Polyacrylonitrile and polylactic acid blend nanofibre spinning using needleless electrospinning technique

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In this work, polyacrylonitrile (PAN) and polylactic acid (PLA) blended polymers have been used to prepare a flexible and partially biodegradable electrospun nanofibre sheet suitable for filtration application. Also, acetone has been used as a replacement of dimethyl formamide (DMF) during spinning and a needleless (wire electrode) electrospinning machine has been used for filament preparation. Initially, PAN fibre is spun with DMF and various parameters, such as polymer concentration, voltage, distance between electrodes and RH%, are standardised. With these standard parameters, PLA is then added with PAN, and PLA concentration is optimised without affecting the desired fibre diameter. Further, the amount of acetone with DMF is also standardised without affecting the fibre diameter. Finally, polymer concentration of 2.5% PAN with 0.5% of PLA, a potential difference of 55 kV, electrode distance of 125mm at 35% RH and 10% acetone are found suitable for getting the desired nanofibre with minimum diameter.

Keywords: Filter fabric, Nanofibre, Needleless electrospinning, Nonwoven, PAN/PLA blend, Polyacrylonitrile, Polylactic acid, Polypropylene, Wire electrode

1 Introduction

Nanofibre technology involves the synthesis, processing, manufacturing and application of fibres with nanoscale dimension[1-3]. Electrospun fibres are typically in the range of several nanometers to a few microns in diameter[4,5]. Electrospun nanofibre webs can be modified to a desired porous structure. There is a huge range of polymers that can be used to make nanofibres[6]. The main features of nanofibres are a large surface area to volume ratio, excellent flexibility, and high porosity[7,8]. The nanofibres have potential applications nowadays in the areas of medical and filtration[9]. Generally, two types of electrospinning techniques are available in the market, viz. needle-based electrospinning and needleless electrospinning[10,11]. The disadvantage of the needle spinning process is needle chocking during mass production[12] and non-uniform deposition. Hence, needle-less spinning technology is suitable and gaining interest in the mass production of nanofibre[13,14]. There is a provision of different electrodes, such as cylindrical, multiple wires, oval shape and single wire system[15-17]. Here in this study,

we have used a single wire type electrode with closed carriage for the production of nanofibres[18-20]. Among the different polymers, the spinnability of polyacrylonitrile (PAN) in the dimethyl formamide (DMF) system is better than other polymers[21,22]. From the application point of view, PAN nanofibres can be applied in various applications. But based on the nature of the polymer, PAN nanofibres are more fragile[23-25]. On the other hand, polylactic acid (PLA) is a biodegradable electro-spinnable polymer and flexible in nature[26,27]. In this work, an attempt has been made to prepare the nanofibre with a blend of both the polymer (PAN/PLA) to achieve an optimised property[28]. Simultaneously, acetone has been used to replace the possible amount of DMF without affecting fibre properties and spinnability[29,30].

2 Materials and Methods

2.1 Materials

Polyacrylonitrile (PAN), having an intrinsic viscosity (5 dL/g) and molecular weight (1×10^5), was procured from Techno Orbit (Kanpur) and the PLA fibre grade was procured from the local market of Mumbai (India). Dimethylformamide (DMF) (Mm 73.09 g/mol) and acetone (Mm 58.08 g/mol) were obtained from Merck Life Science Pvt Ltd, Mumbai (India). Polypropylene

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spunbonded nonwoven fabric was obtained from Techfab (India) Industries Ltd, Daman (U.T).

2.2 Methods

2.2.1 Spinning Solution Preparation

2.2.1.1 PAN with DMF

The measured quantity of solvent DMF was taken in a conical flask. Initially, solvent DMF was stirred for 10min using a magnetic stirrer and then PAN was added gradually, and finally, the conical flask's cap was sealed by para film. After the addition of the polymer, the rotational speed of the stirrer was increased to 600 rpm, and the temperature of the heating plate was kept at 40˚C. This was continued till the dissolution of the polymer properly.

2.2.1.2 PAN and PLA Blend with DMF

Similarly, the blend solution of PAN and PLA polymer was prepared with DMF[31,32]. The measured quantity of solvent DMF was taken, and then PAN and PLA polymer in variable ratios were added gradually to the solvent on stirring. The rotational speed of the magnetic stirrer was increased up to 600 rpm, and the temperature of the heating plate was kept at 70˚C. The solution was heated at the same temperature and stirred until the complete dissolution of polymers.

2.2.1.3 PAN and PLA Blend with DMF and Acetone

In this case, a blend of PAN and PLA polymers in the required ratio was prepared with DMF and acetone mixture. The measured quantity of solvents DMF and acetone was taken in a conical flask and stirred for some time to prepare a homogeneous mixture of solvents. After 10 min, the polymer blend was added gradually to the flask and the rotational speed of the stirrer was increased up to 600 rpm. The temperature was kept at 70˚C and stirred until the complete dissolution of the polymer.

2.3 Electrospinning

The nanofibres from PAN and PAN/PLA blend were prepared using an electrospinning machine from ELMARCO Nano Spider (NS 1WS500U Series, version 03), made in the Czech Republic with needleless wire electrode technology. The nanofibres were deposited on the spunbonded polypropylene fabric. The parameters, such as concentration of polymers, voltage, distance between two electrodes and relative humidity, were standardised, one by one. Simultaneously, wire speed, carriage speed, the linear speed of the substrate material, and temperature were kept fixed during spinning.

2.4 Analysis of Fibre Surface Morphology

The surface morphology of PAN/PLA blend nanofibres was examined by scanning electron microscope (JSM-IT200 Series) JEOL Ltd., made in Tokyo, Japan. All samples were sputter coated with gold prior to SEM analysis. Fibre diameter was measured by image software Image J, based on images obtained from SEM analysis. The diameter of a minimum of 150 fibres was measured, for each sample at different positions. The average diameter of 150 readings of respective samples and the diameter distribution chart is reported.

2.5 Pore Size Analysis

Quantachrome's capillary flow 3G series porometer with standard test method ASTM D 6767, operating under Windows® and the 3G win software, was used for pore size analysis. This technique is based on a capillary flow test. Atmospheric conditions, such as temperature and relative humidity, were kept at 21±2˚C and 65±5 % respectively, during the test.

3 Results and Discussion

3.1 Effect of PAN Concentration on Fibre Diameter

The effect of polymer concentration on spinnability and fibre diameter was investigated by changing the concentration percentage of the PAN in DMF. Different concentrations, such as 1%, 2%, 3%, 4% and 6% wt/wt are taken in a set of experiments. During this experiment, other parameters, such as voltage, relative humidity and distance between electrodes are kept fixed at 40 kV, 45% and 130mm respectively. Fibre fineness and morphology have been investigated by SEM. The SEM images of fibre, and the plot of fibre diameter, corresponding to PAN concentrations are given in Figs 1 and 2(a) respectively. Few beads are observed at 1% and 2% concentrations, whereas fibres are found bead free from 3% to 6% of polymer concentration. The diameter of the fibres is found to be increased with an increase in polymer concentration. Based on fibre morphology and uniformity of fibre diameter distribution, 3wt% is kept fixed for a further set of experiments.

3.2 Effect of Potential Difference between Electrodes on Fibre Diameter

The effect of potential difference on the nanofibre diameter and pore size of the deposited nanofibre mat has been investigated by varying the voltages from
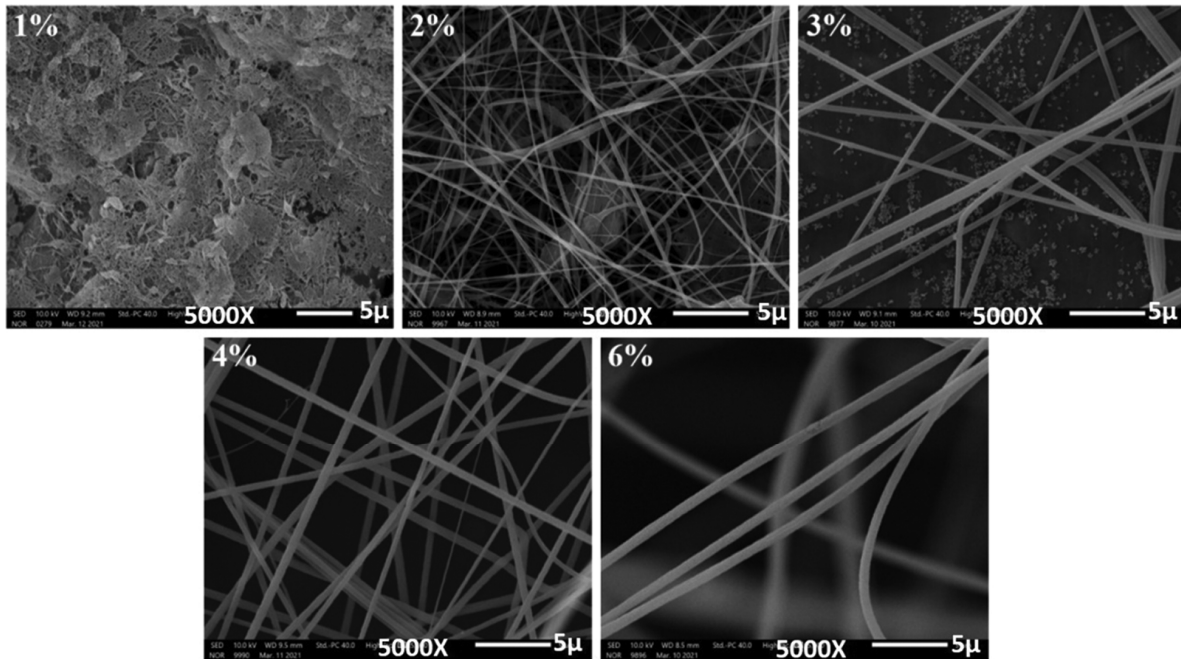
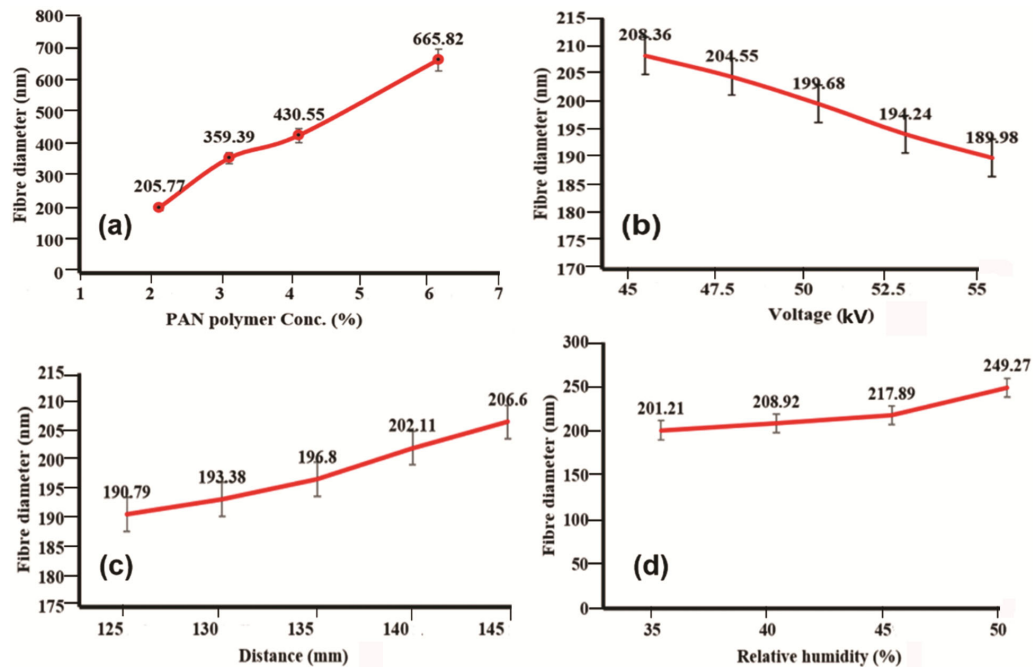Fig. 1 — SEM images of nanofibre at different concentrations of PAN in DMF

Fig. 2 — Diameter of nanofibres at different (a) PAN concentrations, (b) voltages, (c) distance between electrodes and (d) RH

45 kV to 55 kV at intervals of 2.5 kV. During spinning, other parameters, such as concentration, the distance between two electrodes, wire speed, carriage speed, the linear speed of the substrate material, relative humidity (RH), temperature and deposition time have been kept fixed at 3%, 130 mm, 1.0 mm/s, 300 mm/s, 360.0 mm/min, 45% RH, 21±2°C and 3 min respectively. Fibre surface morphology has

been investigated by SEM and the diameter of the fibre is measured by using image J software. The plot of fibre diameter at respective voltage is shown in Fig. 2 (b). Morphology of the fibres is found bead free in all the cases, but a decrease in diameter is observed up to 55 kV due to high stretching force on the spinning jet. Beyond the 55 kV, spinning is not done due to the limitation of voltage, with respect to

electrode distance. Based on the finding, 55 kV is kept fixed for a further set of experiments.

3.3 Effect of Distance between Two Electrodes

The effect of distance between the two electrodes on the nanofibres quality and diameter of the nanofibre mat during spinning has been investigated by changing the distance from 130mm to 145 mm at the interval of 5 mm. During this study, other parameters, such as concentration, bottom electrode voltage, top electrode voltage, wire speed, carriage speed, the linear speed of the substrate material, relative humidity percentage, temperature and deposition time are retained fixed at 3%, 45kV, 1.0 mm/s, 300 mm/s, 360.0 mm/min, 45% RH, 21±2°C and 3 min respectively. The plot of fibre diameter with respect to the distance between electrodes is shown in Fig. 2(c). When the voltage between electrodes is fixed, the fibre diameter increases with an increase in distance between electrodes because of a decrease in the strength of the electric field. When field strength decreases at a higher distance, it applies a low stretch to the polymer solution, leading to a higher fibre diameter. As there is no significant difference in diameter at 125 mm and 130mm, the distance of 130mm is kept fixed for a further set of experiments.

3.4 Effect of Relative Humidity on Fibre Diameter

The influence of environmental relative humidity percentage on the spinning and fibre quality has been investigated by altering the relative humidity percentage from 35% to 50% inside the spinning chamber at intervals of 5%. During this study, other parameters, such as polymer concentration, bottom electrode voltage, top electrode voltage, distance between two electrodes, wire speed, carriage speed, linear speed of the substrate material, temperature and deposition time have been kept fixed at 3wt%, 45kV, 130 mm, 1.0 mm/s, 300 mm/s, 360.0 mm/min, 21±2°C and 3 min respectively. SEM images at different RH% and plots of fibre diameter versus RH% are shown in Figs 3 and 2(d) respectively. Fibre quality and morphology are found similar at the above ranges of RH%. With the increase in RH %, a gradual increase in diameter is observed. The charge transfer between the environment and solvent is faster with an increase in moisture due to the charge diffusion. Thus, the fibre solidifies before further elongation and causes thicker fibre. From the result of this set of experiments, RH % is kept fixed at 35% for further experiments.

3.5 Effect of Blending of PLA with PAN and DMF on Fibre Quality

The effect of polymer concentration on spinnability and fibre diameter has been investigated by adding PLA within and above the standardised concentration of PAN. The PAN/PLA blend with DMF in the different concentrations, such as 3% (2% PAN and
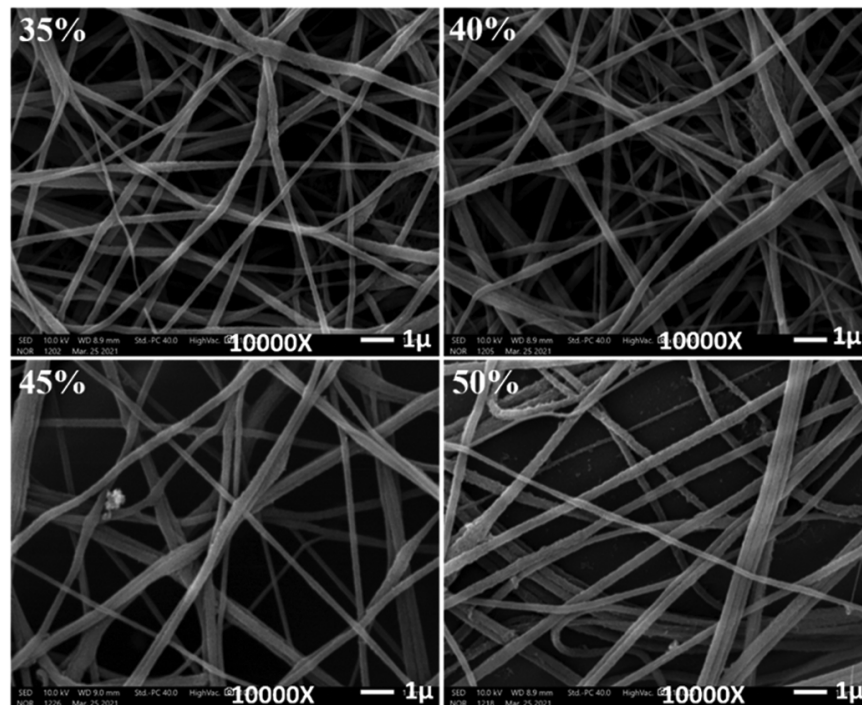

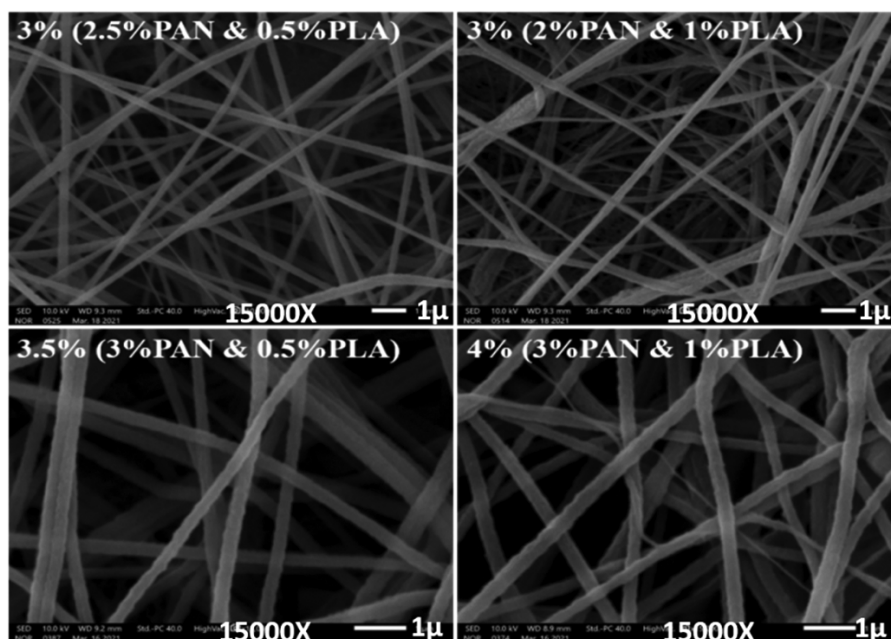Fig. 3 — SEM images of nanofibre at different RH (%) of PAN in DMF

Fig. 4 — SEM images of nanofibre at different concentrations % of PLA and PAN blend in DMF

1% PLA), 3% (2.5% PAN and 0.5% PLA), 3.5% (3% PAN and 0.5% PLA) and 4% (3% PAN and 1% PLA) wt/wt has been prepared in DMF. During the spinning, other parameters such as distance between two electrodes, voltage of top electrode, voltage of bottom electrode, carriage speed, wire speed, relative humidity percentage, temperature and deposition time, are kept fixed. The SEM images of fibre at different polymer concentrations and plot of fibre diameter with respect to PLA and PAN concentration are shown in Figs 4 and 5 respectively. An increase in diameter in both cases within and above 3% PAN is observed by increasing the blend percentage of PLA. Hence, 2.5% PAN and 0.5% PLA (total 3% concentration) are kept fixed to achieve the finer fibre. Based on the calculation, PAN and PLA percentage in the fibre is 83.3 and 16.7% respectively.

To check the flexibility of nano fibre after blending with the PLA, the stiffness of 100% PAN and PAN/PLA blend nanofibre mat of the same dimension is also checked. The modulus of 100% PAN and PAN/PLA blend mat is found 2.1 MPa and 1.1 MPa respectively. The reduction in modulus shows the increase in flexibility of the nanofibre after blending with PLA.

3.6 Effect of Acetone on Spinnability and Fibre Diameter of PAN/PLA Blend

DMF solvent is hazardous, and hence attempt has been made in the final part of the study to partially
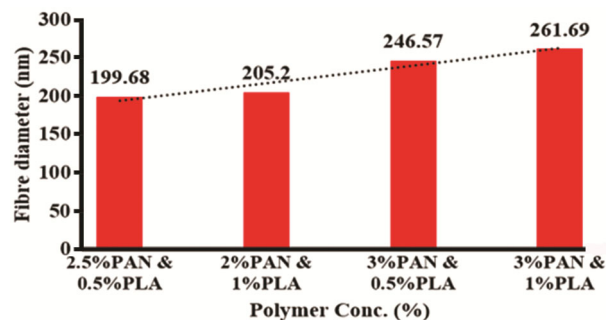

Fig. 5 — Fibre diameter at different concentrations of PAN/PLA blend

replace the DMF with acetone and observe its effect on the fibre properties, such as diameter and morphology. The polymer blend solution is prepared with 10, 15 and 20% of acetone in DMF. All other conditions, such as solution parameters and spinning parameters have been kept fixed as mentioned earlier. The image of the fibre at different concentrations of acetone is shown in Fig. 6. There are no changes found in spinnability, but an increase in fibre diameter from 202 nm to 252 nm is observed with an increase in acetone concentration. This increase in diameter is due to the fast evaporation of acetone; hence, the acetone percentage can be chosen to replace the DMF as per the required fibre diameter.

3.7 Pore Size Analysis of Nanofibre Mat Spun at Standardised Parameters

The pore size of the nanofibrous mat depends on the fibre diameter. The thinner the fibre the smaller is
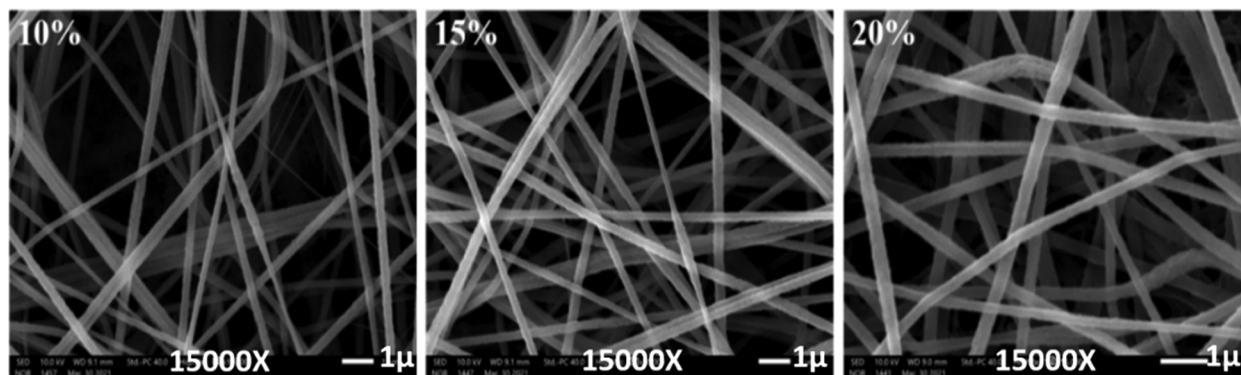
Fig. 6 — SEM images of nanofibres at different concentrations of PAN/PLA blend in DMF and acetone

the pore size. The PAN/PLA blend nanofibrous matt spun at standardized parameters for 3min deposition is taken for the pore size analysis by capillary flow porometer. The mean flow pore size of the mat is found 2.75 μm.

4 Conclusion

The electrospinning of PAN, a fragile polymer blended with PLA has been done successfully to get a flexible mat, in the needleless spinning system with wire electrodes. The process parameters have been optimized to get the least possible fibre diameter. The standardized parameters for the PAN are found to be 3% wt/wt polymer in DMF, 55kV voltage, 130mm distance between electrodes and 35% RH. Other parameters, such as carriage speed and temperature have been kept fixed at 300mm/s and 21±2°C respectively. At these parameters, PAN has been replaced with PLA step by step and it has been found that the diameter of nano fibres increases with an increase in concentration of PLA after 0.5wt%. The concentration of PAN 2.5wt% and PLA 0.5wt% (total concentration of 3wt%) is found suitable to keep the fibre diameter minimum. The addition of PLA above the total blend concentration of 3% could not help to keep the fibre diameter finer. DMF solvent is mildly hazardous, whereas acetone is nonhazardous but more volatile in nature. So, acetone has been added to replace the DMF in the PAN/PLA blend solution. The increase in acetone concentration results in an increase in fibre diameter. This may be due to the increase in the rate of evaporation because of the volatile nature of acetone. To maintain the minimum fibre diameter, acetone concentration is kept fixed at 10%. Finally, the pore size of the mat has been analyzed and the mean flow pore size is found to be 2.75 μm at the standardized parameter. Therefore, it is concluded that the PAN/PLA blend nanofibre can be

spun in mass scale commercially at the above-mentioned parameters and the prepared nanofibre mat can be used for fine particulate filtration.

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