OXYGEN PLASMA MODIFICATION OF POLYESTER-BASED POLYURETHANE SURFACES: STABILITY OF SURFACE FUNCTIONALITIES IN TIME

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Introduction

Polyurethanes are a large family of polymers widely used in medical devices with one common characteristic of the presence of urethane linkages along the large molecular chains. The urethane linkages are formed by the reaction of isocyanates (-NCO) and alcohols (-OH) and in general consist of only a small component of the total chain, with the greatest number of linkages contributed by the macroglycol. Polyurethanes are among the best choices for biomedical applications because of their tunable properties such as durability, elasticity and fatigue resistance, connected with their segmented polymeric character. Thus, polyurethane can be tailored to meet the desired properties for a wide range of applications.
Owing to their versatility of chemical composition, polyurethanes are now the highest-performing biomedical-grade elastomers. For biomaterial applications, the interaction of a material's surface with cells is of critical importance. The interaction strongly depends on the physicochemical properties of the surface, such as its hydrophilicity, roughness, or presence of functional groups, microstructure, and mechanical properties. Such properties determine cell attachment, as well as cell spreading behavior, proliferation, and differentiation.
The surface characteristics of a material can be adjusted to a specific application by surface modification techniques, without changing the material bulk properties. The capacity of polyurethanes to undergo modifications increases their suitability for biomedical applications. The functionalization can be obtained with the use of plasma treatment by the generation of surface functional groups. The superiority of the proposed method is based on its simplicity, efficiency, and environmental friendliness.

Materials and Methods

The commercially available aromatic polyester polyurethane samples provided by American Polyfilm, Inc were modified using oxygen plasma using a Diener electronic Femto plasma system (Diener Electronic GmbH, Nagold, Germany) at variable parameters (oxygen partial pressure, generator power, modification time). The changes within the surface were followed by contact angle measurements, using a Surftens universal instrument (OEG GmbH). Static contact angles of water were calculated using Surftens 4.3 — windows image processing software for digital images for the determination of contact angles and surface tension. The chemical surface composition of the polyurethane samples was examined with the use of XPS (SES R4000, Gammadata Scienta).

Results and Discussion

One of the most common techniques for improving biocompatibility of polymeric surfaces is oxygen plasma treatment. The most important issue is to adjust plasma parameters for particular polymeric material and its application. Detailed characterization of the oxygen plasma-treated surfaces is crucial because the biological moieties are rigorously sensitive to the geometrical and chemical factors of the material surface.
The introduction of oxygen functional groups has a significant influence on the wettability of the investigated material. Unmodified polyester polyurethane remains hydrophobic, with a water contact angle slightly above 90°. In this work, several oxygen plasma modification parameters were tested (pressure 0.12, 0.2, 0.3 mbar; plasma generator power 25, 50, 75, 100 W, and plasma treatment time 6s -10 min). It was revealed that the strongest impact on surface modification has the oxygen partial pressure in the plasma chamber (FIG. 1A). A fully wettable surface was obtained for the lowest modification pressure (0,12 mbar). A slight modification was observed for 0,3 mbar and even after a long modification time (10 min) the water contact angle does not exceed 50°. It was also revealed that plasma generator power has no significant effect in the investigated range.

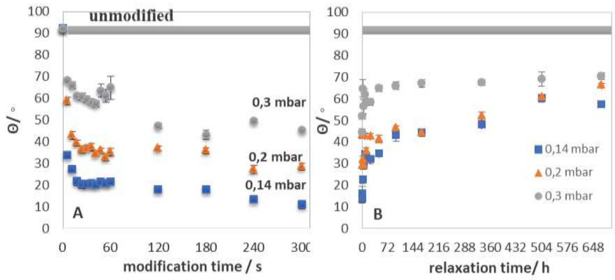

FIG. 1. Experimental water contact angles (θ) for different gas partial pressure (A), and the corresponding kinetic curves of plasma relaxation of activated polyurethane surfaces (B).

To identify the chemical nature of the generated surface functional groups on the polyurethane were investigated with the use of XPS. The results revealed the significant changes between oxygen plasma modified and unmodified surfaces. The XPS spectra (C1s) for both surfaces were deconvoluted, and the characteristic binding energies for oxygen-containing groups were assigned (C=O, C-O, COOH, OH).
The oxygen plasma treatment leads to fully wettable polyurethane surfaces. The modification effect is, however, not stable in time, and the relaxation kinetic curves of hydrophobicity are presented in FIG. 1B. The increase of water contact angle in time was observed for 2 weeks after plasma treatment from ~10 to 60°, yet, never reached the initial value for the unmodified sample.

Conclusions

The oxygen plasma modification on polyurethane surfaces is an efficient technique for increasing hydrophilicity and has a significant impact on biocompatibility. The presented studies revealed oxygen partial pressure as a crucial parameter for polyester-based polyurethane modification. The oxygen-containing groups incorporated in the polyurethane surface provide a suitable platform for further modification. Since the assumptions for the functionalization procedure are of a general nature, the obtained results can be easily extended for other plasma feed gases and polymeric materials.

Acknowledgments

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