

Supplementary Materials

Improvement of mechanical properties and self-healing efficiency by *ex-situ* incorporation of TiO₂ nanoparticles to a waterborne poly(urethane-urea)

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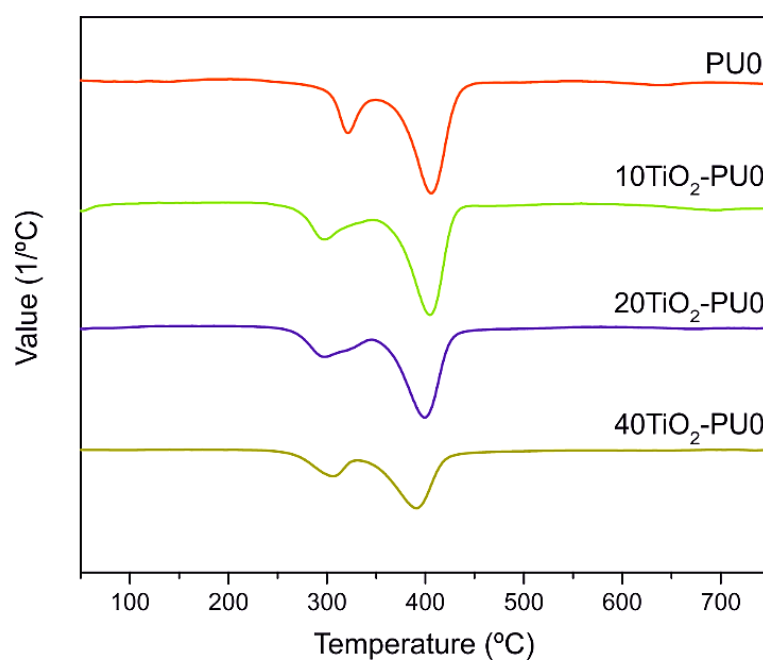


Figure S1. dDTGA curves of the PU0 and TiO₂-PU0 nanocomposite films.

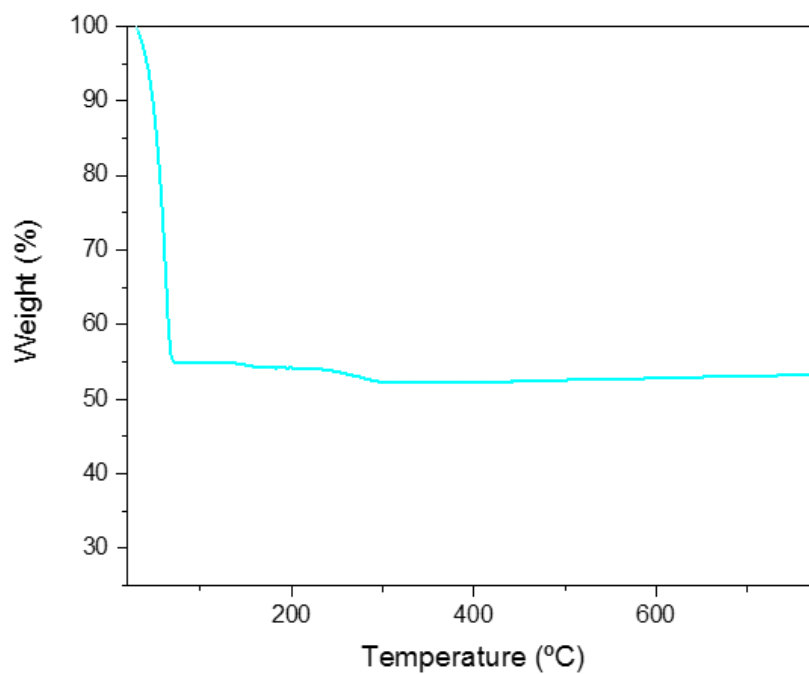


Figure S2. TGA curve of TiO₂ nanoparticles.

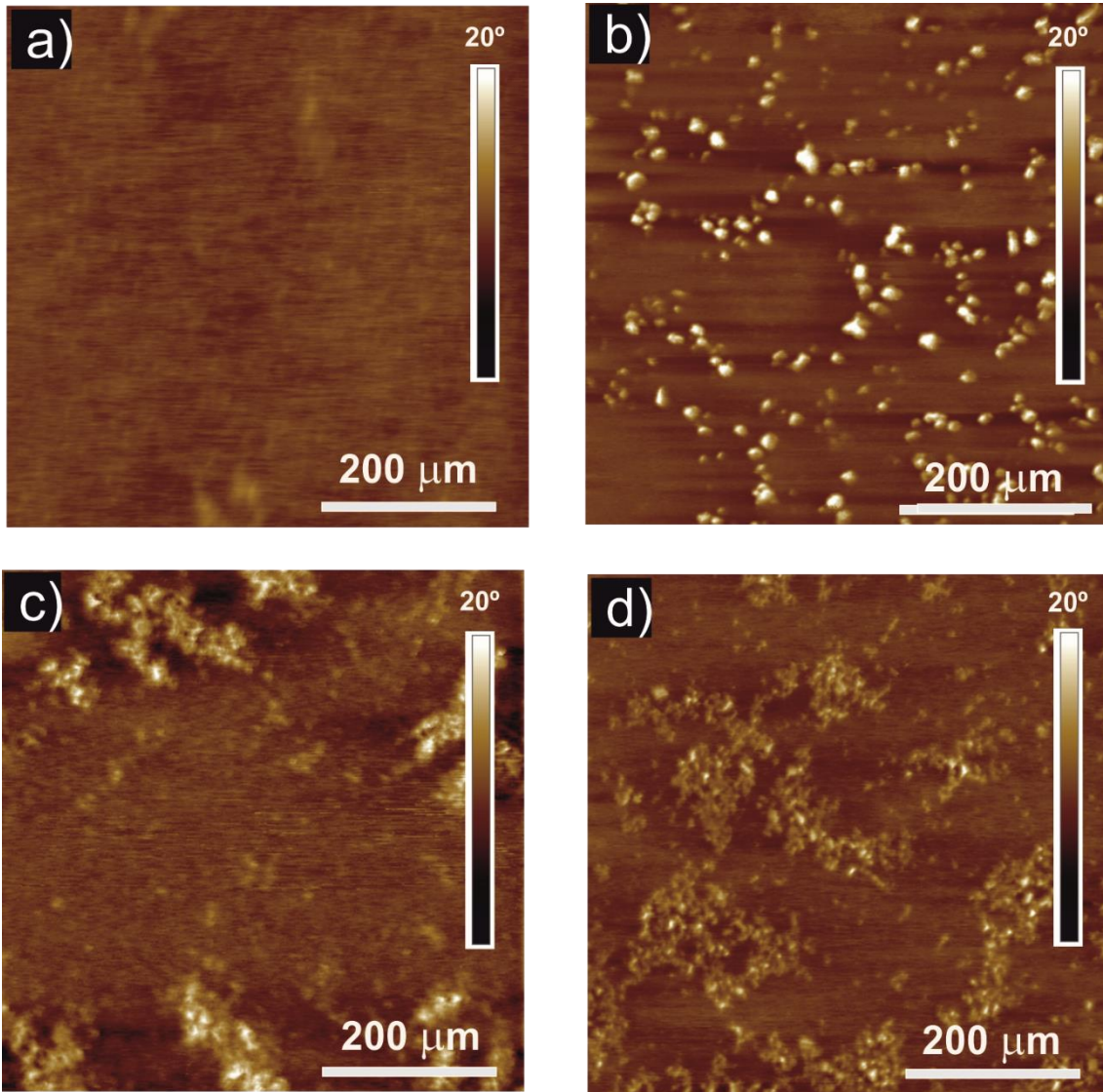


Figure S3. AFM phase images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of (a) PU0, (b) 10TiO₂-PU0, (c) 20TiO₂-PU0 and (d) 40TiO₂-PU0.

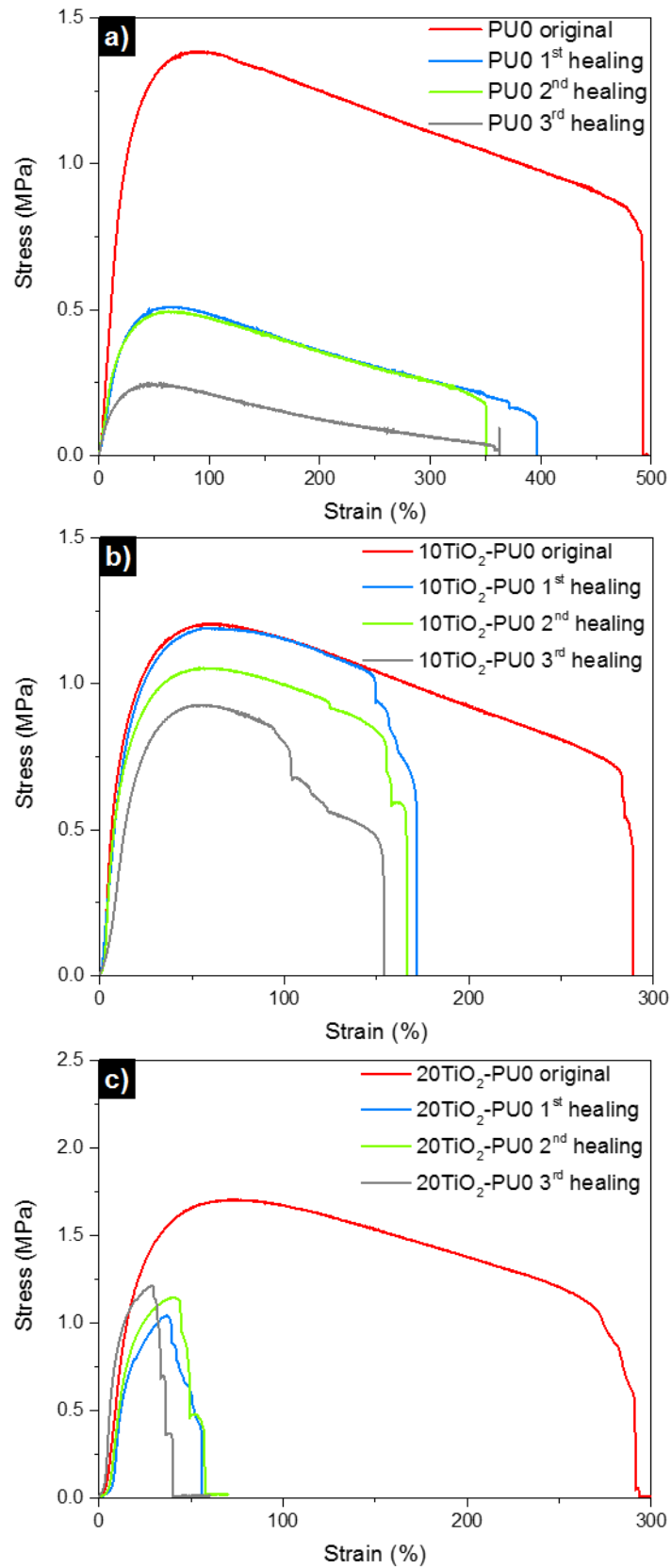
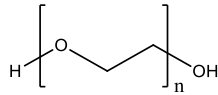
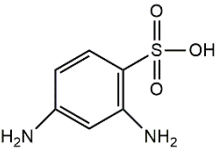
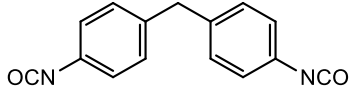


Figure S4. Stress-strain curves of original and self-healed films of (a) PU0, (b) 10TiO₂-

PU0 and (c) 20TiO₂-PU0.

Table S1. Chemical structure, molecular weight and nanoparticle concentration in water.

Raw materials	Chemical structure	Molecular weight (g mol⁻¹)	Concentration in water (wt%)
Poly(ethylene oxide) (PEO)		1023.00 ^a	-
2,4-Diamino- benzenesulfonic acid (DBSA)		188.20	-
4,4'- Diphenylmethane diisocyanate (MDI)		250.25	-
Titanium dioxide nanoparticles^b (TiO₂)	O=Ti=O	79.86	33-37

a) Molecular weight calculated from the hydroxyl index value determined by ASTM D4274-99

b) Commercial aqueous solution of TiO₂ nanoparticles

Table S2. Glass transition temperature of the PU0 and TiO₂-PU0 nanocomposite films.

Sample	T_{gss} (°C)
PU0	0
10TiO₂-PU0	-1
20TiO₂-PU0	-1
40TiO₂-PU0	-8

Table S3. Decomposition temperatures and TiO₂ nanoparticles content of the investigated PU0 and TiO₂-PU0 nanocomposites.

Sample	T₁^a (°C)	T₂^a (°C)	TiO₂ wt% content (%)
PU0	323	406	0
10TiO₂-PU0	302	403	12.6
20TiO₂-PU0	302	402	18.3
40TiO₂-PU0	311	394	37.2

a) Determined from dTGA

Table S4. Surface energy of the original PU0 and TiO₂-PU0 nanocomposite films and after each healing process.

Sample	Original (mN m⁻¹)	1st healing (mN m⁻¹)	2nd healing (mN m⁻¹)	3rd healing (mN m⁻¹)
PU0	72.78 ± 0.05	72.76 ± 0.03	72.79 ± 0.03	72.80 ± 0.03
10TiO₂-PU0	72.79 ± 0.03	72.80 ± 0.03	72.80 ± 0.04	72.79 ± 0.03
20TiO₂-PU0	72.80 ± 0.03	72.78 ± 0.05	72.81 ± 0.02	72.74 ± 0.18