Design of polyurethane-based temperature- and pH-responsive hydrogels

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INTRODUCTION: Polyurethanes (PUs) are very tunable polymers due the high versatility of their chemistry that allows the synthesis of materials with very different properties by simply changing their building blocks. With the final aim to design thermo- and pH-responsive hydrogels for injectable or 3D-printing applications, an amphiphilic PU was first synthesized and its powder were then plasma-treated in the presence of acrylic acid (AA) vapor to graft acid groups along polymer backbone.

METHODS: An amphiphilic PU was synthesized according to [1] and its powder with controlled diameter were plasma-treated with Ar and AA vapor to expose –COOH groups (P-PU), thus enhancing hydrogel sensitivity to alkaline pH. Chemical characterization was performed by Size Exclusion Chromatography (SEC), Infrared (IR) Spectroscopy, Toluidine Blue O (TBO) assay and Proton Nuclear Magnetic Resonance (^{1}H-NMR). PU and P-PU gels (15% w/v) were characterized in terms of sensitivity to temperature (tube inverting and gelation time tests at 37°C, rheology) and external pH (hydrogel pH change in response to external pH, swelling test in contact with buffers at pH 5 or 8). Finally, an innovative investigation of hydrogel thermo- and pH-sensitivity was conducted by Low-Field NMR.

RESULTS: SEC and IR assessed the successful PU synthesis, while TBO assay, ^{1}H-NMR and IR demonstrated the grafting of –COOH groups to PU chains and evidenced a high intra- and inter-synthesis repeatability of the plasma treatment. Tube inverting, gelation time and rheological tests showed the ability of both PU and P-PU solutions (15%w/v) to undergo a sol-to-gel transition at about 27 °C. However, frequency sweep tests showed different storage and loss moduli crossover frequencies at each analyzed temperature (58 *vs* 82 rad/s, 4 *vs* 6 rad/s and 0.25 *vs* 0.15 rad/s for PU and P-PU gels at 25, 30 and 37 °C, respectively), suggesting that the exposure of -COOH groups slightly slowed down gelation kinetics. Concerning sensitivity to basic pH, P-PU gels transferred alkaline pH from the external medium to the gel core with a significantly faster kinetics, resulting from an increased sensitivity of almost the 60% compared to PU gels. Conversely, both systems behaved similarly in the presence of acid buffers. Swelling test against an alkaline buffer confirmed the improved absorption ability of P-PU gels compared to the control (3.3% *vs* 1.1%, respectively). These results were further proved by LF-NMR that allowed the investigation of hydrogel structural changes at the micro/nano-scale in response to temperature and pH changes in terms of micelle nucleation and organization and their interaction with water molecules.

DISCUSSION & CONCLUSIONS: PUs are promising candidates for the design of stimuli-responsive hydrogels, as their properties can be easily tuned by changing their building blocks. In this work, stimuli-sensitive PU-based hydrogels were successfully designed and their thermo- and pH-responsiveness was thoroughly investigated.

REFERENCES
[1] Boffito M. et al. Polym Int. 2016; 65:756-769