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Post-processed chemical treatment of polyimide electrospun nonwovens with ethylenediamine for biomedical applications

Abstract: The generation of electrospun nonwovens from polyimide (PI) is challenging as the fibers are prone to distinct delamination. In consequence, the resulting nonwoven material has particularly low structural integrity and loose fibre interlocking, demanding for a follow-up treatment, such as high temperature thermal treatment.

In this work, a facile method for a post-processed treatment of PI nonwoven is presented in order to obtain a mechanically stable material while maintaining the characteristics of the electrospun nonwoven. The procedure was performed using a solution of EDA in methanol at 37 °C and ambient pressure to achieve a modified fiber interaction. Overall, the developed protocol opens new possibilities in the processing of PI into delamination-free nonwovens. Potential adverse effects of a high temperature thermal treatment are being avoided, and new applications in the field of medical devices may become accessible.

Keywords: Electrospinning, post-treatment, polyimide, nonwoven

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1 Introduction

Electrospun polymer based nonwovens represent a prominent class of high performance fabrics for a variety of applications in the field of biomedical engineering [1, 2]. Depending on the choice of the underlying polymer, it is possible to adjust many desired properties of the target material. Moreover,

alterations in the operating parameters for the electrospinning process result in highly distinct characteristics of the nonwoven fabrics, allowing for tailor-made products.

In terms of polymers, PI provides highly beneficial properties such as high thermal and chemical stability in combination with excellent biocompatibility. The generation of PI nonwovens *via* electrospinning directly from a polymer solution has already been reported by our group [3]. However, mainly due to the low solubility of the polymer itself it remains difficult to achieve a resilient PI nonwoven material [4].

A well-established approach exploits PI precursors for the electrospinning process, such as polyamic acid, followed by thermal imidization, to obtain PI nonwovens [5, 6]. Moreover, increased fibre adherence in combination with surface smoothing has been reported when heat treating PI nonwoven at 1200 °C under nitrogen atmosphere [7]. In biomedical applications in particular, this leads to the demand for alternative post-processed treatments that stabilize the nonwoven structure.

In 2006, Qiao and Chung reported about the effective chemical crosslinking of P84 PI membranes, destined for pervaporation dehydration, using diamines [8]. They showed a strong influence of the diamine treatment on the surface morphology as well as on the chemical structure of the PI membranes.

2 Materials and methods

2.1 General information

Polyimide P84 granules were kindly provided by HP Polymer GmbH (Lenzing, Austria). Ethylenediamine was purchased from Fluka, Germany. All chemicals were used as received without further purification.

FTIR-ATR-measurements were performed using a Bruker Vertex 70 IR-Spectrometer equipped with a DLaTGS-detector. Data were collected in the range of

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$\tilde{\nu} = 700 \text{ cm}^{-1}$ to 4000 cm^{-1} with a resolution of $\tilde{\nu} = 4 \text{ cm}^{-1}$ averaged over 32 scans in reflection mode using a Graseby Golden Gate Diamond ATR-unit. All spectra were subsequently baseline corrected and atmospheric compensation was performed by Bruker's OPUS software.

Polyimide nonwovens were all manufactured *via* electrospinning process on an individually designed electrospinning device from 20 wt% polyimide P84 granules dissolved in DMF following the procedure of [3]. Briefly, the process was carried out using a high voltage setup around 15 kV and a feed rate of 0.4 mL/h with a process time of 30 min.

2.2 General procedure for the postprocessive treatment of PI nonwovens

Ethylenediamine (EDA) was dissolved in technical methanol at a ratio of 1 wt%. Subsequently, the mixture was poured into a petri dish. The PI nonwoven was placed in the solution, covered with the lid and sealed with parafilm. The EDA solution was then allowed to soak into the nonwoven for 18 hours under moderate agitation at 37°C . After the diamine treatment, the nonwoven was taken out and carefully rinsed three times with technical ethanol to remove residual diamine. In the last step, the samples were dried at 40°C under reduced pressure. To evaluate the effect of the solvent and the thermal treatment on the nonwovens, a reference sample was treated in the same manner, but without the addition of EDA.

3 Results and Discussion

3.1 Effect of EDA treatment

To our delight, after the EDA treatment, the nonwoven showed a substantial increase in structural stability compared to the untreated specimen and it was able to be handled without delamination in comparison to the reference sample. Especially detaching the nonwoven from the collector unit used in the electrospinning process was considerably facilitated. However, a decent shrinking could be observed as shown in Figure 1. However, when detaching PI nonwoven without further treatment from the collector, the material shows remarkable disintegration.

Figure 1: a) Macrophotography of PI nonwoven directly after electrospinning on aluminium collector. b) PI nonwoven sample after treatment with 1 wt% EDA in MeOH detached from collector. c) PI nonwoven without treatment after detachment from collector

Following to the treatment, the nonwoven samples were analysed *via* ATR-IR spectroscopy to evaluate the effect on the chemical composition on the PI as shown in Figure 2.

Figure 2: ATR-IR spectra of PI nonwoven reference with band assignment according to Xu et al. [10] in comparison to nonwoven sample after treatment with 1 wt% EDA in MeOH.

A drastic decrease of the intensity of the characteristic imide bands was observed, accompanied by the formation of new, strong bands at $\tilde{\nu} = 1654 \text{ cm}^{-1}$ and $\tilde{\nu} = 1539 \text{ cm}^{-1}$, which can be assigned to amide C=O stretching and N-H bending vibration, respectively [9]. These changes indicate the successful and very fast reaction of the imide functionality with EDA to yield a phthalamide structure (Figure 3 I).

Regarding the reported reaction time of several days for thin film membranes in [8], the accelerated and well proceeded reaction process can be explained with a much higher inner surface of the nonwoven compared to a membrane, thus faster swelling with methanol and ingress of the diamine occurs. Furthermore, the presence of the second amine group offers the possibility to form interchain linkage and thus, stabilizing the polymer material (Figure 3 II).

Figure 3: Assumed reaction of polyimide with diamines to form a phthalamide moiety (I) and subsequent crosslinking (II)

4 Conclusion

In summary, a follow up treatment with EDA has proven to be suitable to achieve stable, delamination-free nonwoven from electrospun PI. Though shrinkage was observed, the material was able to be handled after the treatment without damaging the nonwoven structure. However, it has been shown that for the chosen conditions a transformation to *o*-phthalamide moieties has occurred.

In future work, the effect of the treatment on the mechanical and thermal properties alongside the biocompatibility will be investigated. As it was shown, the reaction was already on a high extent for a concentration of 1 wt% EDA in MeOH. Furthermore, decreasing the diamine amount, as well as a shortened reaction time paired with different diamine moieties may also lead to a change in the reaction outcome. Thus, different properties of the nonwoven may occur, especially regarding physico-chemical behaviour and implant tissue interaction when used for implants.

Author Statement

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