Surface characterization of novel biodegradable poly(peptide-urethaneurea) block copolymers

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Introduction: Polyurethanes (PUs) have been widely used in the field of biomaterials [1-2] as they exhibit excellent mechanical properties. However, as with other polymers, their biocompatibility with living tissues is not ideal. One approach to improving their biocompatibility is to incorporate peptide-like segments into the PU backbone. A combination of such segments mimics natural amino acid sequences and together with conventional hard segments (HS) and soft segments (SS) provides an elastomeric material with excellent mechanical and specifically biodegradable properties. As biodegradation processes are normally initiated at the interface between biomaterials and living tissues, control of the polymer surface composition can be used to optimize the biodegradation processes.

This study investigates the surface composition of novel linear segmented poly(peptide-urethaneurea) (PPUU) block copolymers. These segmented PUs are based on a L-lysine diisocyanate (LDI) HS, a polycaprolactone (PCL) SS, a hydrazine (Hyd) chain extender and an oligopeptide segment (OPS). The latter consists of proline (Pro), hydroxyproline (Hyp) and glycine (Gly).

Methods: Two compositions of PPUU and two corresponding control compositions of poly(urethaneurea) (PUU) without OPS were synthesized via the standard procedure of multi-step addition polymerization in dimethylacetamide (DMAc)[1]. The control polymers were synthesized with LDI/PCL/Hyd molar ratios of 4/1/3 and 8/1/7 (PUU 413 and 817). The PPUUs were synthesized based on PUU 413 and 817 compositions with the addition of a collagen-like OPS (Gly/Pro/Hyp molar ratio of 2/1/2). The total PCL/LDI/Hyd/(Gly/Pro/Hyp/Hyd) molar ratios were 4/1/2/(1) and 8/1/6/(1) (PPUU 4121 and 8161).

Smooth and uniform polymer layers for surface analysis were obtained by spin coating the four synthesized PUs onto glass slides from 2.5 wt% solutions in DMAc. The spin-coated samples were then characterized with Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) and Time of Flight Secondary Mass Ion Spectroscopy (ToF-SIMS). The ToF-SIMS data were processed with Principal Component Analysis (PCA). This multivariate analysis technique was used to examine differences in the spectra collected from the four PUs.

Results: ARXPS was used to examine how the polymer composition in the near surface region changes with sampling depth. This analysis showed a decrease of the N/C ratio at the smallest sampling depth for both the control PUUs and main PPUUs. Among the three segments, the PCL is the only one that does not contain nitrogen and therefore the ARXPS results suggest that the PCL SS concentration is higher at the outermost surfaces of all four PUs.

Due to their difference molecular structures, ToF-SIMS can differentiate between the nitrogen containing HS and OPS segments. Applying PCA, like the example shown in Fig. 1, was used to determine a list of characteristic ions in Fig. 2a that are unique to each of the segments. A comparison among the relative intensities of the characteristic ions is shown in Fig. 2b. The ToF-SIMS data in Fig. 2b is consistent with the SS surface enrichment observed in the ARXPS experiments.

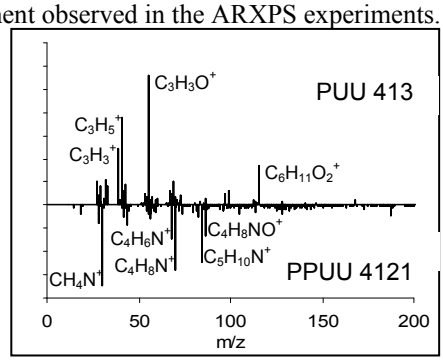

Figure 1. ToF-SIMS/PCA results for PUU 413 vs. PPUU 4121.

(a) SS	39.0232	C_3H_3
	41.0368	C_3H_5
	55.0168	C_3H_3O
	69.0725	C_5H_9
	115.089	$C_6H_{11}O_2$
HS	18.0359	NH_4
	28.0193	CH_2N
	30.0346	CH_4N
	32.0378	N_2H_4
	33.048	N_2H_5
	84.0856	$C_5H_{10}N$
OPS	68.0516	C_4H_6N
	70.0705	C_4H_8N
	86.0628	C_4H_8NO

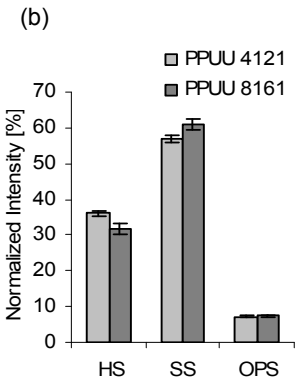

Figure 2. (a) Characteristic ions of the SS, HS and OPS and (b) normalized intensities of these ions for PPUU 4121 and 8161

Conclusions: The ARXPS and ToF-SIMS experimental data show that the surfaces of these four new PUs are enriched with the PCL SS, the most hydrophobic segment of these PUs. The combination of ToF-SIMS and PCA allowed characteristic fragments for each segment to be identified.

Future Studies: Currently the mechanism and kinetics of surface degradation after exposure of these novel block copolymers to different biological environments is being studied.

References:

1. Simonovsky FI. J Biomater Sci Polymer Ed. 2005;16: 267-284.
2. Sanders JE. Biomaterials 2005;26:813-818.