its solubility in various solvent system have been evaluated. Molecular weight of PLA under investigation was evaluated by using Gel Permeable Chromatography (GPC) which is a type of size exclusion chromatography that separate the analytes on the basis of size, in organic solvents. 1mg/mL PLA solution was prepared in tetrahydrofuran under long exposure to sonication and injected in GPC and molecular weight was detected using Refractive Index Detector. The results showed that M_w of ~83000 and M_n in the tune of ~66000.

Initially, solvents tried were Dimethyl formamide, Acetone, Dichloromethane, Chloroform as individual and in combination. Its insoluble in DMF and Acetone whereas in chloroform it is soluble after prolonged sonication and in DCM found to be soluble. However, using DCM with or without combination of DMF showed droplet deposition during electrospinning at different concentrations and fibre web formation was found better with chloroform at and above 5% concentration at both with or without presence of acetone as diluent in spinning dope. With these preliminary trials it was decided to use 10% PLA solution in chloroform and 5% solution in chloroform and acetone combination (60 : 40 volume ratio). In solvent combination, first PLA was dissolved in calculated volume of chloroform and then desired acetone was added to achieve the predetermined volume ratio. Using these spinning dopes, electrospinning was carried out and nano fibre web obtained was characterized as follows.

Morphology of PLA nanofibrous web

To study the morphology and average diameter of the electrospun nanofibrous nonwoven web the scanning electron microscopy was carried out. To measure the average diameter of the nanofibres 50 readings were taken from the SEM images. Fig.1 shows the morphology of electrospun PLA nanofibres.

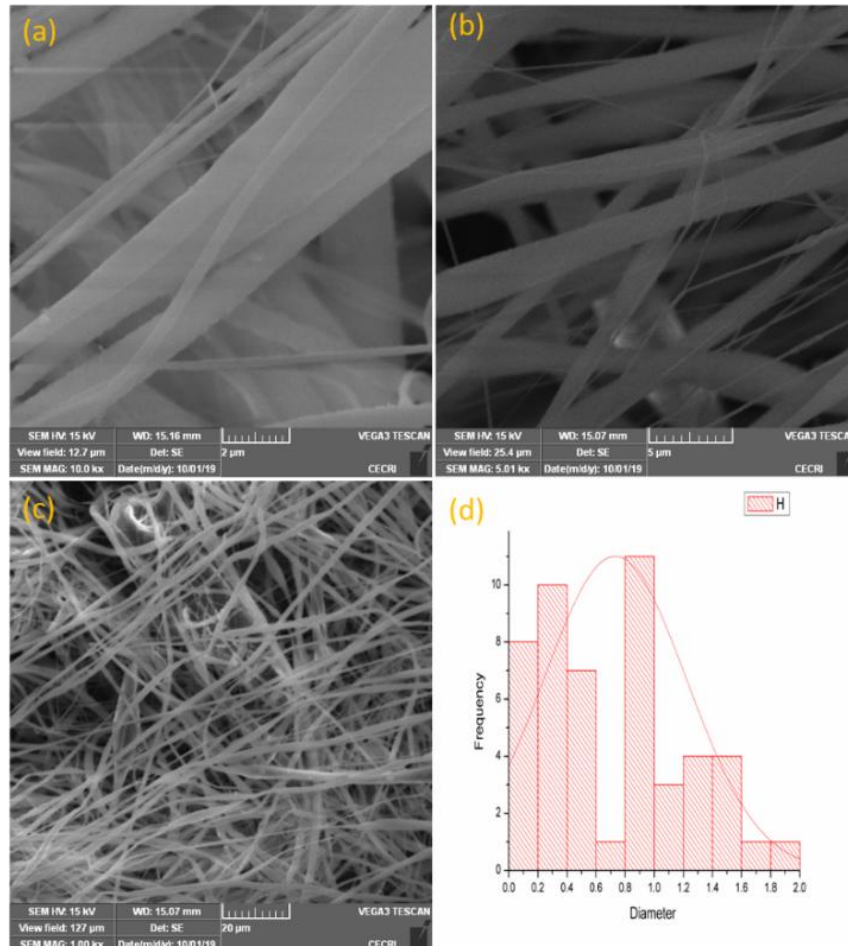


Fig.1 SEM images of nanofibrous nonwoven webs synthesized by using 10% PLA in chloroform as single solvent system

Fig.1 shows the morphological behavior of 10% electrospun nanofibres produced by using chloroform (single solvent system). From figure it is clear that the dissolution of poly lactic acid (PLA) produces the smooth and defect free nanofibres having an average diameter in the range of 731 ± 473 nm. Also, one can say that there is aligned fibre deposition is observed under the experimental condition.

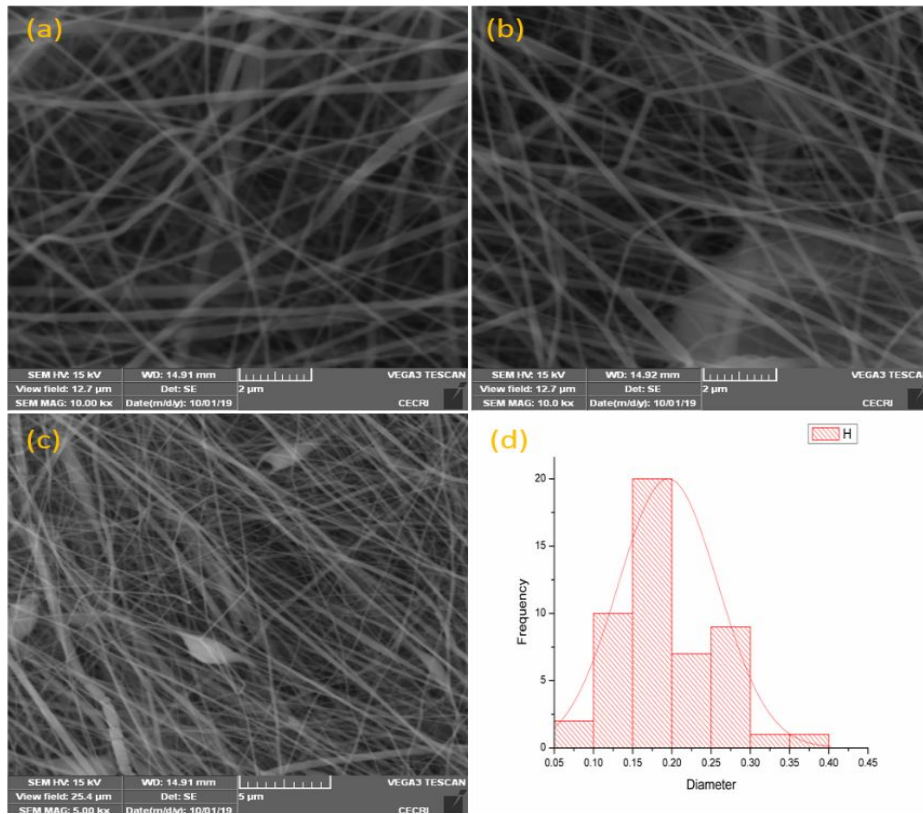


Fig.2 SEM images of nanofibrous nonwoven webs synthesized by using 5 % PLA in binary solvent system (chloroform and acetone at 60 : 40 volume ratio)

From the Fig. No. 2 one can say that the 5% PLA nanofibres synthesized by using chloroform and acetone (binary solvent system) at a volume ratio of 60:40 produces the nanofibres having an average diameter in the range of 195 ± 06 nm. As compared to single solvent system, binary solvent system produces finer nanofibres with more evenness in diameter. However, in the binary solvent system, nano fibres were found with beads formed. This may be due to lower solid content in spinning dope. The beads can be seen clearly in fig. 2 c.

XRD analysis of PLA Nano fibrous web

The Fig.3 shows the XRD patterns of nano fibrous web synthesized using 5 and 10% PLA concentration dope in respective solvent system.

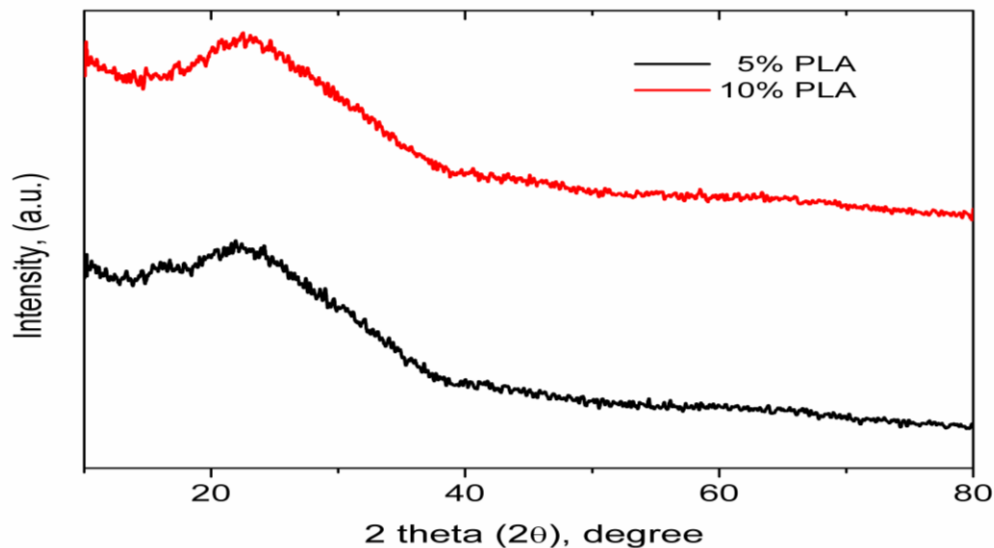


Fig.3 X-Ray Diffraction pattern of nanofibrous webs using 5 and 10% PLA in respective solvent systems.

From the Fig.3 it is clear that there is no crystal aggregate observed in either case of PLA nanofibres. It shows a broad hollow spectrum which means that both PLA nanofibrous nonwoven webs under investigation lies in amorphous phase.

IV. CONCLUSION

The electrospinning is most efficient and simple method of producing nanofibres. To study the effect of solvent system on the morphology and mean diameter the characterization of the electrospun nanofibrous nonwoven webs was carried out. From the analysis it can be conclude that the single solvent system at 10% concentration of PLA produces the smooth and defect free nanofibres however, the range of diameter distribution was wider. Whereas the binary solvent system at 5% PLA concentration the nanofibres produced were having comparatively finer structure with narrow distribution of fibre diameter, they produced with beads as irregularity. The nanofibres produced in either case found to be amorphous in nature.

REFERENCES

- 1 Hale Karakaş, *Funtex*, 2012, 1–35.
- 2 K. P. Matabola and R. M. Moutloali, *J. Mater. Sci.*, 2013, **48**, 5475–5482.
- 3 P. Heikkilä and A. Harlin, *Eur. Polym. J.*, 2008, **44**, 3067–3079.
- 4 C. J. Angamma and S. H. Jayaram, *Part. Sci. Technol.*, 2016, **34**, 72–82.
- 5 B. Pant, M. Park and S.-J. Park, *Pharmaceutics*, 2019, **11**, 305.
- 6 I. Garcia-Orue, G. Gainza, F. B. Gutierrez, J. J. Aguirre, C. Evora, J. L. Pedraz, R. M. Hernandez, A. Delgado and M. Igartua, *Int. J. Pharm.*, 2017, **523**, 556–566.
- 7 M. Rahmani, S. Arbabi Bidgoli and S. M. Rezayat, *Nanomedicine J.*, 2017, **4**, 61–70.
- 8 P. K. Baumgarten, *J. Colloid Interface Sci.*, 1971, **36**, 71–79.
- 9 I. Jun, H. S. Han, J. R. Edwards and H. Jeon, *Int. J. Mol. Sci.*, , DOI:10.3390/ijms19030745.
- 10 X. Qin and D. Wu, *J. Therm. Anal. Calorim.*, 2012, **107**, 1007–1013.
- 11 M. A. Jahangir, T. M. Rumi, A. Wahab, M. A. Rahman and Z. Bin Sayed, *Am. J. Chem.*, 2017, **2017**, 177–186.
- 12 N. Goonoo, A. Bhaw-Luximon and D. Jhurry, *J. Biomed. Nanotechnol.*, 2014, **10**, 2173–2199.
- 13 D. J. Subach, *Chemist*, 1997, **74**, 7–9.
- 14 F. Rancan, D. Papakostas, S. Hadam, S. Hackbarth, T. Delair, C. Primard, B. Verrier, W. Sterry, U. Blume-Peytavi and A. Vogt, *Pharm. Res.*, 2009, **26**, 2027–2036.
- 15 A. J. Gavasane, *Clin. Pharmacol. Biopharm.*, , DOI:10.4172/2167-065x.1000121.