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Water uptake of various electrospun nonwovens

Abstract: In recent years, nanofiber based materials have emerged as especially interesting for several biomedical applications, regarding their high surface to volume ratio. Due to the superficial nano- and microstructuring and the different wettability compared to nonstructured surfaces, the water absorption is an important parameter with respect to the degradation stability, thermomechanic properties and drug release properties, depending on the type of polymer [1]. In this investigation, the water absorption of different non- and plasma modified biostable nanofiber nonwovens based on polyurethane, polyester and polyamide were analysed and compared. Also, the water absorption by specified water wetting, the contact angle and morphology changes were examined. The results show that the water uptake is highly dependent on the surface modification and the polymer composition itself and can therefore be partially changed.

Keywords: nanofiber, water absorption, wetting, PCU-co-Si, TPC-ET, PA 6, PA 6.12

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1 Introduction

The water absorption of polymers acting as carrier for drugs, such as drug delivery systems (DDS) or implant coatings, is very important. The water absorption can significantly influence the thermomechanical properties, the degradation or the drug release of the used polymers. For instance, the water absorption of polymer coatings for implantable medical devices should be rather low in most cases. There, the water diffusion through the coating of the implant starts with the contact to water. Adhesion losses at the coating-implant interaction may eventually lead delamination of the coating. The implant is thus directly exposed to the environment. Hence, with a low water uptake the coating should be able to minimize delamination [2]. In contrast, the water uptake of wound dressings or DDS for a high initial drug release may need to be rather high. Thus, the biomedical application of polymers, amongst others, is dependent on the water absorption [3].

The water uptake is highly dependent on the fabrication method of the polymer, such as solvent cast films, scaffolds or nonwoven. In recent years, electrospun polymeric nonwoven have emerged as an interesting strategy for tissue engineering scaffolds, drug release systems, wound dressings, and others. In contrast to polymer films, the high surface to volume ratio of nonwovens can be ideal for maximising surface conjugation and encapsulated drug release, while the biomimetic fiber structure can lead to improved cell attachment [4].

In these studies, the water absorption of different non- and O_2-plasma modified non-degradable electrospun polymers was investigated via Karl-Fischer titration (KFT). Besides water absorption during 24 hours, the contact angles and morphology changes were analysed. The water uptake is highly dependent on the surfaces modification and the polymer type itself.

2 Materials and Methods

2.1 Materials

A thermoplastic silicone polycarbonate elastomer (PCU-co-Si) was provided by AdvanSource (Wilmington, USA). The thermoplastic polyester elastomer (TPC-ET) and one polyamide (PA 6.12) were provided by (DuPont, Wilmington, USA). Another polyamide (PA 6) was purchased by BASF (Ludwigshafen, Germany). The used solvents, such as chloroform, acetic acid and formic acid, were purchased by Roth (Karlsruhe, Germany).

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2.2 Methods

The electrospinning process was performed according to [5]. Homogenous polymer solutions were obtained by dissolving 7.5 - 14% (w/w) of the respective polymer in a specific solvent combination, such as formic acid and acetic acid (1:1 v/v). For the process of electrospinning, the commercial device 4Spin C4S LAB2 (Contipro, Dolní Dobrouč, Czech Republic) was used. Fibrous nonwoven were fabricated from polymer solution by the use of needle electrospinning. For this a single jet capillary emitter (gauge 19) and a static continual collector were used at an emitter collector distance in a range of 16 -24 cm resulting in nonwoven samples with random fiber formation. The applied high voltage was 25 - 54 kV, at a feed rate of 15 - 200 µL/min for ambient conditions of 25 °C and humidity of 40%. The spinning process was performed for approx. 1 h to reach a workable layer thickness. The nonwoven surfaces were activated using a radio frequency (RF) plasma generator (Diener electronic GmbH & Co. KG, Ebhausen, Germany) at a frequency 13.56 MHz, with oxygen plasma for 30 s at 40 W and 0.3 mbar, according to [6]

The nonwoven surfaces were examined inQuanta FEG 250 (Thermo Fisher Scientific, FEI Deutschland GmbH) scanning electron microscope (SEM). A mobile surface analyzer (MSA; Krüss, Hamburg, Germany) was used for analyzing the contact angles and the derived results of the surface energy. Presented mean values and standard deviations were calculated from n = 5 of all investigated polymer samples.

The specific water content of each polymer was determined via a Karl Fischer titrator (METTLER TOLEDO, Giessen, Germany). The polymer samples were weighed, given into a furnace (250 °C), which was connected to the KTF, the resulting water vapor was introduced into the electrolyte solution by a glass tube and the amount of water was determined (n =3).

The water absorption after 24 h of the polymer samples were tested based on the DIN EN ISO 62. The polymer samples were added to distilled water for 24 h at room temperature. Afterwards, the polymer samples were removed, dried for 5 min and analysed as described above.

3 Results

In these studies, the water absorption of non- and modified permanent polymer nonwovens was investigated. The polymer samples were produced via electrospinning and modified by O_2-plasma.

Table 1: Mean fiber diameter and standard deviation in µm of the investigated non- and modified electrospun nonwoven polymers (n = 10).

Polymer	non-modified [µm]	O_2-plasma modified [µm]
PCU-co-Si	1.28 ± 0.37	1.34 ± 0.35
TPC-ET	0.96 ± 0.16	1.24 ± 0.22
PA 6	0.12 ± 0.01	0.12 ± 0.01
PA 6.12	0.20 ± 0.02	0.16 ± 0.02

Besides the water absorption, the influence of the plasma modification on the fiber diameters, the contact angle and morphological changes were analyzed. The fiber diameters are shown in Table 1. Thereby the generation of the O_2-containing groups did not show a substantial influence on the fibers. Furthermore, it was shown that PCU-co-Si and TPC-ET as well as PA 6 and PA 6.12 have very similar fiber diameters.

No substantial changes of the fiber surface were detected via SEM. Several SEM images of the non- and modified polymers are presented in Figure 1. The fiber similarity of PCU-co-Si and TPC-ET, as well as PA 6 and PA 6.12, is also illustrated here.

Although hardly any morphological changes are visible due to the O_2-plasma modification, the surfaces of the polymers became more hydrophilic (Figure 2).

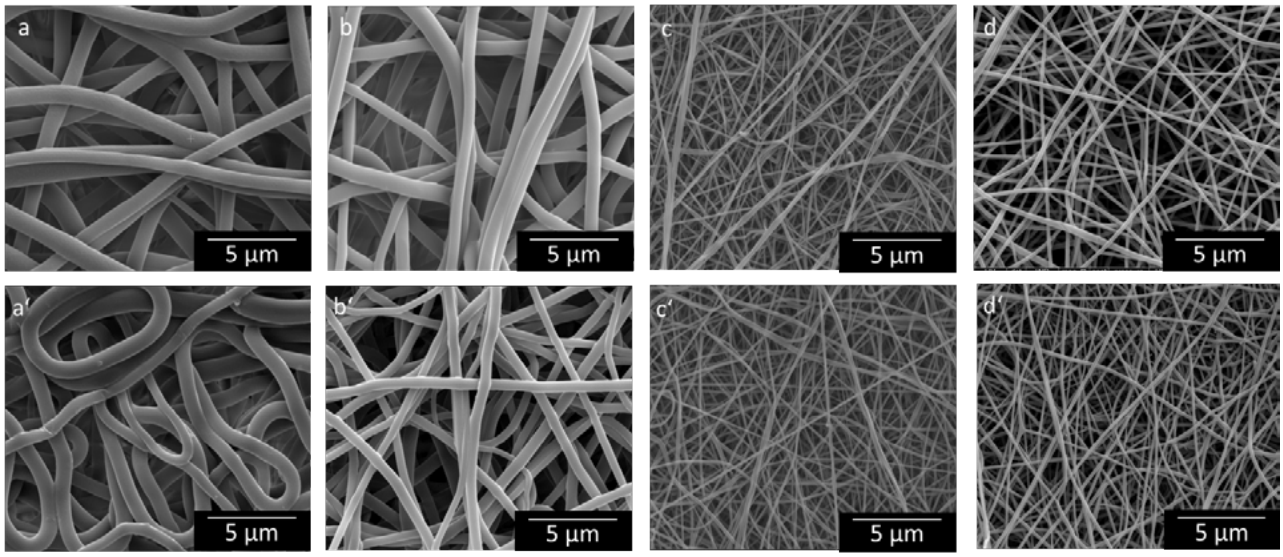

Figure 1: Representative SEM images of all investigated non- (a,b, c, d) and modified (a´, b´, c´, d´) nonwoven polymers samples (a) PCU-co –Si, (b) TPC-ET, (c) PA 6, (d) PA 6.12

The contact angles for PCU-co-Si and TPC-ET decreased about 16 ° and 20 °, respectively. The contact angle for PA 6 and PA 6.12 decreased about 56 ° and 97 °, respectively.

The water absorption of the different polymers is shown in Figure 3. Except for TPC-ET the water absorption of the non-modified polymer samples after 24 h of wetting is in the range of 6.5 - 8%. For TPC-ET, the water absorption was only 0.1%. The water absorption for all polymers was higher after the O_2-plasma modification in comparison to the non-modified polymer samples.

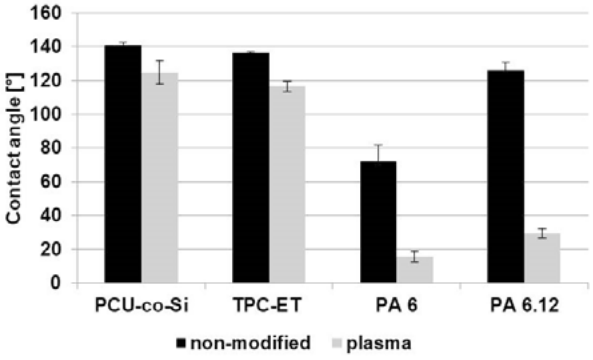

Figure 2: Water contact angle Θ_W ± standard deviation (SD) of the investigated non- and modified polymeric nonwoven determined with the sessile drop method (n = 5).

The water absorption for PCU-co-Si and TPC-ET were rather similar with around 13% after O_2 plasma activation and wetting over 24 h. Surprisingly, for PA 6 and PA 6.12 the water absorption was much lower with 2% and 0.3% compared to the unmodified samples after wetting over 24 h with 7 to 8%.

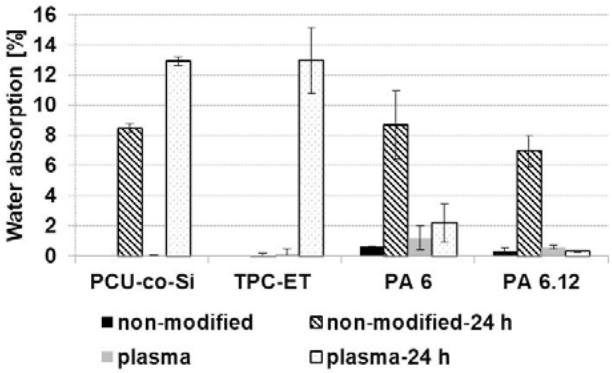

Figure 3: Water absorption of the non- and modifed polymer samples after water wetting (24 h, n = 3)

4 Discussion

Within this research the water absorption of different polymers was investigated. Although PCU-co-Si and TPC-ET show similar ranges of fiber diameter, contact angle and morphology, only the water absorption is rather different. The PCU-co-Si and TPC-ET are based on different types of polymer. PCU-co-Si is a silicone-based copolymer and TPC-ET is a thermoplastic polyester elastomer

The non-modified TPC-ET absorbs only 0.1% after 24 h wetting in contrast to PCU-co-Si with around 8%. This may be caused by the wetting ability of the surface. While the most electrospun nonwoven are hydrophobic due to their surface geometry, the O_2-plasma modification leads to an increased wettability, which is also supported by the change in the contact angle. This leads to an increased contact area

between the nonwoven and the surrounding water. Therefore, the water absorption increases substantially.

PA 6 and PA 6.12 are similar in morphology and fiber diameter, but the contact angles and water absorption are different. The contact angle for PA 6.12 is higher which indicates a more hydrophobic surface compared to PA 6, which is also reflected in the water absorption. The water absorption for all investigated PA 6.12 samples was less than for PA 6 samples. This is probably caused by the molecular structure of the polymers. PA 6 has a higher ratio of heteroatoms in the polymer chain. These are responsible for the interaction with water and thus the water absorption ability. This ratio is lower for PA 6.12 resulting in a lower water uptake (Figure 4).

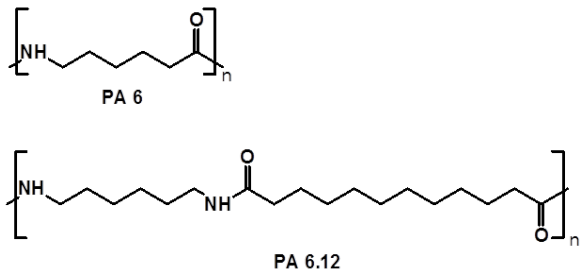

Figure 4: Chemical formula structures of PA 6 and PA 6.12

Within this study alternative promising polymers in comparison to PCU-co-Si and PA6 were investigated in view of their water absorption. TPC-ET and PA 6.12 have relatively similar properties compared to PCU-co-Si and PA 6, respectively. The observed unusual effect of PA 6 and PA 6.12 of the lower water absorption after the modification will be subject of further investigations. The ability to alter water absorption of implants may open new applications in biomedical engineering.

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