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# **Electronic Supplementary Information**

## Improved properties of composite collagen hydrogels: protected oligourethanes and silica particles as modulators

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#### 1. Scheme of the composite hydrogel formation

Figure S1 schematizes the steps of the hybrid hydrogel formation and their derivative materials.



*Figure S1*. Schematic description of the simultaneous process of fibrillogenesis/crosslinking of type I collagen to generate composite hydrogels (a). Schematic drawing of the urea linkages between collagen and oligourethanes (b). Aspect of the final composite material (c and d).

### 2. ATR-FTIR characterization of oligourethane-silica crosslinker

Figure S2 illustrates the IR signals for Si-O-Si bonds in oligourethane-silica in both liquid and solid states, indicating that the mild drying process does not contribute significantly to the silica

condensation. This confirms that small colloidal silica particles are dispersed in the oligourethane solutions.



*Figure S2*. ATR-FTIR spectra for crosslinker based on P(IPDI) oligourethane and silica, in liquid and solid states (a). Extension of the typical region for Si-O-Si bond (b).

#### 3. Polymerization of collagen in presence of silica-oligourethanes

Figure S3 illustrates change of absorbance over time for different materials. Figure S4 shows that hydrogels with silica have lower nucleation time ( $t_{lag}$ , 9.5 min) than silica-free materials (19.3 min). Besides the polymerization rate (S) is higher for materials with silica (0.0123 min<sup>-1</sup>) than for silica-free materials (0.0109 min<sup>-1</sup>). Thus, the incorporation of silica particles to collagen-oligourethane hydrogels accelerates the polymerization of type I collagen.



*Figure S3*. Turbidimetric gelation analysis of collagen hydrogel crosslinked with silicaoligourethanes. The legend indicates the COL hydrogels composited with silica-oligourethanes derived from TEOS, PEG and hexamethylene (P(HDI)), isophorone (P(IPDI)), trimethylhexamethylene (P(TMDI)) or L-lysine (P(LDI)) diisocyanates.



Figure S4. Turbidimetric gelation analysis of the hydrogels without or with silica (5 wt.%). The legend indicates the COL hydrogels composited with oligourethane (30 wt.%) based on isophorone diisocyanate (IPDI).

#### 4. SEM images

COL

Figure S5 illustrates the SEM images indicating the pore size by means of the yellow line highlighting the biggest pore in each SEM micrograph. Figure S6 shows additional SEM micrographs (enlarged zones) to compare the various microstructures in the biocomposites. The surface of the composite materials is featured by a fibrillar structure. The silica deposited on materials are also observed.





3

*Figure S5*. SEM images indicate the pore size in the materials (Scale bar: 300 µm).



*Figure S6*. SEM images indicate the fibrillar structure of the materials and the deposition of the silica particles in the materials (Scale bar:  $10 \ \mu m$ ).

#### 5. Scheme of the working hypothesis

Figure S7 illustrates that isocyanate groups with low degree of substitution in neighboring groups, such as HDI and LDI, increase the urethane oligomerization and the collagen crosslinking, compared to the isocyanate groups impeded by steric hindrance, such as IPDI and TMDI.



*Figure S7.* Graphical summary of the influence of the chemical structure of the aliphatic diisocyanates on the crosslinking capacity of collagen with oligourethanes.