Stefanie Kohse*, Niels Grabow, Klaus-Peter Schmitz and Thomas Eickner

Electrospinning of polyimide nanofibres – effects of working parameters on morphology

Abstract: The use of the electrospinning technique is a promising and versatile method for producing fibrous nonwovens from various polymers. Here we present fibre formation via direct electrospinning of a soluble polyimide, a class of polymers that is typically insoluble. In this study solution parameters as the solvent and the polymer concentration are investigated. Furthermore relevant process parameters are varied for optimization of the performance. The presented data indicate polyimide as a promising material for the fabrication of nanofibrous nonwovens via direct electrospinning.

Keywords: electrospinning, nanofibres, nonwoven, polyimide.

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1 Introduction

Implant development can be highly featured by the use of innovative technologies like electrospinning for processing of various polymers. So produced polymeric nanofibrous nonwoven fabrics can be applied in drug delivery systems as well as for the use as fundamental structures in permanent implants.

The class of polyimides holds a number of superior properties such as their high mechanical strength and thermal stability as well as their great chemical and dielectric properties. [1,2] Furthermore a negligible cytotoxicity for some representatives of commercially available polyimides indicates a good biocompatibility. [3] Therefore its potential application in biomedical engineering is of high interest.

Electrospinning of polyimide is challenging due to missing solubility in common solvents of this class of polymers. In the past different solutions were reported as for example the electrospinning of polymer-precursors, core shell-electrospinning or synthesis of fluorinated derivatives. [1] But also one commercial soluble polymer is available, that can be used for electrospinning. [4] In the presented work we focussed on parameter study performed in order to evaluate the influence of solution as well as process parameter on the nanofibrous polyimide material.

2 Materials and methods

2.1 Materials

Polyimide P84 Powder Solution Grade was kindly provided by HP Polymer GmbH (Lenzing, Austria). N,N-Dimethylformamide (DMF), 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) and Dimethylsulfoxide (DMSO) were purchased by Carl Roth GmbH + Co. KG (Karlsruhe, Germany). All used solvents were applied without further purification.

2.2 Methods

Clear and homogenous polymer solution of 5 – 25 wt% was obtained by dissolving the polymer in all used solvents at 37 °C. Fibrous nonwovens were fabricated from polymer solution by the use of both, needle as well as needleless electrospinning. For the process of electrospinning a device of Contipro (Dolní Dobrouč, Czech Republic) 4Spin® C4S LAB2 was used, respectively. For fabrication of randomized fibres a static continual collector and for aligned fibres a static patterned collector was used. For needle-electrospinning a single jet capillary emitter with cannulas from gauche 15 to gauche 23 were used. For needleless electrospinning a rod emitter was used. For each single solution process parameter like high voltage and feed rate

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were optimized until a stable process was achieved. All trials were performed at an emitter collector distance of 22 cm. The high voltage was varied for needle electrospinning between 15 kV and 22 kV and for needleless spinning between 35 kV and 45 kV.

The feed rate was varied for needle electrospinning between 2 µL/min and 30 µL/min and for needleless spinning between 75 µL/min and 100 µL/min. In **Table 1** all performed processes are summarized.

Table 1: Summary of processed polyimide polymer solutions.

Entry	$c_{polymer}$ [wt%]	Solvent	Emitter/Collector
1	5	HFIP	needle, g19/static
2	10	HFIP	needle, g19/static
3	10	DMSO	needle, g19/static
4	20	DMSO	needle, g19/static
5a	10	DMF	needleless /static
5b			needle, g19/static
6	15	DMF	needleless /static
7a	20	DMF	needleless /static
7b			needle, g19/static
7c			needle, g19/static, patterned
8	25	DMF	needleless /static

Upon completion of the process morphological structure was examined by scanning electron microscopy. The evaluation of the process was done in consideration of process stability, shape of the fibres and fibre diameter.

3 Results and discussion

3.1 Impact of the solvent

For all solvents electrospinning process was achieved. The choice of the solvent has thereby a high impact on the shape of the formed fibres. While smooth but stucked fibres are formed with polymer solutions in DMSO (Entry 3, 4) , by the use of HFIP as solvent (Entry 1, 2) only ribbon shaped fibres are formed. Such ribbon shaped fibres are formed out of a liquid jet with a thin polymer skin on the outer side. [5] On this way a tube is formed by solvent evaporation in the inside. This leads to collapse of tube and finally to formation of the ribbon fibre.

The formation of double-grooved fibres is reported from binary solvent systems leading to phase separation. [6,7] In this study only single solvent systems were used. Furthermore SEM micrographs (**Figure 1C, D**) indicate that the shape of the fibre is not grooved, in contrary two or more fibres seem to accumulate.

Smooth and round shaped fibres are formed with polymer solution in DMF (Entry 7b). In **Figure 1** SEM images of the electrospun nonwovens are presented, showing the impact of solvent on the shape of the formed fibres.

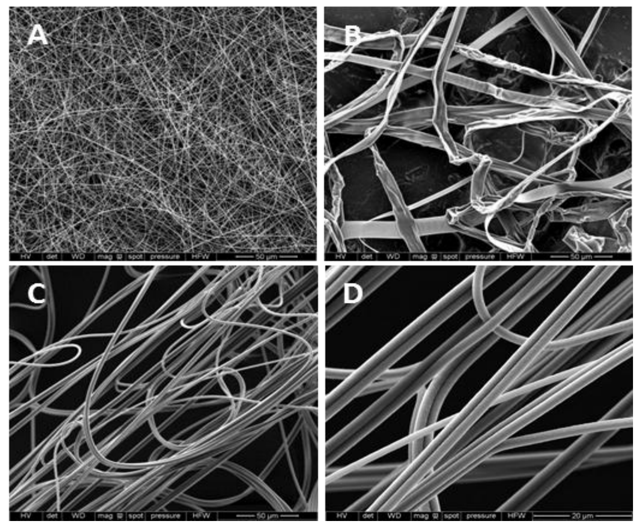


Figure 1: SEM images of the electrospun polyimide – Influence of the solvent on the shape of fibre (**A**: DMF (Entry 7b) smooth and round shaped fibres, **B**: HFIP (Entry 2) ribbon shaped fibres, **C,D**: DMSO (Entry 4) double attached fibres).

3.2 Impact of the polymer concentration

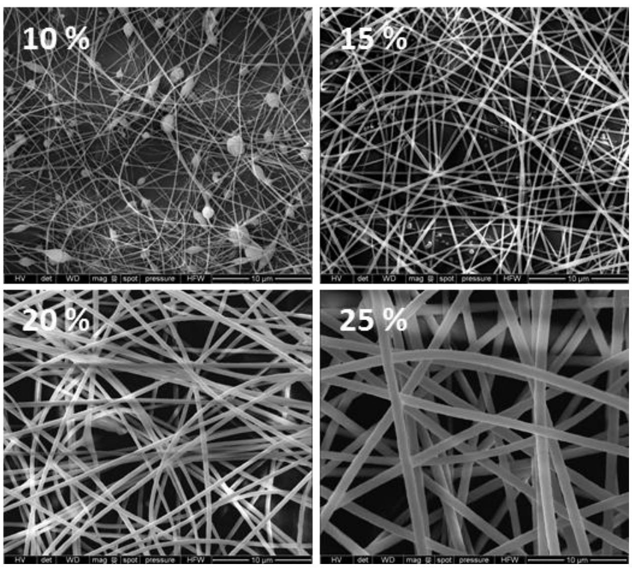
Variation of polymer concentration leads to rising fibre diameter with increasing polymer concentration as shown in **Table 2**.

However, for a concentration of 10 wt% only beaded fibres are obtained. This can be solved by increasing the concentration of the polymers. Exceeding a concentration of 15 wt% the fibres become smooth (**Figure 2**).

Table 2: Fibre diameter of the fabricated polyimide nonwovens.

$c_{polymer}$ [wt%]	Fibre diameter [nm]
10	132 ± 35
15	287 ± 66
20	423 ± 75
25	1001 ± 71

Furthermore, process stability is influenced by concentration of the polymer. The higher the polymer concentration, the more stable the process becomes up to a concentration of 20 wt%. At higher concentrations polymer surface dries quickly at the emitter resulting in an instability of the process. For a concentration of 20 wt% it was possible to keep the process stable for about one hour, reaching a nonwoven in dimensions of 20 cm x 22 cm with a layer thickness of 50 µm to 100 µm.



3.3 Impact of the emitter and collector

Comparing needle- with needleless electrospinning no differences in shape and diameter of fibres can be determined, although spinning parameter differ. For needle electrospinning a high voltage of 21 kV and a feed rate of 16 µl/min was applied. For needleless electrospinning a high voltage of 41 kV and a feed rate of 81 µl/min was used. Fabrication of aligned fibres is normally done by rotating collectors, while orientation is controlled by rotation speed. By the use of a patterned, static collector of Contipro the orientation of the fibres can be controlled by static operation. With this collector we were able to produce aligned fibres without the use of a rotating collector as shown in **Figure 3**.

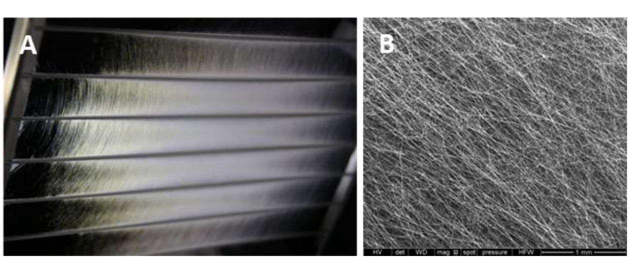


Figure 3: A: Aligned electrospun polyimide fibres **B:** SEM image of the aligned fibres

4 Conclusion

Fabrication of nanofibrous polymer nonwovens of a soluble polyimide via direct electrospinning process was successfully performed. Due to the choice of solvent the shape of the formed fibres can be controlled. By the use of DMF smooth and round shaped fibres were produced. The stability of the process is highly affected by the concentration of the polymer. Here maximum process stability was determined at concentrations of 20 wt%. A nonwoven in dimensions of 20 cm x 22 cm with a layer thickness of 50 µm to 100 µm was produced. Furthermore the diameter of the produced fibres can be controlled in the range of 280 nm to 1 µm. Also the successful fabrication of aligned fibres by the use of a patterned static collector was shown. Therefore, polyimide can be considered as a promising material for the fabrication of nanofibrous nonwovens. So the next objective, its potential for application in biomedical engineering should be given attention in further studies.

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