Characterization of Dynamic Shape-Memory (Meth)Acrylate Networks for Tissue Engineering Applications

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Statement of Purpose: Micro-scale roughness has been shown to increase osteoblast cell differentiation over smoother surfaces but decrease cellular proliferation [1]. Thus, a smart material that can provide a smooth surface to promote initial cell attachment, spreading and proliferation, and over time display micro-scale roughness to enhance differentiation could be beneficial for tissue engineering applications. In this study, we create one such polymer by fine-tuning the properties of an acrylate based shape-memory network and mimicking the topography of control and grit-blasted titanium through soft lithography.

Methods: Acrylate solutions were achieved by first combining varied ratios of benzyl methacrylate (BZMA) and benzyl acrylate (BZA) with 5% w/v 1,12-dodecanediol dimethyacrylate (DDDMA) as the crosslinker and 0.5% w/v 2,2 dimethyoxy 2-phenylacetophenone (DMPA) as the photoinitiator. PDMS molds were made using a Sylgard 184 kit with a base to curing agent ratio of 10:1, poured over titanium sheets (control "PT" or grit-blasted "GB"), allowed to de-gas, and baked at 150° C for 10 min. Sheets of shape-memory polymer were created by photopolymerizing the previous networks between glass slides with or without PDMS molds with 1-mm glass spacers. Glass transition temperature (T_g) was determined by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Laser-cut 15 mm disc samples were then compressed using an MTS Insight for up to 40% strain and allowed to recover in phosphate buffered saline at 37° C for up to 7 days, and roughness measured via laser confocal microscopy.

Results: To achieve a shape-memory polymer that would recover at body temperature, networks were created with seven weight ratios of BZA:BZMA at a constant wt% DDDMA (Fig. 1). Wet samples for DSC were soaked in ddH_2O to determine if water uptake would decrease the T_g (7 day data were not statistically different from 24 hour data). The onset of the T_g determined by DMA for BZA:BZMA:DDDMA 30:65:5 (boxed in Fig 1) falls near this temperature (Fig 2),. This composition was used for subsequent compression and recovery experiments.

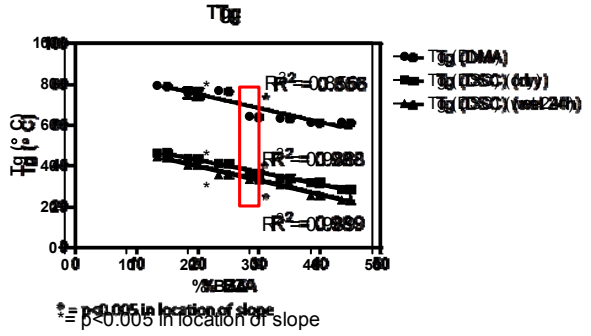

Fig 1 – T_g dependence on soaking and BZA concentration from 15 to 45 wt%

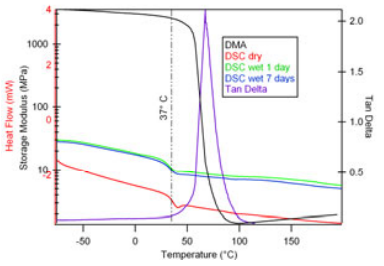

Fig 2 – DMA and DSC data for 30:65:5 polymer network

Figure 3A shows roughness and height recovery of the 30:65:5 polymer made from GB Ti (pGB) with up to 40% strain compared to the smoother polymer made from PT Ti (pPT, dashed line). Transfer and recovery of the complex microtopography can be seen in Fig 3B.

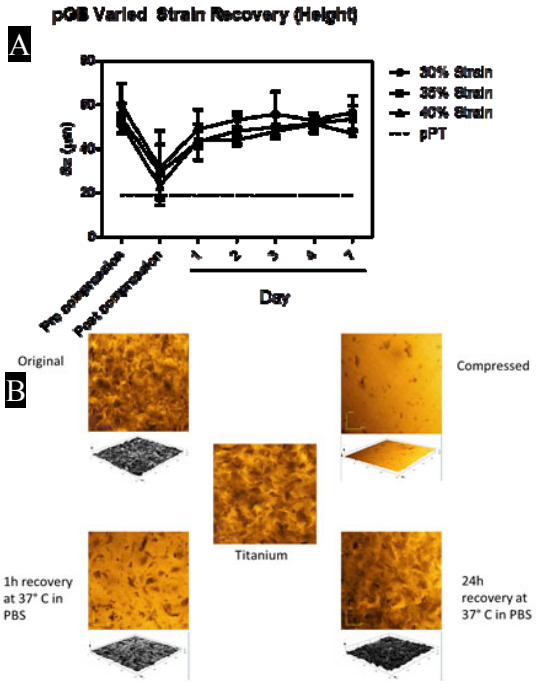

Fig 3 – (A) 7 day recovery ~~of roughness (Sa) and~~ peak-to-valley height (Sz) for strains from 30-40%. (B) Confocal images of polymer network recovery and initial titanium surface

Conclusions: We have developed a process for transferring micro-scale surface features from metals to shape-memory polymers (SMPs) via soft lithography and have shown that these polymers recover over time irrespective of compressive strain of up to 40%. We are able to tune the ~~glass transition temperature~~Tg of these SMPs to that of homeostasis for future biological experiments on this ~~non-toxic~~ SMP, and are in the process of tailoring recovery rate at that temperature.

References: Olivares-Navarrete, R, *et al.* PNAS 2008;105(41):15767-72