Supplementary Figure S1.

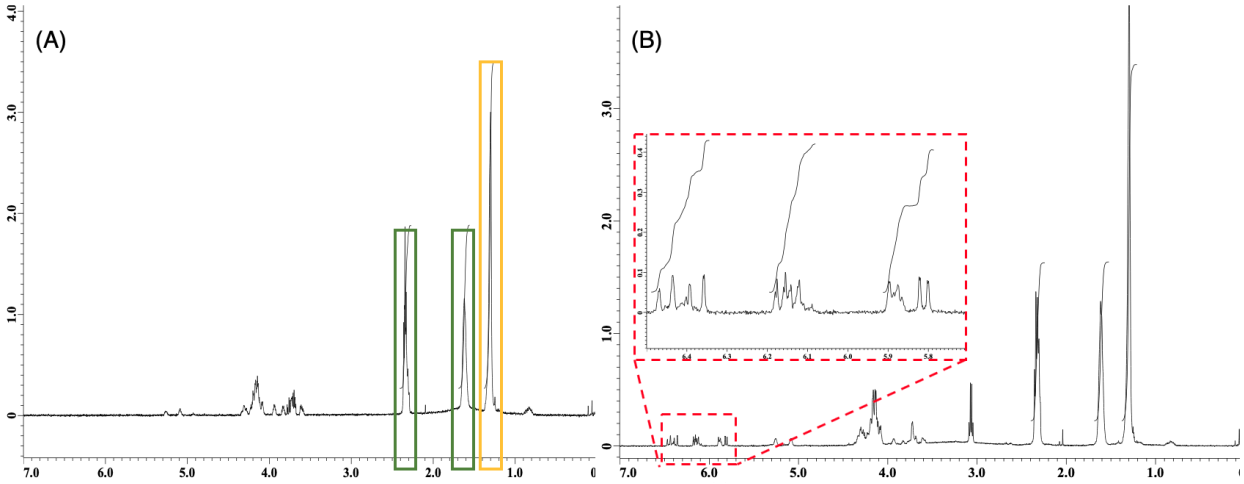

Figure S1. Characterization of PGS and PGSA. (A) ^{1}H NMR results of PGS polymer. The peaks marked in yellow are from alkyl groups on the polymer backbone and ones marked blue are from ester group. (B) ^{1}H NMR results for PGSA. The peaks represent acrylate groups are zoomed in for view. The acrylate ratio was calculated by the average of integrals at δ = 6.4 ppm, 6.15 ppm, and 5.85 ppm over δ = 1.4 ppm.

Supplementary Figure S2.

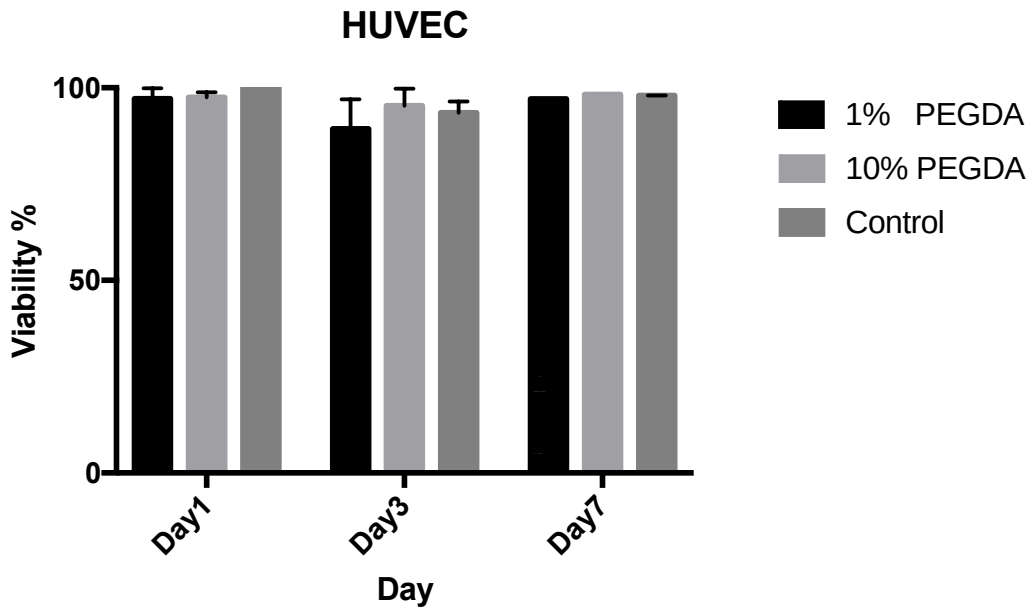

Figure S2. Summary of HUVEC viability seeded on different surfaces at each time point. Both LoResin (1% PEGDA) and HiResin (10% PEGDA) has demonstrated high biocompatibility (>90%) during the 7-day test.

Supplementary Figure S3.

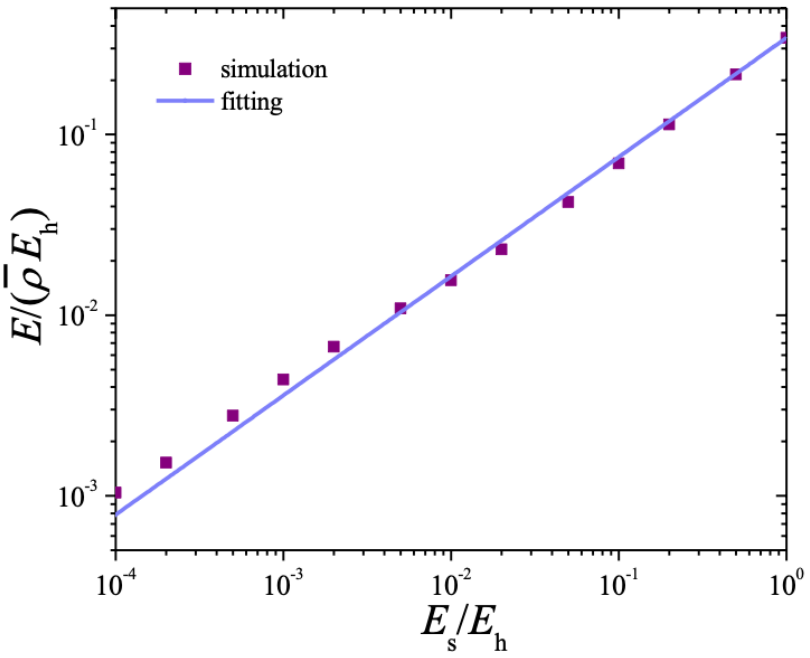

Figure S3. Simulation results of network structural elastic modulus (E) vs the ratio between the elastic modulus of the soft segment (E_s) and that of the hard segment (E_h). A function of E was developed by curve fitting.

Supplementary Figure S4.

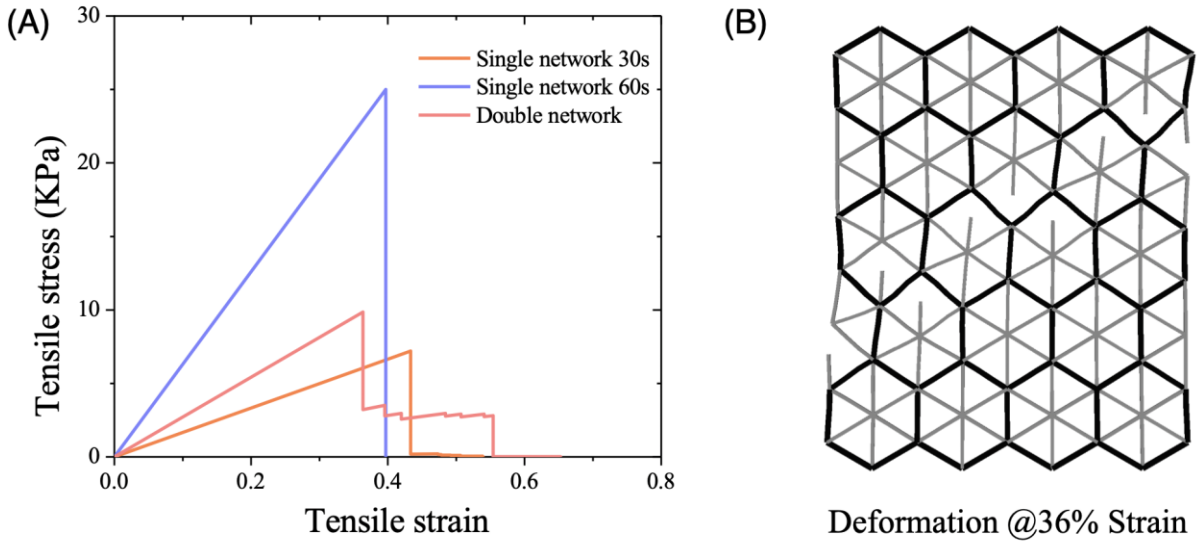

Figure S4. (A) Stress-strain curve of the network structures calculated from model simulation. Noted that the SN structure with hard segments only (SN 60s) did not undergo elongation processes as observed in the other two structures. A similar distinction was observed on 3D printed structures. (B) Simulated deformation of DN structure at 36% strain where the soft segments have reached their fracture limit but hard segments remain intact.

Supplementary Figure S5.

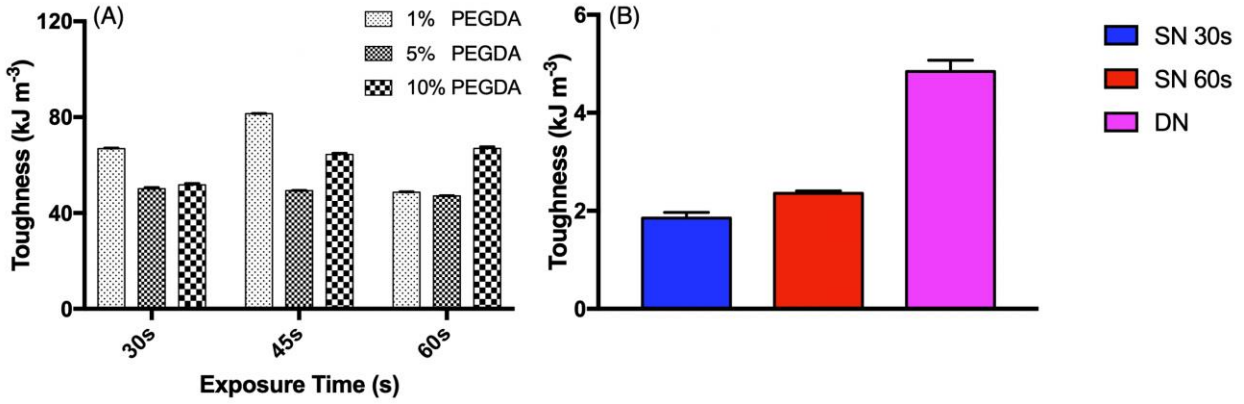

Figure S5. (A) Toughness of the printed PGSA tensile bars with different compositions and exposure conditions. (B) Toughness of the network structures printed.