In Vitro Studies Of Polydimethylsiloxane Based Polyurethanes: Correlation With Microstructure

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Statement of Purpose: Polydimethylsiloxane (PDMS) based polyurethanes (PU) present excellent long-term biostability compared with other commercially available polyurethanes[1]. In this study we mimic *in vivo* conditions through *in vitro* accelerated tests[2] in order to investigate the resulting microstructure of annealed and non-annealed PDMS-PUs. Polytetramethylene oxide (PTMO)-PU films are used as a control.

Methods: PDMS-PUs were prepared from methylendiisocyanate (MDI), butanediol (BDO), and polyhexamethylenoxide (PHMO) and PDMS as the soft segment (20/80(w/w))[3]. Thermal annealing was carried out at 120 ^{0}C for 6 h. In vitro accelerated tests were performed on films (40 wt% hard segments, 120 µm thickness). Samples of each polymer were withdrawn at regular intervals of 24, 48 and 72 days. All samples were examined using scanning electron microscope (SEM). ATR-FTIR and small-angle X-ray (SAXS) experiments were also conducted on untreated and oxidized samples.

Results / Discussion:

In vitro experiments Physical degradation of all the samples was observed by SEM (Figure 1). As can be observed the control surface is totally eroded and presents large cracks. In contrast, PDMS-PUs present a much less eroded surface and the annealed sample is less damaged than the non annealed sample.

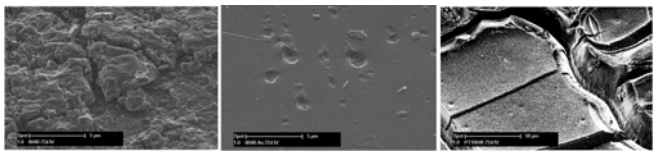

Figure 1 Surface structure after 72 days *in vitro*: (a) PDMS-PU40. (b) PDMS-PU40annealed. (c) control

The decrease in absorbance of the IR band at 1110 cm^{-1} and the appearance of a shoulder at 1171 cm^{-1} (Figure 2) indicate degradation of the polyether soft segments in the control materials[2]. The spectra of PDMS-PUs present two large Si-O-Si stretching bands at 1072 and 1016 cm^{-1} and no evidence of PDMS degradation is observed after 72 days *in vitro*. Any PHMO oxidation cannot be followed due to overlap of the band at 1110 cm^{-1}. Hard segment degradation is observed in non-annealed PDMS-PU40 as evidenced by the decreased intensity of the bands at 1530 and 1229 cm^{-1}, assigned to the urethane amide[2]. Changes in microstructure upon oxidation were studied in further detail using SAXS (Figure 3). The observed scattering peak arises from the difference in electron density between the hard and the soft domains, and its position is related to the mean interdomain spacing, d ($d = 2\pi/q_{max}$).

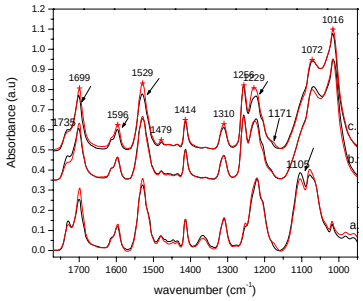

Figure 2. ATR-FTIR of the untreated (black) and after 72 days *in vitro* (red). (a) control; (b) PDMS-PU40a; (c) PDMS-PU

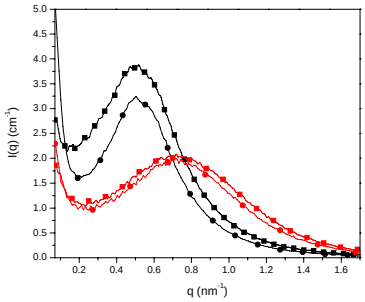

Figure 3 Background corrected SAXS intensities as a function of scattering vector, q, for PDMS-PU40 (red) and PTMO-PU (black) (■) untreated,(●) after 24 days *in vitro*

The interdomain spacing and the total scattering intensity (absolute units) do not change for the PDMS-PUs after 24 days *in vitro* treatment, indicating no significant change in the hard/soft domain organization. In contrast, the total scattering intensity of the oxidized control decreases with respect to the untreated sample. The origin of this change might be due to a reduced electron density contrast arising from a higher electron density of the oxidized soft phase.

Summary: The *in vitro* biostability of PDMS based PU was related to its microstructure through ATR FT-IR and SAXS experiments. In contrast to PTMO-based materials, PDMS-based PUs exhibited almost no degradation under strongly oxidative conditions and the degradation was less severe in annealed samples.

References

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3. Martin DJ., *et al*. Biomaterials. 2000; 21:1021