Supporting information

Highly transparent polyurethane thermosets with tunable properties and enzymatic degradability derived from polyols originating from hemicellulosic sugars

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This supporting information contains 14 pages with 11 Figures and 3 Tables.

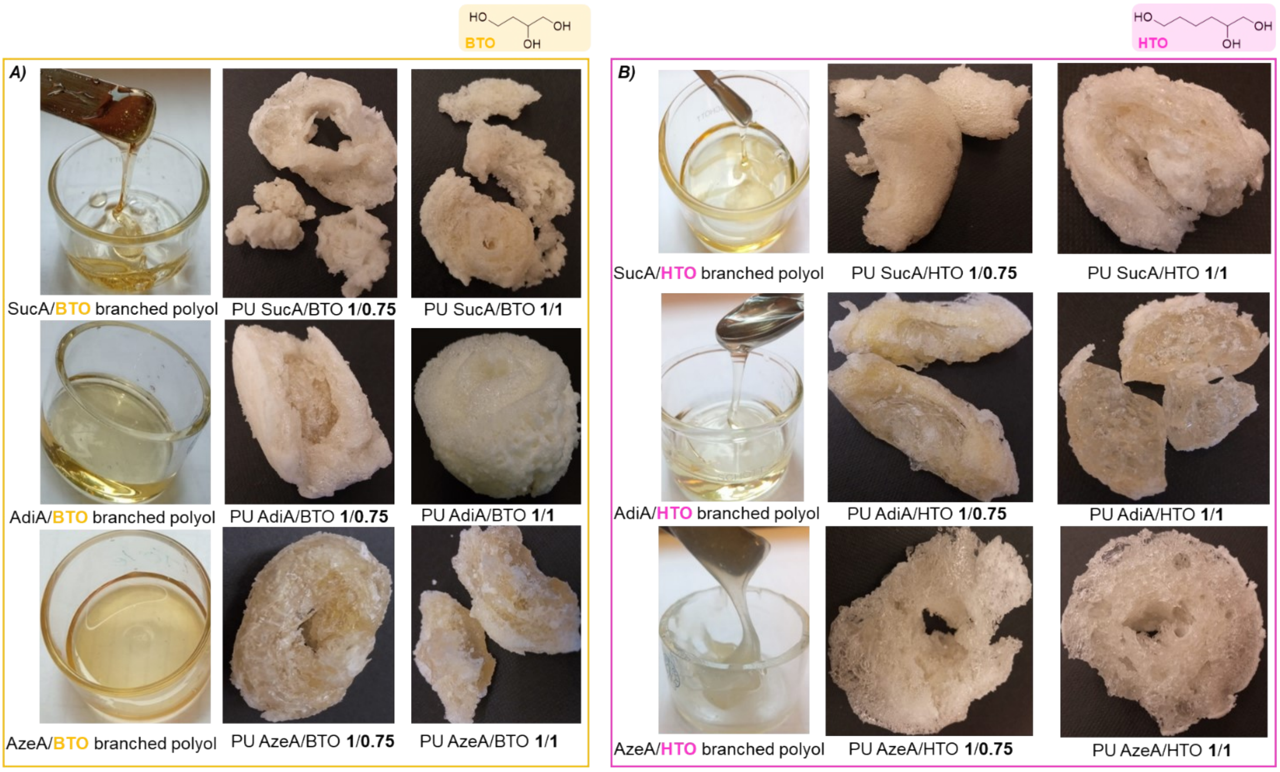

Figure S1. Photos of the PU networks with different crosslinking degrees made from fully renewable polyols based on *A)* 1,2,4-Butanetriol (BTO) and *B)* 1,2,6-Hexanetriol (HTO)

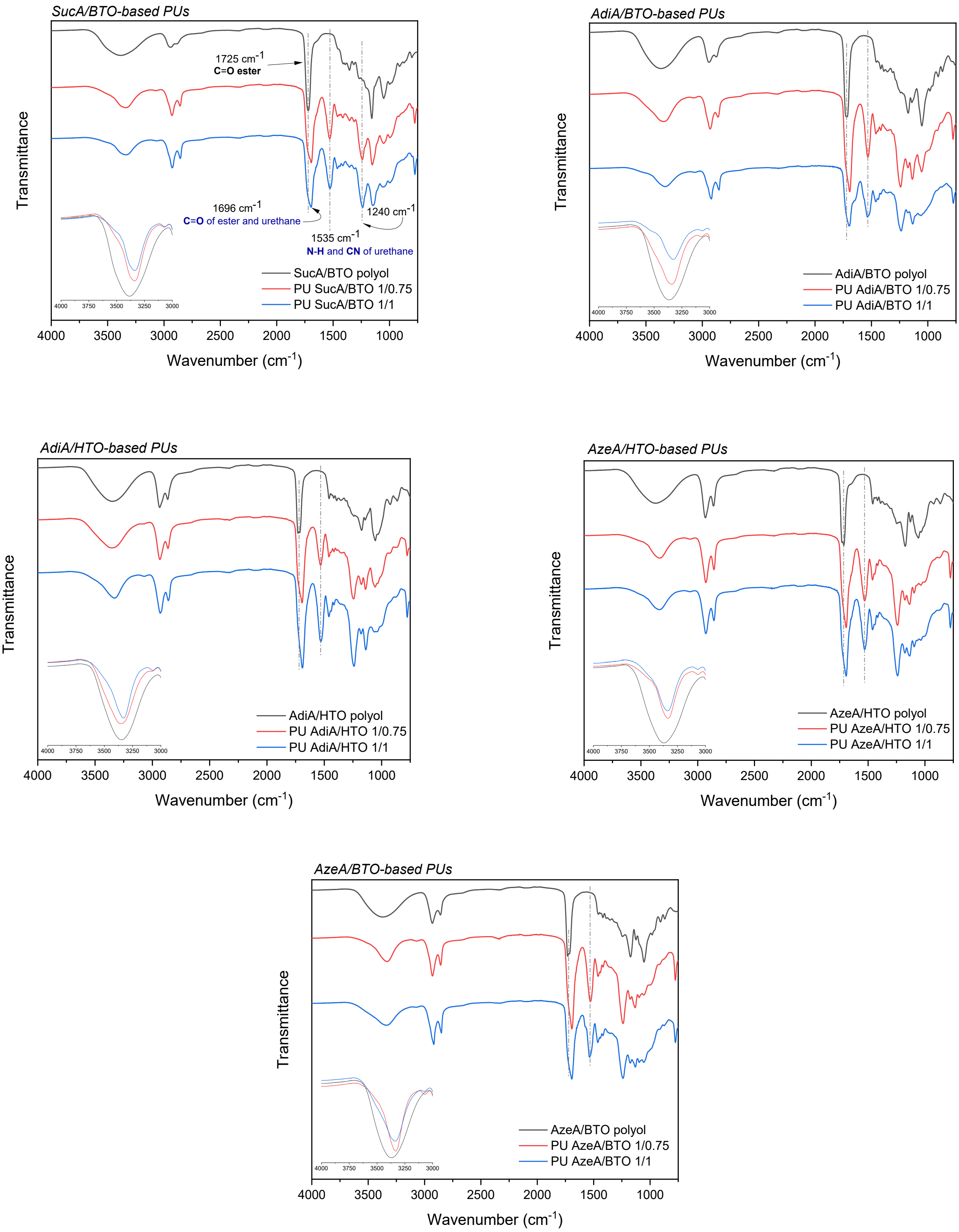

Figure S2. FTIR spectra of partially and fully crosslinked PUs derived 100% from renewable-based branched polyols

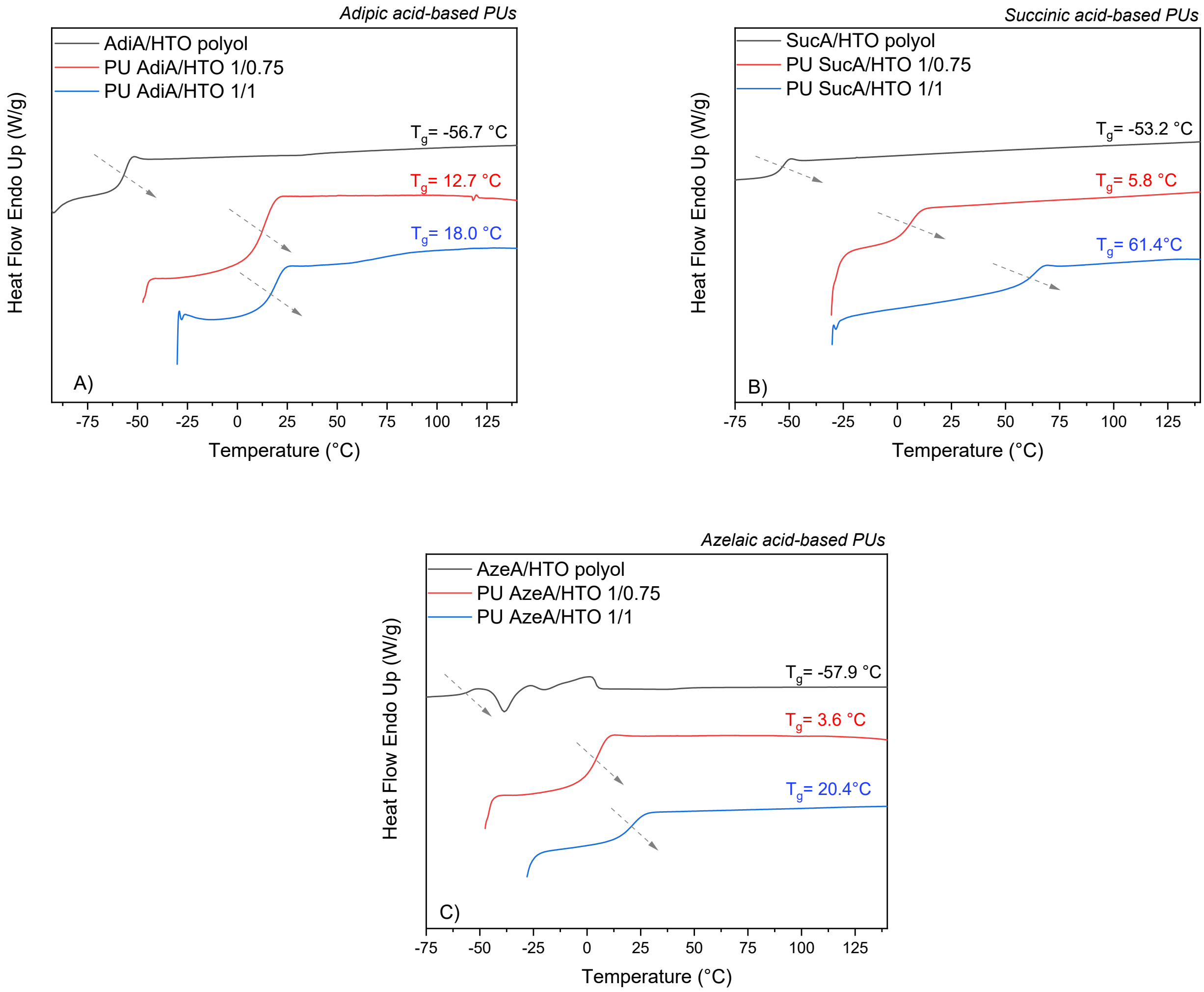

Figure S3. DSC thermograms of the PU thermosets with different degree of crosslinking derived from: *A)* SucA/HTO polyol, *B)* AdiA/HTO polyol, and *C)* AzeA/HTO polyol

Table S1. Quantities of branched polyol and HDI involved in the gram-scale synthesis of the new aliphatic PU thermosets

PU sample	Amount of polyol (g)	Amount of HDI (g)
PU SucA/BTO 1/0.75	5	2.96
PU AdiA/BTO 1/0.75	5	4.09
PU AzeA/BTO 1/0.75	5	3.47
PU SucA/HTO 1/0.75	5	3.13
PU AdiA/HTO 1/0.75	5	4.60
PU AzeA/HTO 1/0.75	5	2.82
PU SucA/BTO 1/1	5	3.95
PU AdiA/BTO 1/1	5	5.45
PU AzeA/BTO 1/1	5	4.63
PU SucA/HTO 1/1	5	4.18
PU AdiA/HTO 1/1	5	6.13
PU AzeA/HTO 1/1	5	3.76

Table S2. Thermal properties of purified the branched polyols and their corresponding polyurethane networks with different compositions

Samples	T_g (°C)	$T_{d,5\%}$	$R_{500°C}$ (%)
SucA/BTO polyol	-18.6	187.8	4.1
PU SucA/BTO 1/0.75	10.9	235.0	6.1
PU SucA/BTO 1/1	70.4	263.1	4.5
AdiA/BTO polyol	-52.1	168.3	4.3
PU AdiA/BTO 1/0.75	6.3	247.0	4.2
PU AdiA/BTO 1/1	45.1	265.0	4.9
AzeA/BTO polyol	-57.2	193.1	1
PU AzeA/BTO 1/0.75	18.5	267.8	0.7
PU AzeA/BTO 1/1	23.5	275.5	1.2
SucA/HTO polyol	-53.2	179.3	0.8
PU SucA/HTO 1/0.75	5.8	244.0	1.1
PU SucA/HTO 1/1	61.4	264.6	1.9
AdiA/HTO polyol	-56.7	226.3	2.9
PU AdiA/HTO 1/0.75	12.7	261.1	0.5
PU AdiA/HTO 1/1	18.0	270.5	1.2
AzeA/HTO polyol	-57.9	236.7	1.3
PU AzeA/HTO 1/0.75	3.6	266.1	0.8
PU AzeA/HTO 1/1	20.4	273.6	1.7

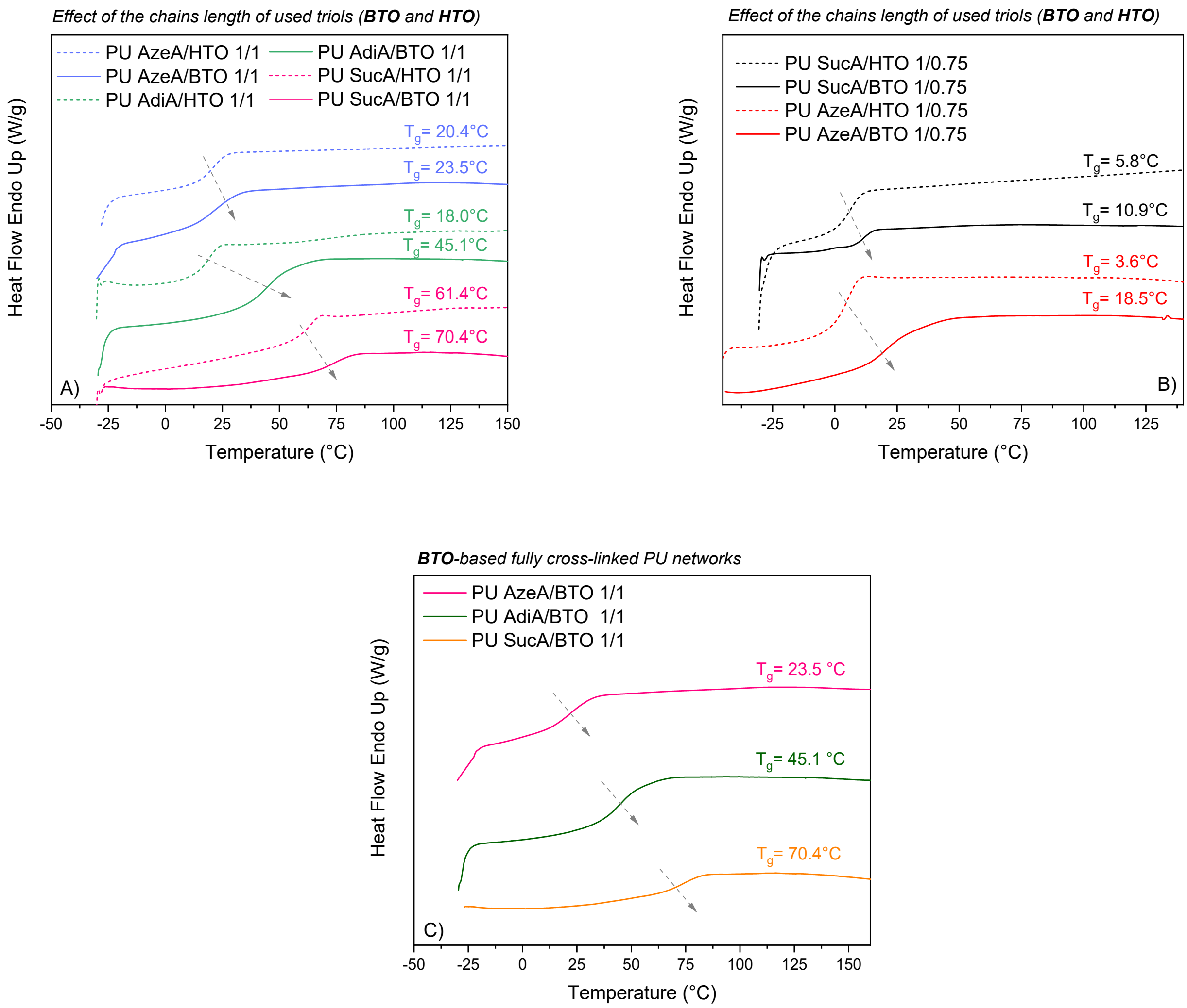

Figure S4. *A)* and *B)* Effect of the chain length of used triols (BTO and HTO), *C)* Effect of diacid type into BTO-based polyols on the T_g increase of PU networks

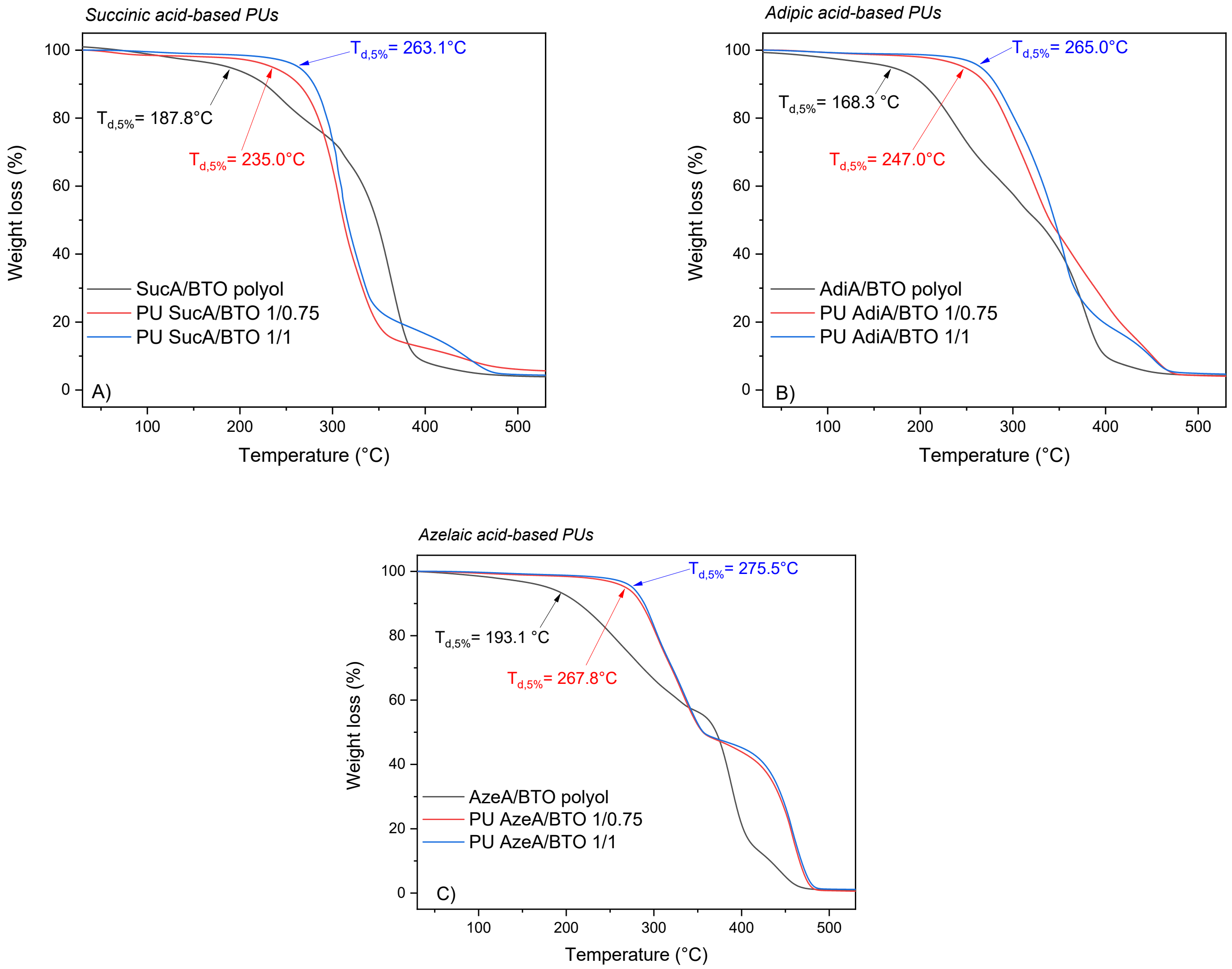

Figure S5. TGA thermograms of the PU networks with different degree of crosslinking derived from: *A)* SucA/BTO polyol, *B)* AdiA/BTO polyol, and *C)* AzeA/BTO polyol

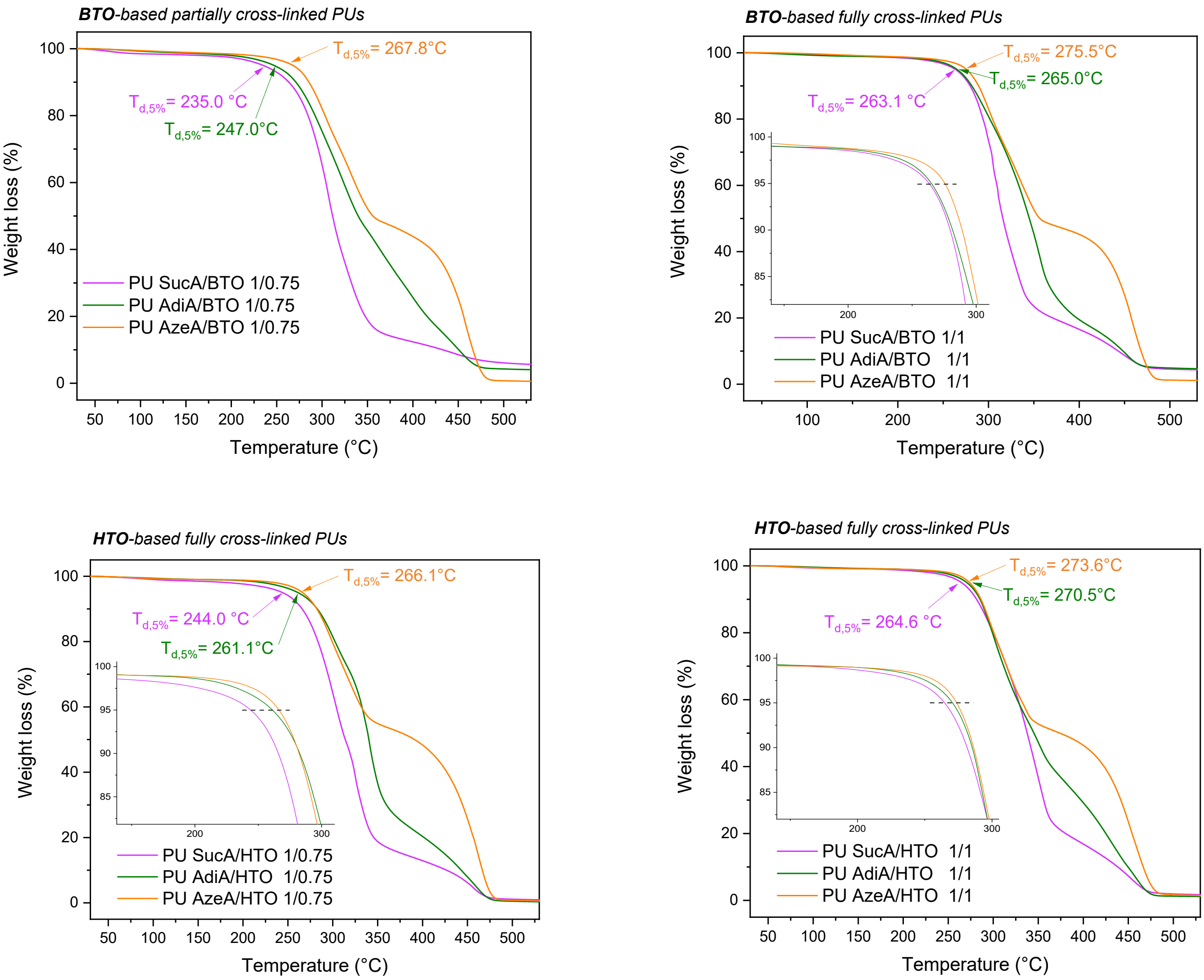

Figure S6. Effect of diacid type into branched polyols on the heat resistance of PU networks with different degree of crosslinking

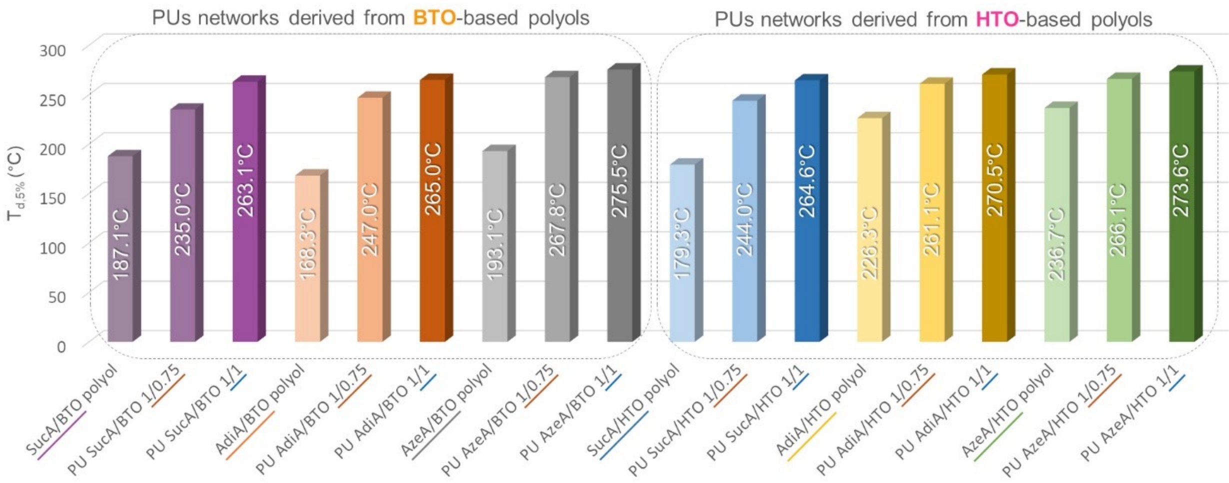

Figure S7. Effect of the crosslinking degree of the prepared PU networks on their thermal stability ($T_{d,5\%}$)

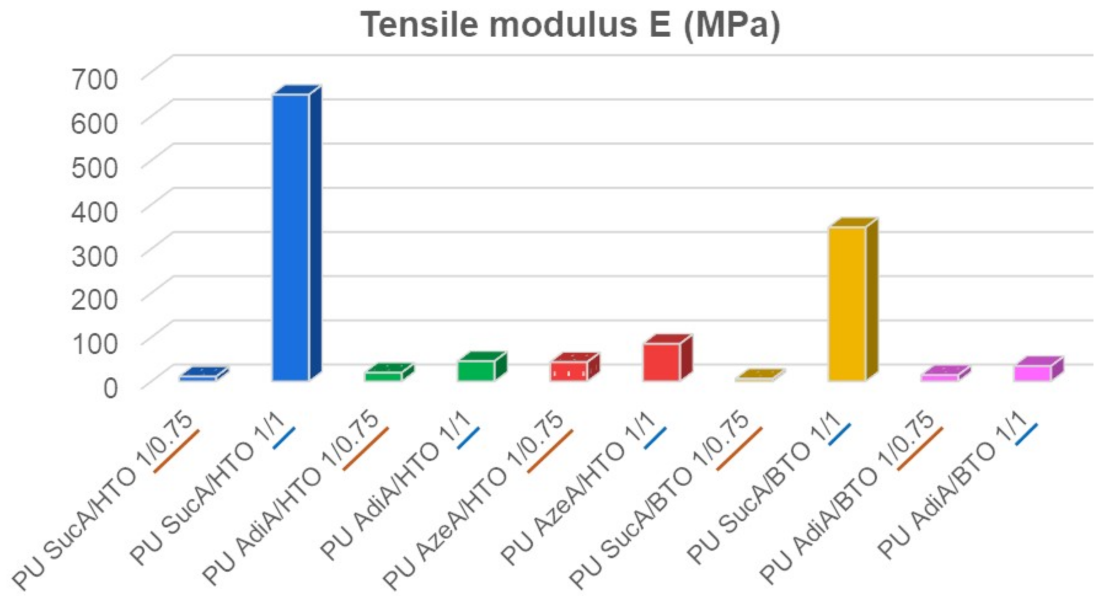

Figure S8. Comparison of tensile modulus of prepared polyurethane thermosets as a function of their crosslinking degrees

Table S3. Mechanical parameters of the prepared polyurethane networks

PU networks	Tensile modulus *E* (MPa)	Tensile strength *σ* (MPa)	Elongation at break *ε* (%)
PU SucA/HTO 1/1	648.8 ± 100.9	31.1 ± 3.05	22 ± 3.8
PU SucA/HTO 1/0.75	11.2 ± 0.14	9.0 ± 1.22	188 ± 7.3
PU AdiA/HTO 1/1	45.8 ± 0.1	14.9 ± 0.7	52 ± 1.5
PU AdiA/HTO 1/0.75	19.9 ± 2.0	7.6 ± 0.4	58 ± 0.9
PU AzeA/HTO 1/1	85.2 ± 5.1	26.2 ± 0.2	52 ± 4.7
PU AzeA/HTO 1/0.75	43.7 ± 0.8	12.1 ± 1.5	62 ± 7.9
PU SucA/BTO 1/1	348.6 ± 78	25.9 ± 1.5	15 ± 1.5
PU SucA/BTO 1/0.75	6.1 ± 0.2	3.3 ± 0.04	74 ± 1.5
PU AdiA/BTO 1/1	34.9 ± 7.2	24.1 ± 2.2	130 ± 4.4
PU AdiA/BTO 1/0.75	14.4 ± 0.7	9.1 ± 1.3	170 ± 16.8
PU AzeA/BTO 1/1	56.0 ± 9.2	15.0 ± 2.2	38 ± 0.5
PU AzeA/BTO 1/0.75	84.9 ± 2.5	18.3 ± 2.9	44 ± 0.2

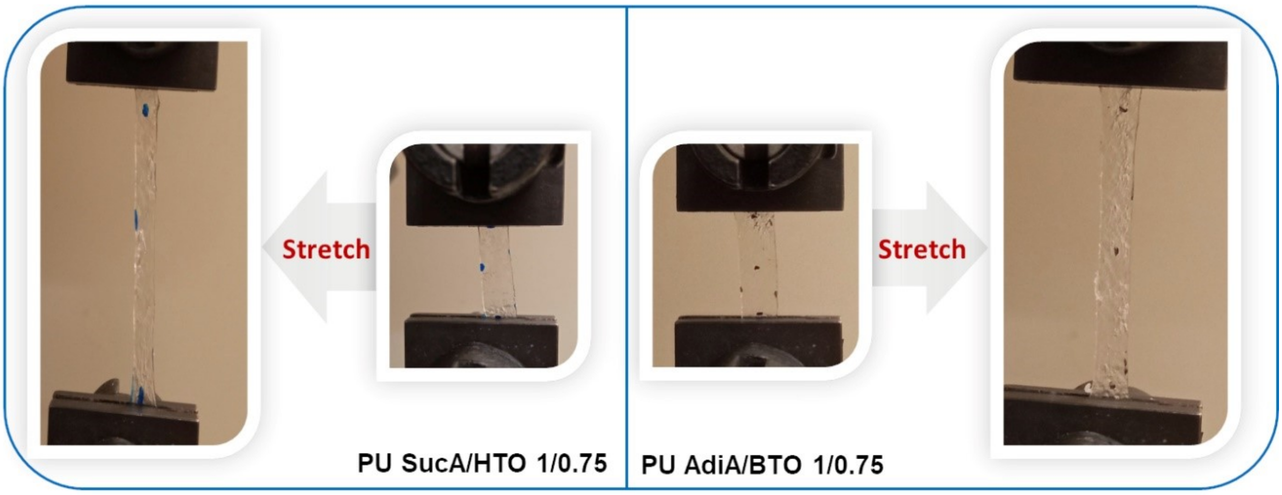

Figure S9. Highly stretchable polyurethane samples with elastomeric behavior at room temperature: PU SucA/HTO 1/0.75 (*left*) and PU AdiA/BTO 1/0.75 (*right*)

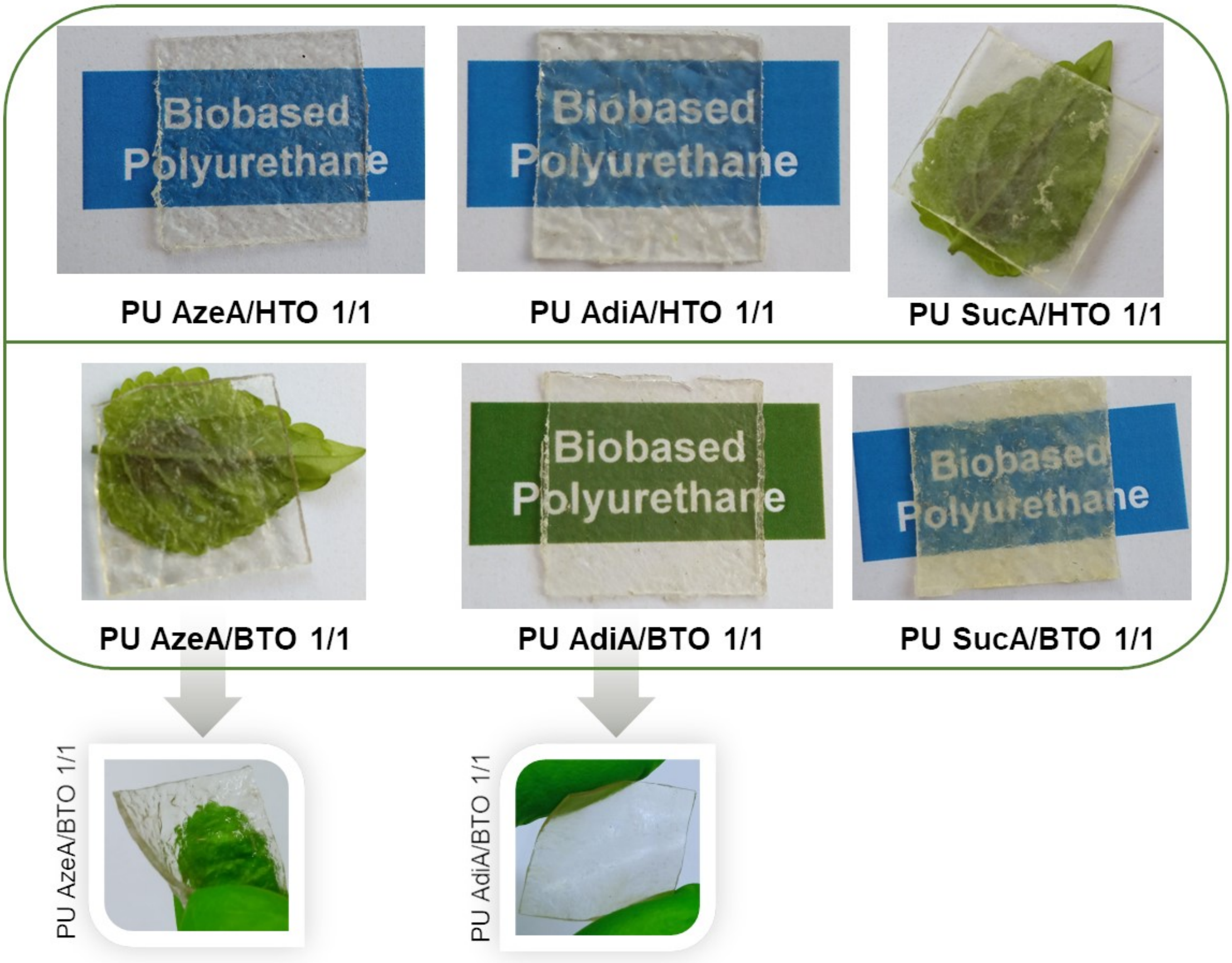

Figure S10. Photographs of fully crosslinked renewable polyurethane films

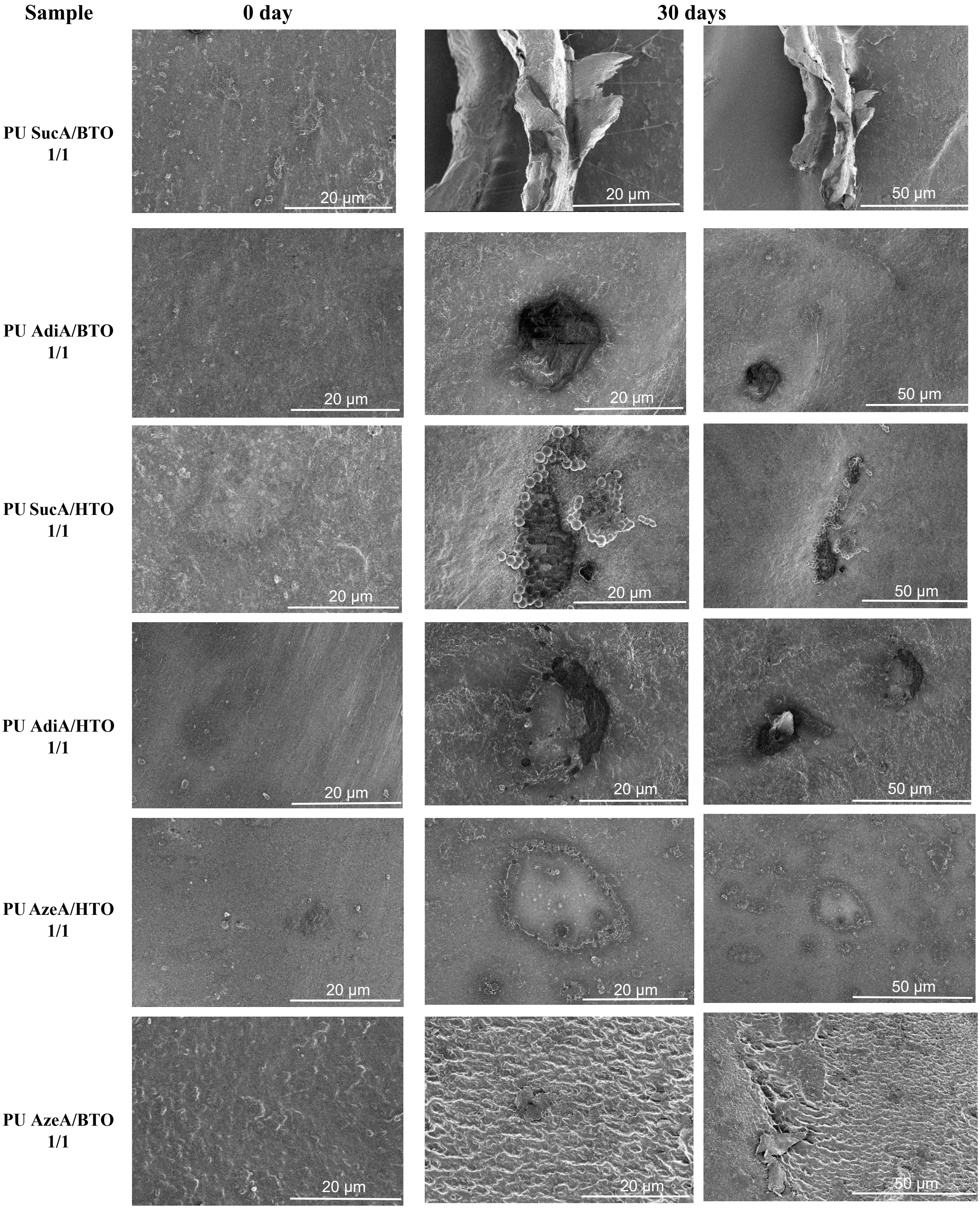

Figure S11. SEM micrographs of fully crosslinked polyurethane networks before (0 days) and after 30 days of enzymatic degradation