# ADHESION IMPROVEMENTS OF FUNCTIONAL NANOFIBROUS LAYERS

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***Abstract:*** Nanofibrous web adhesion is a critical issue for the application of nanofibres in different market sectors (i.e. Filtration, Membrane for sportswear application, sound absorption textiles, reinforcement etc.). Within this study, the combination of thermoplastic Polyurethanes with Polyester has been investigated assuring good adhesion performances.

**Key Words:** Nanofibres; Adhesion; Sealant; Electrospinning

## 1. Introduction

Among nanomaterials, nanofibers represent one of the most attractive nano-device for the production of high added values products (i.e. thin fibres for filtration application, bone tissue engineering, drug delivery, catalyst supports, fibre mats serving as reinforcing component in composite systems, and fibre templates for the preparation of functional nanotubes). When the diameters of polymer fiber materials are shrunk from micrometers to sub-microns or nanometers there appear several amazing characteristics such as very large surface area to volume ratio flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material.
Polymeric nanofibers can be processed by a number of techniques such as Drawing, Template Synthesis, Phase Separation, Self-Assembly and Electrospinning. The latter is the cheapest and the most straightforward way to produce nanofibrous material[1].
Despite the fact nanofibrous material can be exploited in different market sectors [2], they have limited mechanical properties[3] and they are often deposited on resistant substrate such as porous woven fabrics and nonwovens that can provide structural support without affecting nanoweb morphology[4]. Since a composite material must be produced, a big challenge to promote market uptake of nanofibers is to assure proper adhesion of the mats onto the substrates in working conditions. In this work, different amounts of the polyurethanes (PUs) adhesive were used to alter the properties of electrospun polymeric fibers, and the effects of the adhesive were studied by applying the sealant on polyester nanofibres. In fact, applications involving nanofibers are limited due to their insufficient mechanical properties derived from the nonbonded structure of the electrospun mats[5].
The effects of different blending rations on morphology and structure of the electrosun fibers have been investigated. The composite mats formed with the proper amount of adhesive can broaden the practical application: point-bonded structure in nonwoven mats can increase the surface area as well as decrease the pore size by increasing the number of interconnected pores throughout the mat. Therefore, the modified fibrous mats of the polymer should have greater potential in filtrations, tissue engineering, protective clothing and construction materials than the non-bonded structure.

## 1. Material and Methods

### 1.1 - Materials and Equipment used for the production of the nanofibrous web

Polyester granules (provided by UNIPI, Pise) have been used as raw material for the production of Polyester nanofibres.

A thermoplastic polyurethane has been used and combined with polyesters since it can assure proper sealant properties according to its Glass Transition Temperature. Polymers and their combinations have been solubilised in a mixture of tetrafluoro acetic acid (TFA) and dichloromethane (DCM) and they have been purchased by Sigma Aldrich.

Polyester nets have been used as support for the deposition of the nanofibrous web.

Elmarco's NanospiderTM Production Line NS LAB200 based on needle-less electrospinning process available at Next Technology Tecnotessile (NTT) has been used for the production of the nanofibrous layer. Technical parameters of the machinery are listed in table 1.

**Table 1. Main technical characteristics of the Elmarco apparatus available at NTT**

| | |
|---|---|
| Number of spinning electrodes | 1 |
| Spinning electrode width | 200 mm |
| Effective nanofibre layer width | 200 mm |
| Spinning distance | 70 – 190 mm |
| Substrate speed | 0.13 – 1.57 m/min |
| Spinning voltage | 0 – 80 kV |
| Batch volume | 20 – 200 ml |
| Power | 0.45 kW |

The conditions investigated for the production of RPET nanofibres respectively are listed below (table 2).

**Table 2 – Process Parameters investigated within the study**

| Spinning solution | | Collector substrate material | | Equipment setting | |
|---|---|---|---|---|---|
| Polymer | PET<br>PET/PU<br>PU | Composition | PET net | Electrode | Yarn/Drum |
| Solvent | TFA:DCM (7:3) | Thickness | 0.5 mm | Electrode rotation speed | 0 – 16 rpm |
| Concentration | 5-20%wt. | Resistivity | $10^{13}$ | Distance of the electrodes | 7 – 19 cm |
| Additive | None | | | Voltage | 20 – 80 kV |
| | | | | Collector electrode | Yarn/Drum |

Produced fibrous webs have been thermal treated in a ventilated oven at optimal conditions in the range 120 – 160 °C for 3 – 5 minutes.

### 1.2 Characterisation methods

The morphological structures of the different structures (nanofibres; films; beads; microfibrous layer) and the diameters of the nanofibres were investigated by Scanning Electron Microscope (SEM; Phenom G2 pure desktop apparatus) working in the magnification range 20-17,000.

Open porosity has been determined by assessing a gravimetry analysis and a Capillary flow porometry, respectively.
The adhesion of the layer has been evaluated performing a peel test similar to the ISO 10373 by identifying the minimum force required to separate the nanoweb from the support.

**Results**
Pure PET fibers as well as their composite fibers with different amounts of PU adhesive were produced. Optimal process and products parameters have been defined for all the prepared polymer solutions.

**Table 3 – Optimal process and system parameters for the production of electrospun nanofibres**

| Polymer | Concentration | Voltage | Electrode | Distance |
|---|---|---|---|---|
| PET | 10%wt. | 70 kV | Yarn | 16 |
| PET-PU (3:1) | 7.5%wt. – 2.5%wt. | 73 kV | Yarn | 15 |
| PET PU (1:1) | 4%wt. – 4%wt. | 76 kV | Yarn | 14 |
| PU | 7% wt. | 80 kV | Yarn | 12 |

Morphological tests are showing than homogeneous nanolayers can be produced with all polymers at optimal process and system electrospinning parameters.

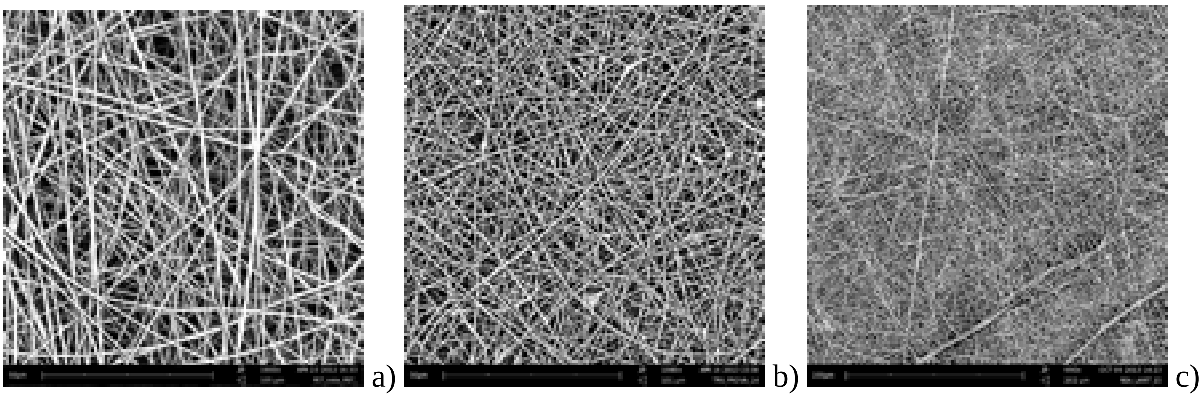


**Figure 1 – Morphology of the PET (a); PET-PU (b) and 100% PU (c) nanofibres**

In order to allow to bond the fibres all the samples were thermobonded at 150 °C for 5 minutes and the effect of the thermal treatment on fibres morphology has been investigated.
As shown in the SEM images, pure electrospun fibrous mats of PET did not possess any bonded structure between the fibers. The average fiber diameter of pure PET was approximately 300 - 400 nm and fiber diameter is increased by increasing the amount of with the amounts of PU in polyesters (600 – 700 nm) and depended on the viscosity and conductivity of the polymer solutions. The viscosity of pure polymer solutions increases with the amount of PU, inducing an increase in the electrical field required to spun nanofibres (Figure 2).

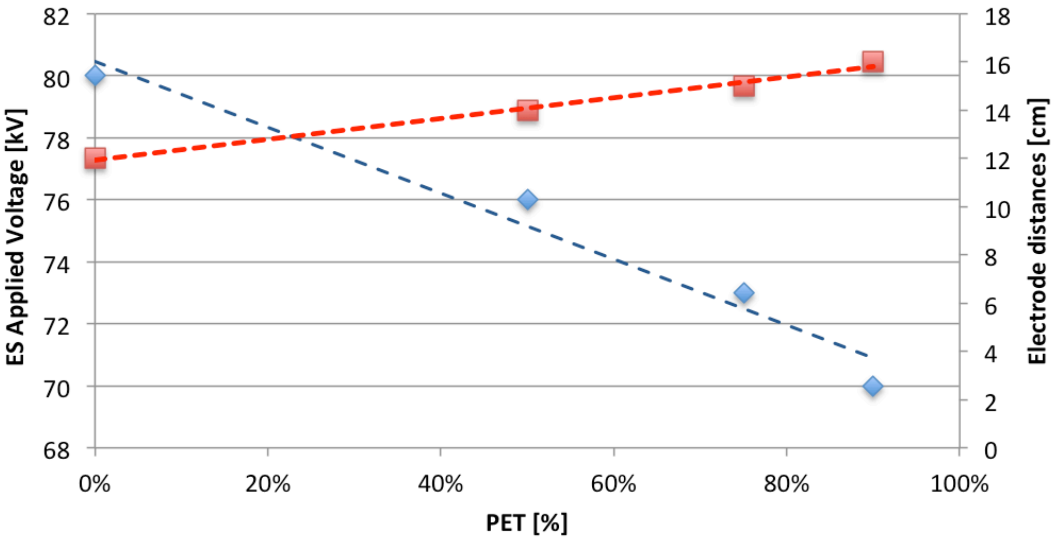
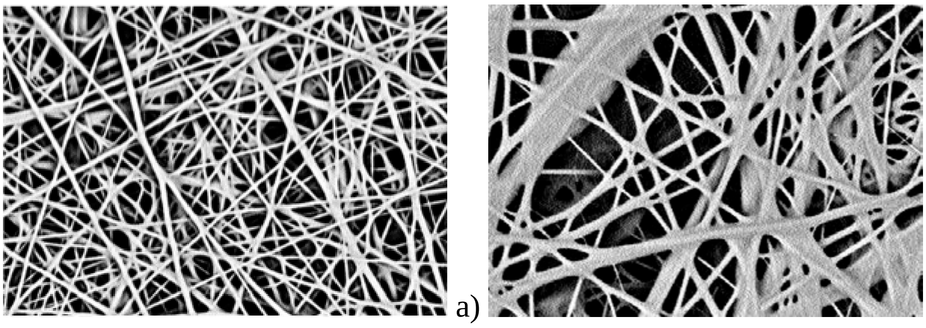



**Figure 1 – Trend of ES Voltage and Electrode distance with the amount of PET in the ES solution.**

At the same time, by increasing the fiber diameters a slight reduction of the open porosity and available superficial area is available.
However increasing the amounts of PU highly interconnected fibers throughout the mats can be produced.



a) b)

**Figure 3 – PU nanofibres before (a) and after thermal treatment (b). It is eveident that the thermobonding polyurethane is promoting point-bonded structure.**

The plot of the delamination tests performed on both PET, PET-PU 75:25 nanoweb is showing that in the overall there is any benefit on the average delamination force that it is around 0.25 N, but there is a significant improvement of the point bonded structures represent the to reinforce the non-woven fabrics since an homogeneous force must be applied.

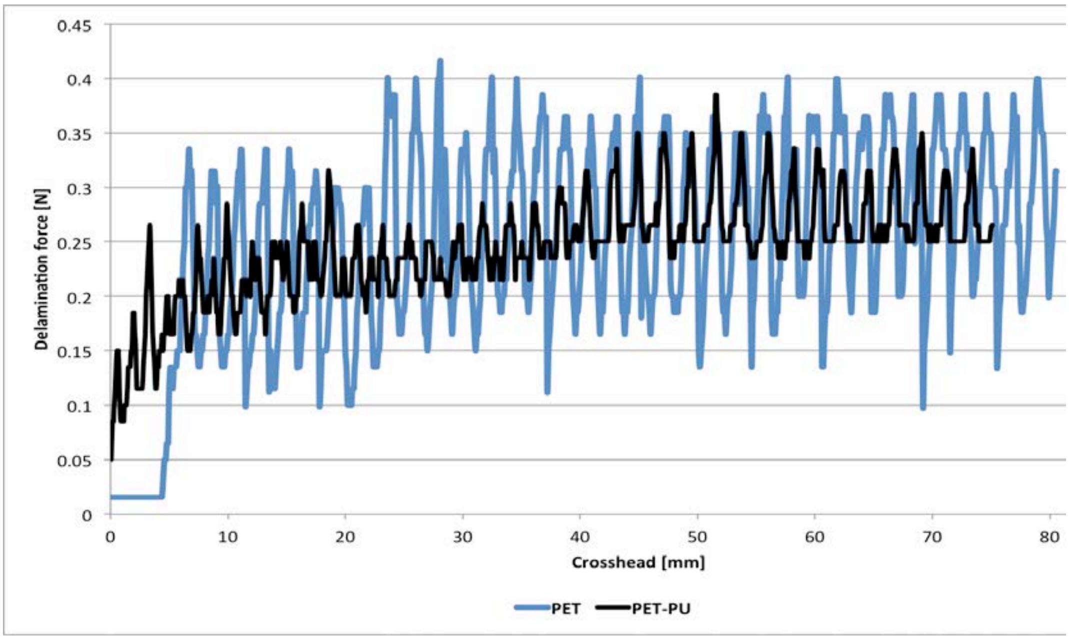



**Figure 4 – Delamination profile for virgin PET and PET-PU blend (75%-25%). The point bonded structure of the PU containing nanofibres is allowing to increase the resistance of the layer**.

In fact, three different types of bonding structures have been identified in non-woven mats: segmented, agglomerated, and point-bonded structures. Since the average values and maximum values is the same, it seems that there is no effect in the agglomeration and segmentation whilst the improvement on minimum force is related to with the non-bonded structure to the point-bonded fiber structure caused by PU.
By increasing PU content a significant improvement on the adhesion can be recorded, since a delamination force of 7.1 N is required to delaminate the nanolayer.

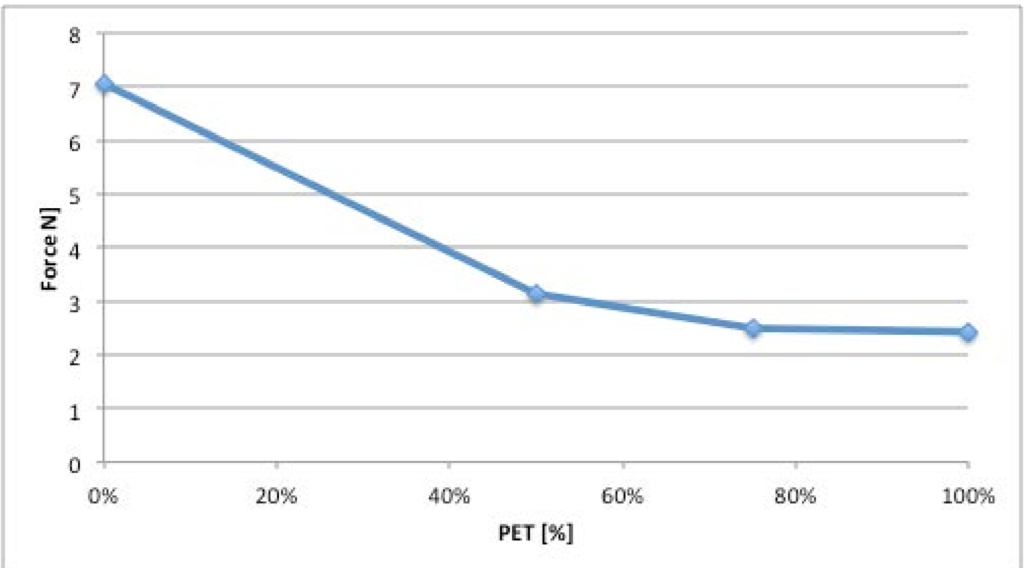



**Figure 5 – Trend of the average peel forces requested to remove the nanoweb from the support in function of the PET content in the blends**.

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**References**


[1] Composites Science and Technology 63 (2003) 2223–2253. A review on polymer nanofibers by electrospinning and their applications in nanocomposites; Zheng-Ming Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna

[2] Applications of Electrospun Fibers. P. Lu; B. Ding. Recent Patents on Nanotechnology 2008; 2: pp. 169-182.

[3] Int J. Nanomedicine. 2006 March; 1(1): 15–30. Nanofibers and their applications in tissue engineering. Rajesh Vasita; Dhirendra S. Katti

[4] The effect of supporting material type on the nanofiber morphology; Baturalp Yalcinkaya; Funda Cengiz Callioglu; 21. – 23. 9. 2011

[5] Uyar T, Balan A, Toppare L and Besenbacher F, Polymer 50:475–480 (2009).