SURFACE FUNCTIONALIZATION OF POLYURETHANE BIOMATERIALS: COMBINED EXPERIMENTAL AND MOLECULAR DYNAMICS SIMULATIONS APPROACH

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[ENGINEERING OF BIOMATERIALS 163 (2021) 41]

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. Properties such as elastomeric and fatigue resistance are the basis of polyurethanes' success in biomedical science. Owing to their versatility of chemical composition, polyurethanes are now the highest-performing biomedical-grade elastomers. The availability of polyurethanes in several forms, i.e. of adhesives, coatings, sealants, rigid and flexible foams as well as textile fibres all of them in wide hardness range (from soft to super hard in Shore hardness scale) allow their use in pacemakers, catheters, vascular grafts, heart assist balloon pumps, artificial heart bladders and wound dressings [1].

The chemical modification strategies to prevent bacterial colonization have employed different types of bactericidal substances (e.g., metallic nanoparticles, peptides, antibiotics), among which antibiotics are most frequently used. Although the worldwide epidemic of antibiotic resistance is in danger of ending the common antibiotic therapy, there is still a lack of better drugs substitutes that can effectively prevent and cure infections. Antibiotic resistance cannot be restrained, but its development and spread can be significantly slowed down by curtailing a large amount of unnecessary antibiotic use in medical treatment. Therefore, implants surface functionalization to prevent biomaterial-centered infection (BCI) states an attractive alternative option to the typical prevention pathways. Therefore, understanding the factors affecting bacterial adhesion to surfaces is crucial for the design of novel and safe biomaterials.

The study aimed to optimize the plasma modification parameters of polyurethane surfaces with oxygen-containing surface groups. Such functionalization enhances the interactions between body fluid ions and the polymeric surfaces, observed experimentally as calcium phosphate formation, peptide (RGD) and protein (casein) adsorption. The experimental investigations were complemented with the use of molecular dynamics simulations which allow for an in-depth understanding of the interfacial processes.

Materials and Methods

Oxygen plasma modification. To modify the polymeric surfaces, oxygen plasma treatment was carried out using a Diener electronic Femto plasma system at 50 W and an oxygen partial pressure of 0.14 mbar. The varied parameter was the time of exposure to the plasma, which was in the range of 0.1−10 min.

Materials characterization. The samples were characterized with the use of spectroscopic (ATR-IR, XPS, SIMS, DSC) and microscopic (fluorescence microscopy, SEM) methods. The adsorption of peptides and proteins was followed by Quartz Microbalance.

Atomistic Molecular Dynamics Simulations. Fully atomistic molecular dynamics simulations were performed to investigate interactions between water molecules and several surfaces modelling polyurethane. In our model, the slab configuration was used with two model surfaces interacting with a slab of water [2].

Results and Discussion

Upon oxygen plasma treatment, the originally hydrophobic polyurethane surfaces (Θw=99º) turn into hydrophilic and a dramatic decrease of water contact angle value to Θw=0.1º (50W, 0.14 mbar, 6 min) was observed. As a consequence, the calculated values of Surface Free Energy (SFE) were changed accordingly. Initially, the SFE of unmodified polymer is 28.1 mJ/m^2 and consists mostly of the dispersive component. Modification with oxygen plasma results in the incorporation of oxygen-containing surface groups such as -OH, -CHO and -COOH, as identified with the use of XPS (FIG. 1A). The functional groups alter significantly the kinetics of RGD and casein adsorption, which is a good measure of biocompatibility of the modified polyurethane surfaces.

Moreover, the experimental measurements were complemented with theoretical studies using MD simulations. A representative image of the N atom distribution of the polyurethane chains in the simulation box is presented in FIG. 1B. The simulations allow determining which surface functional surface coverage is optimal in terms of biocompatibility and in a broader perspective allow to design functionalized implantable polymeric materials and their fine tuning.

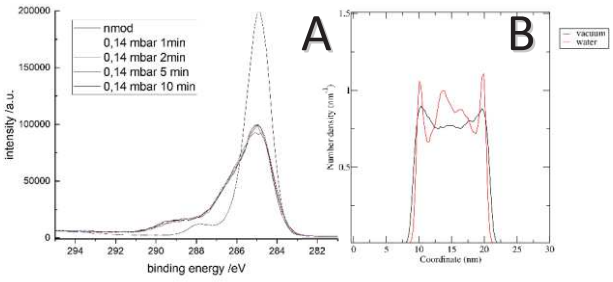

FIG. 1. Representative C1s XPS spectra of unmodified (nmod) and oxygen plasma modified polyurethane (A) accompanied by a representative image of polyurethane chains N atom distribution in the MD simulation box (B).

Conclusions

The study clearly shows that such a comprehensive experimental and theoretical approach allows for knowledge-based design and optimization of polymeric biomaterials interfaces, crucial in terms of biocompatibility and lowering the risk of BCI.

Acknowledgments

This study was financed by the Polish National Science Centre project awarded by decision number DEC-2019/35/D/ST5/03107.

References

[1] Chytrosz P. *et al.* ACS biomaterials science & engineering, 2021, 7.4: 1403-1413.
[2] Golda-Cepa M. *et al.* ACS applied materials & interfaces, 2017, 9.19: 16685-16693.