# POLY(LACTIC ACID) BASED CONDUCTING NANOFIBROUS STRUCTURE THROUGH ELCTROSPINNING

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## Introduction

Electrospinning is an established way to process polymer solutions or melts into continuous fibres with diameter often in the nanometre range. This technique is applicable to virtually every soluble or fusible polymer [1]. It involves a process in which a polymer solution is stretched into fine filaments (Fig. 1) under the action of a high electrical voltage. Nonwoven textiles composed of electrospun fibres have large specific surface areas and small pore sizes compared to commercial textiles, making them excellent candidates for use in filtration and membrane applications [2,3]. This process primarily depends on a number of parameters, including the type of polymer, solution viscosity, polarity and surface tension of the solvent, electric field strength and the distance between the spinneret and the collector. Multi-functionalised micro/nanostructures of conducting polymers or conducting polymer/biopolymer blends have received much attention because of their unique properties and technological applications in electrical, magnetic and biomedical devices [4]. They are of special interest for tissue engineering because new technologies will require biomaterials that not only physically support tissue growth but also are electrically conductive, and thus able to stimulate specific cell functions or trigger cell responses. The present research has included polyaniline (PANi) as the conducting polymer and poly(L-lactic acid) (PLLA) as the biopolymer and both polymers have been successfully electrospun producing bead-free and fine nanofibrous structure.

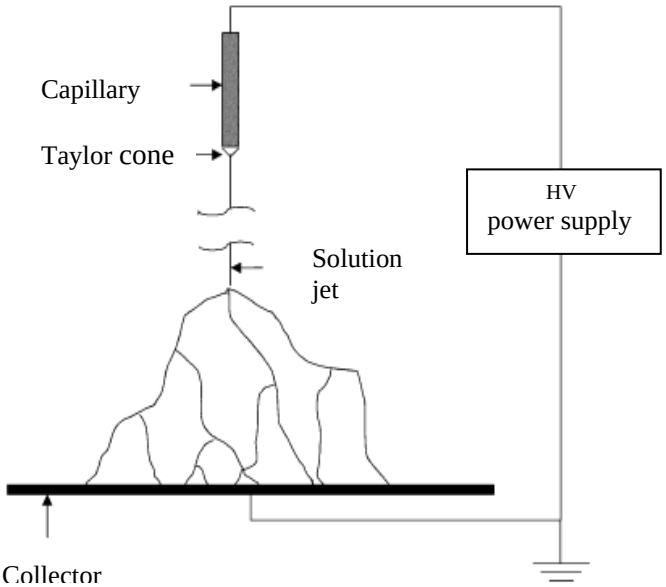


Fig. 1 Basic schematic diagram of electrospinning process [5]

## Experimental Details

*Materials*

Dodecylbenzene sulphonic acid (DBSA) doped PANi and PLLA have been dissolved in common solvents. The PLLA was NatureWorks 3051D material with weight average molar mass $1.044\times10^5$ g $mol^{-1}$ (as measured using gel permeation chromatography). Aniline (99%), procured from Acros Organics, ammonium persulphate (98%), purchased from Ajax Chemicals and DBSA obtained from Acros Organics were used to synthesise DBSA doped PANi (PANi-DBSA). Chloroform (98%), dimethyl formamide (DMF) (98%) and tetra butyl ammonium bromide (TBAB) were procured from Sigma-Aldrich and used without further purification.

*Manufacturing of nanofibrous mat*

PLLA was dissolved in CHCl3/DMF mixtures with proportions (v/v, CHCl3:DMF) (i) 50:50, and (ii) 70:30, to give PLLA concentration 10 % (w/v). PLLA solution (2 parts by volume) was then mixed with DBSA-doped PANi solution (1 part by volume) to give solutions with 6.7 % (w/v) PLLA and 1.7% (w/v) DBSA-doped PANi in (i) 67:33 and (ii) 80:20 CHCl3:DMF. 1% (w/v) TBAB was used as an additive to increase the conductivity of the solution. Polymer solution was delivered to a stainless steel syringe needle by a glass hypodermic syringe. The flow of polymer solution was controlled using a programmable syringe pump (Cole-Parmer Hz 50/60, cat #789100C). The same type of hypodermic needle (20G1TW, 0.9x25 mm from BD PrecisionGlide$^{TM}$ Needle) was used throughout the experimental work. The power supply was a Spellman DEL HVPS INST 230-30R unit that could generate up to 30 kV. As recommended in recent studies [2,3], a solution feed rate (1-2 ml $hr^{-1}$) with constant polymer concentration and molar mass were chosen for this study. The distance between the collector and the needle tip was maintained at 80–100 mm and voltage was kept in the range of 8-10 kV. Microscopic observations of electrospun nanofibres

were performed using Philips XL30S scanning electron microscope (SEM) after being coated with platinum.

**Results and Discussion**

DBSA-doped PANi/PLLA mat exhibits a bead-free network of nanofibres that have extraordinarily smooth surface and diameters in the range 75 to 100 nm. Fig. 2 (a) suggests that the solvent mixture of CHCl3 and

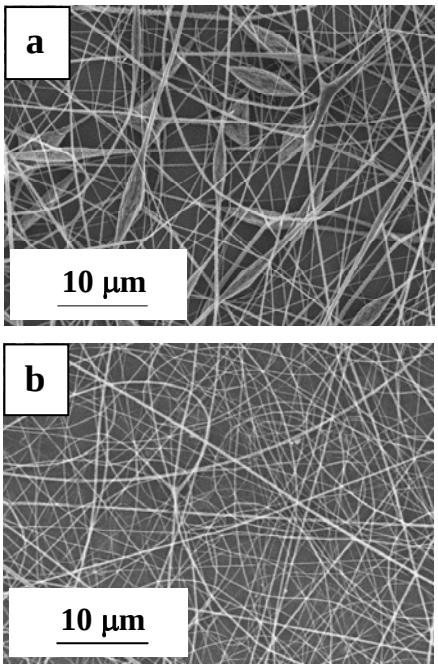


Fig. 2 (a) Nanofibres from an 80:20 CHCl3:DMF solution of DBSA doped PANi and PLLA (b) Bead-free nanofibres from a 67:33 CHCl3:DMF solution with TBAB

DMF at a ratio of 80:20 produces nanofibres with a number of beads. However, increased voltage and distance between needle tip and collector produced a network with relatively small area occupied by small beads. The solvent mixture of same at a ratio of 67:33 gave, with the added electrolyte, almost bead-free networks in Fig. 2(b). The effect of the added electrolyte on the conductivity of DBSA-doped PANi/PLLA solutions is illustrated by the data shown in Table 1. Concentration and salt addition have been

Table 1**.** Solution conductivity of spinnable polymer solutions at 24°C.

| **Polymer(chloroform:DMF volume ratio)** | **Conductivity ($\mu S\ cm^{-1}$)** |
|---|---|
| PANi/PLLA (80:20) | 9.95 |
| PANi/PLLA (67:33) | 24.30 |
| PANi/PLLA(67:33) with1% TBAB | 380.00 |
| PLLA (70:30) | 1.85 |

found to have relatively large effects on the fibre diameter and bead formation compared to those of the other parameters [3,5]. An increase in the polymer concentration results in greater polymer chain entanglements within the solution, which is necessary to maintain the continuity of the jet during electrospinning [6]. In addition, increased polymer concentration increases the surface tension of the solution, which is beneficial because lower surface tension tends to favour bead formation [7]. Patra et al. and Fong et al. [2,7,8] have suggested that the net charge density carried by the electrospinning jet is an important factor that greatly influences the morphology of the electrospun products, together with the viscosity and surface tension of the solution. Their results have also shown that beads become smaller and the shape becomes more elliptical as the net charge density is increased. DMF with high dielectric constant is an effective solvent component. Addition of only 1% of the quaternary ammonium salt TBAB dramatically increases the conductivity of the electrospinning solution of DBSA-doped PANi and PLLA, and facilitates the formation of bead-free nanofibres. DMF has low vapour pressure and high boiling point that have made the solution more effectively spinnable. Significant conductivity has also been found for the PANi based PLLA mat.

**Conclusions**

Solutions of DBSA-doped PANi and PLLA in chloroform/DMF mixtures are readily electrospinnable. Increased solution conductivity by using DMF and electrolyte (TBAB) reduces the average diameter (less than 100 nm) of the nanofibres and successfully produces bead-free nanofibres. Bulk AC conductivity across the fibremat has also been determined.

**References**

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