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DOI:
10.1016/j.eurpolymj.2022.111502

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Document Version
Peer reviewed version

Citation for published version (Harvard):
Djordjevic, I, Wicaksono, G, Singh, J, Singh, M, Ellis, EG, Alraddadi, M, Dove, A & Steele, TWJ 2022, 'Hybrid polymer networks of carbene and thiol ene', *European Polymer Journal*, vol. 178, 111502. https://doi.org/10.1016/j.eurpolymj.2022.111502

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Hybrid polymer networks of carbene and thiol ene

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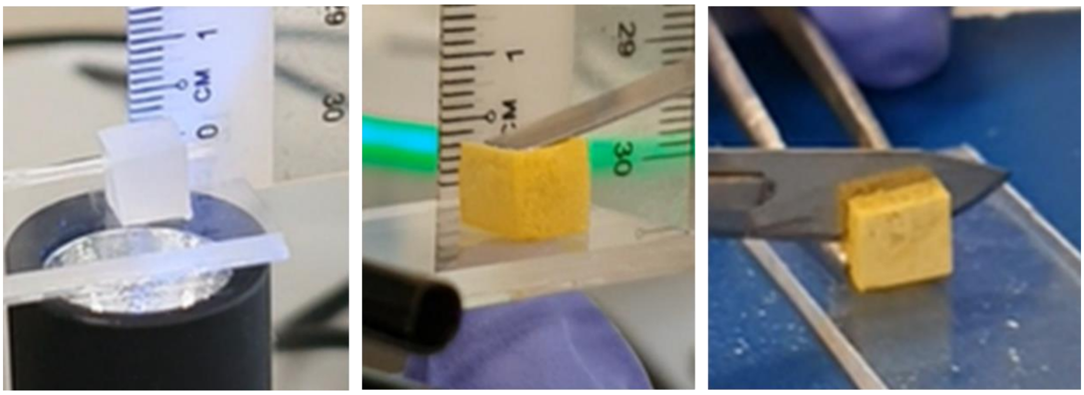
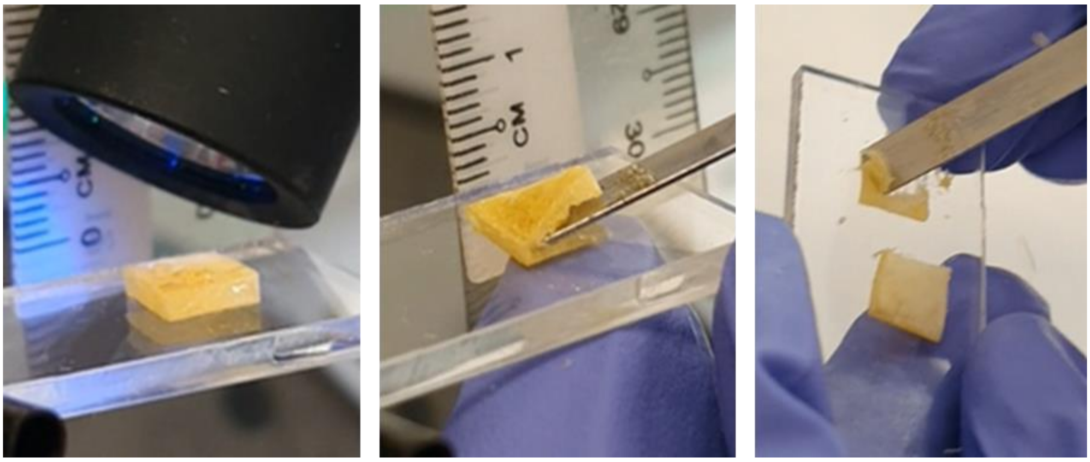
SUPPLEMENTARY INFORMATION



Supplementary video 1. UVA activation of thiol/alkene/CaproGlu hybrid network.



Supplementary video 2. Sample cut for lap shear adhesion test and scratch test demonstration after UVA activation of thiol/alkene/CaproGlu hybrid network.

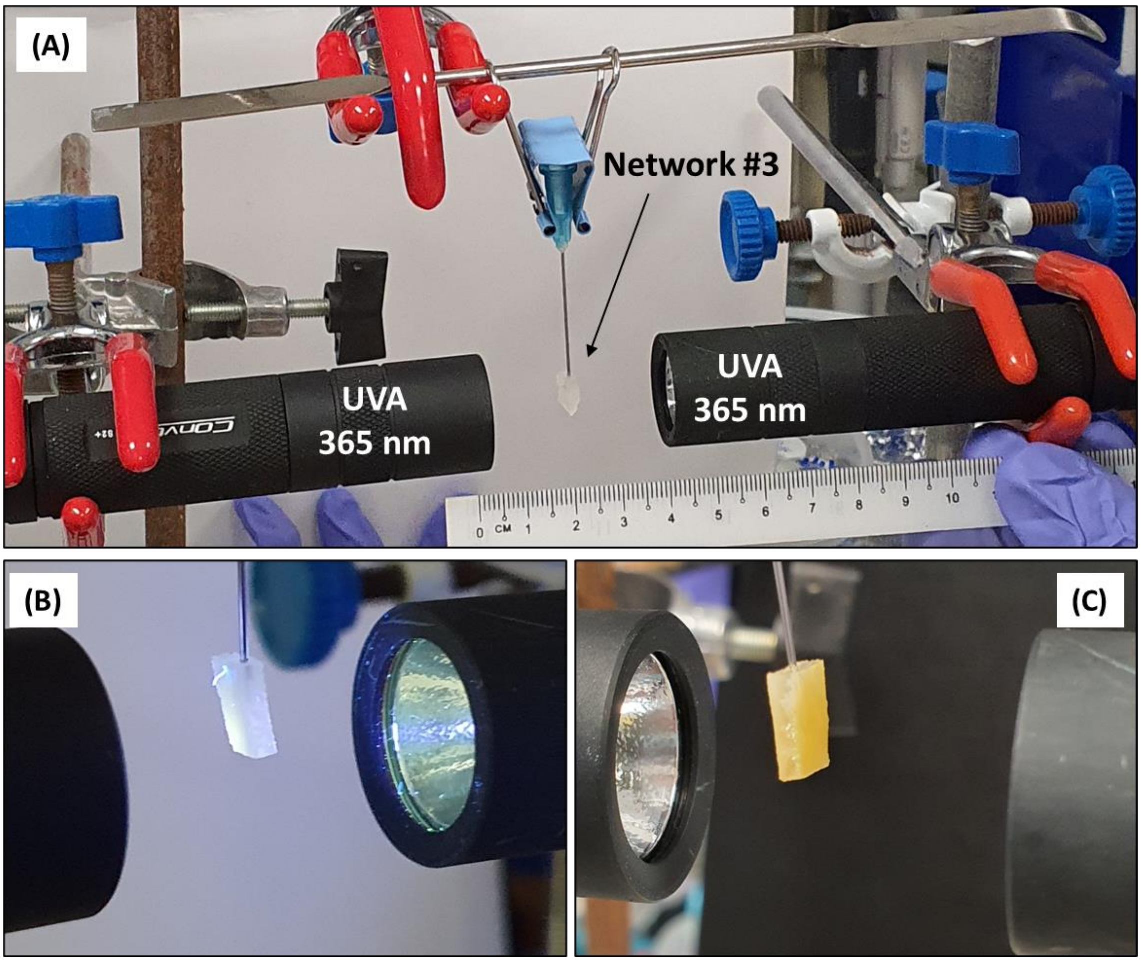


Figure S1. 3-component thiol/alkene/CaproGlu hybrid polymer network (SH1/Ene2/Dz; **Table 1**) sample preparation for FTIR and SEM analysis: (A) sample fixed with needle between 2 UVA diodes (100 mW.cm^{-2}); (B) diodes turned ON simultaneously for 100 sec to deliver 10 J.cm^{-2} to each side of the sample; (C) sample after UVA curing.

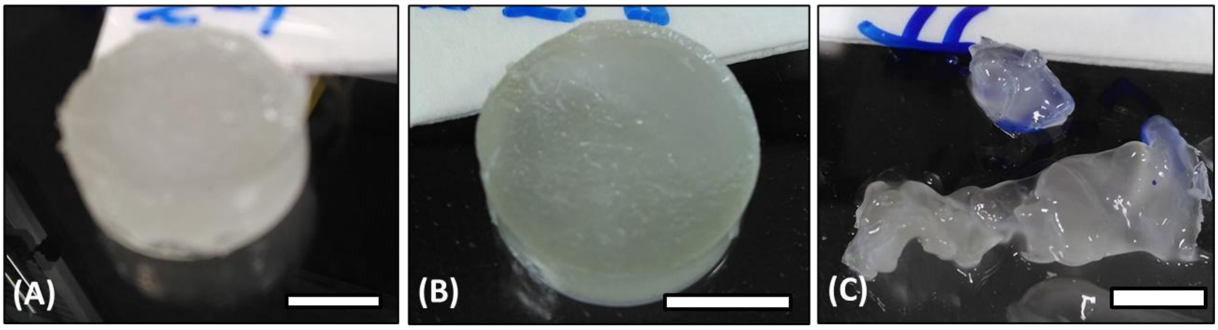


Figure S2. Digital photographs of crosslinked 3-component thiol/alkene/CaproGlu hybrid polymer network samples in ambient conditions 24 h after mixing (no UVA activation; bar = 1 cm): (A-C) SH2/Ene2/Dz, SH1/Ene2/Dz and SH1/Ene1.5/Dz (nomenclature and composition: **Table 1**) respectively.

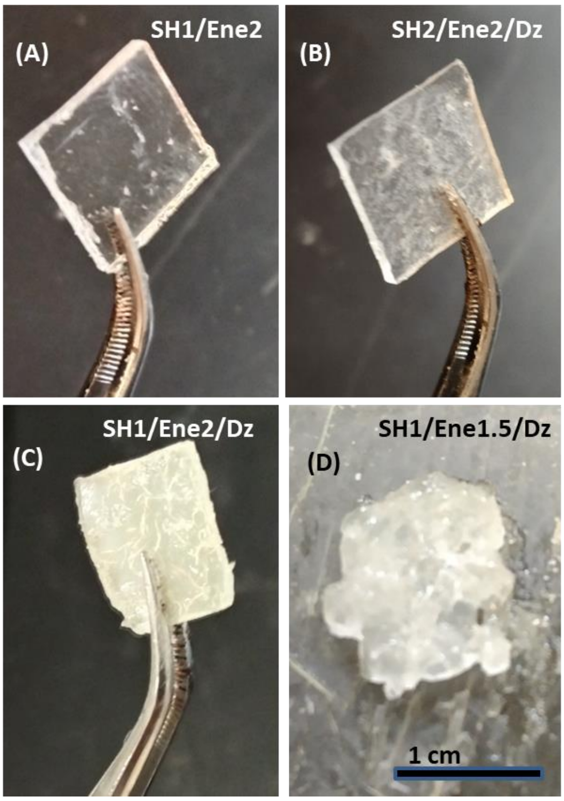


Figure S3. Photographs of samples prepared for peel test: (A) SH1/Ene2 (no CaproGlu) control; (B-D) HPN samples with compositions outlined in **Table 1**.

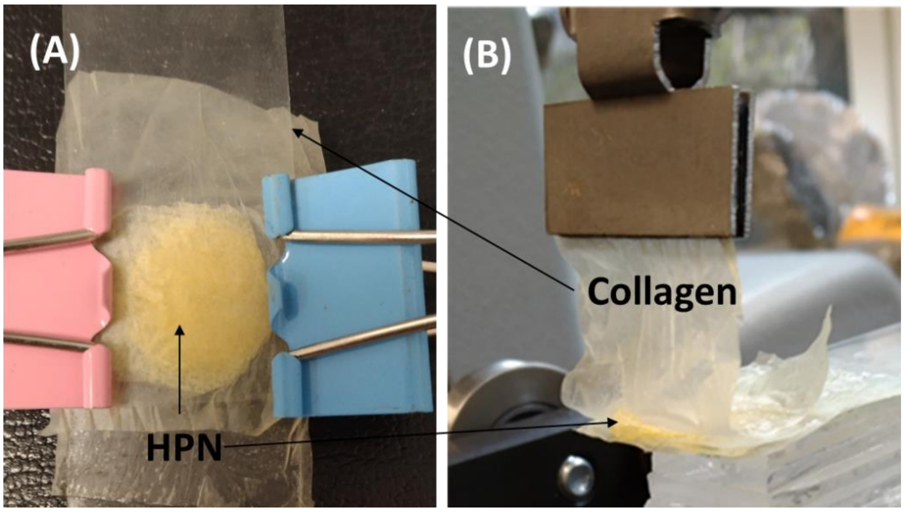


Figure S4. Peel test experimental design for samples placed between 2 collagen sheets: (A) Glass slide/cyanoacrylate/Collagen/HPN/Collagen structure fixed with paper clips after UVA activation (20 J.cm^{-2}: 10 J.cm^{-2} from either side of the sample); (B) Collagen/HPN/Collagen structure mounted on the sample holder for peel strength test.

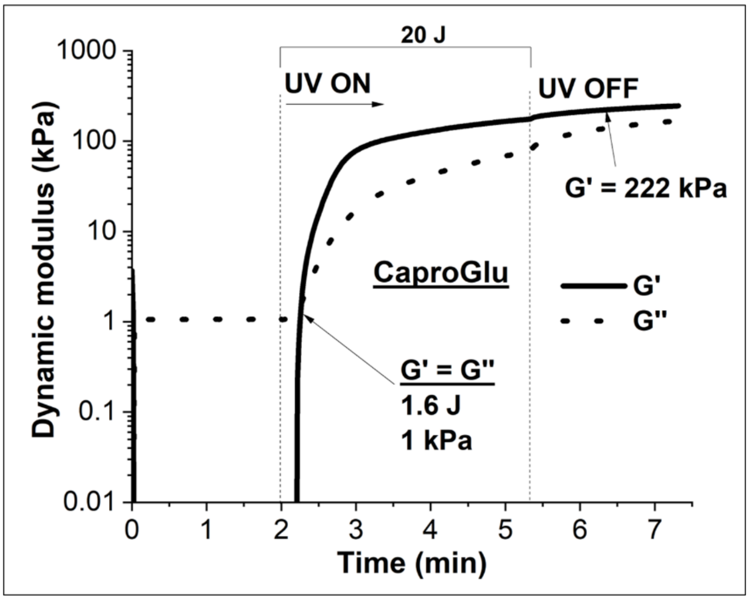


Figure S5. 1-step light-activated crosslinking of pure CaproGlu analyzed with photorheometry – dynamic change of storage (G’) and loss (G’’) moduli over time (bottom) and absorbed energy dose (top’ J.cm^{-2}) with indicated gelation point (G’ = G”) upon light activation (diode wavelength range = 320-500 nm; diode power = 100 mW.cm^{-2}).

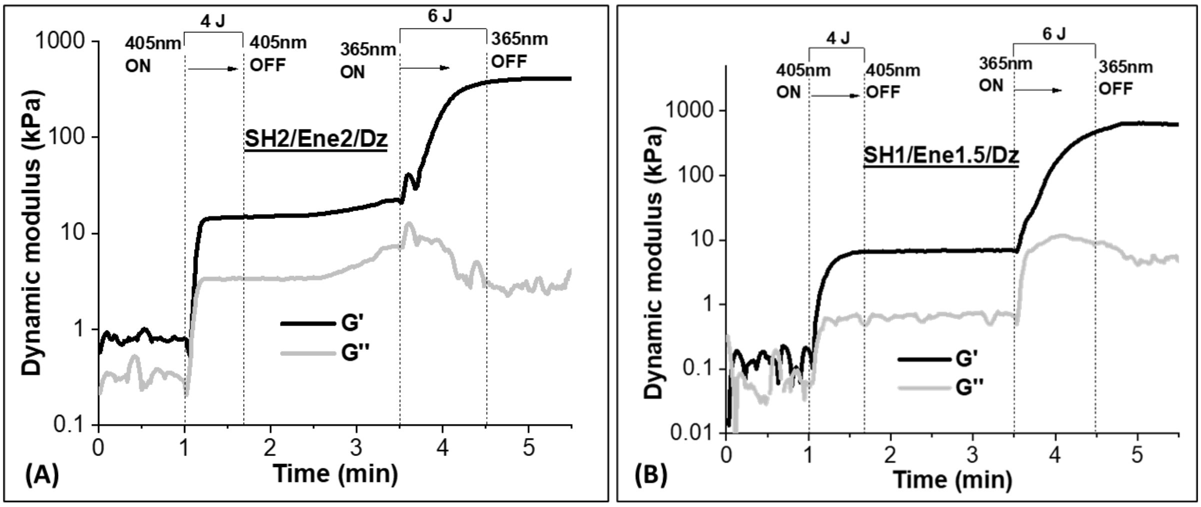


Figure S6. Photorheological profiles of 3-component thiol/alkene/CaproGlu hybrid polymer networks (Table 1) SH2/Ene2/Dz and SH1/Ene1.5/Dz (A and B respectfully) with dynamic change of storage (G’) and loss (G’’) moduli upon 2-step light activation at 405 nm and 365 nm (light diode power: 100 mW.cm^{-2}) over time (bottom) and absorbed energy dose (top; J.cm^{-2}).

Table S1. Dynamic (storage) modulus (G') of hybrid networks and controls recorded 1 min after the light diodes are turned off (see **Fig. 3**; **Fig. S3**) and gelation points expressed as light energy (J) dose required to reach G' = G'' value.

Hybrid network composition	G' (405 nm; kPa)	G' (365 nm; kPa)	Gel. Point (J.cm^{-2})
CaproGlu (Control-1)	-	170	2
SH/Yne (Control-2)*	-	5750*	6
SH2/Yne2/Dz*	-	500*	4
SH/Ene (Control-3)	1520	1530	-
SH2/Ene2/Dz	16	410	-
SH1/Ene2/Dz	28	920	-
SH1/Ene1.5/Dz	7	630	-

**Measured upon 1-step activation at polychromatic light: 320-500 nm; 30 J.*

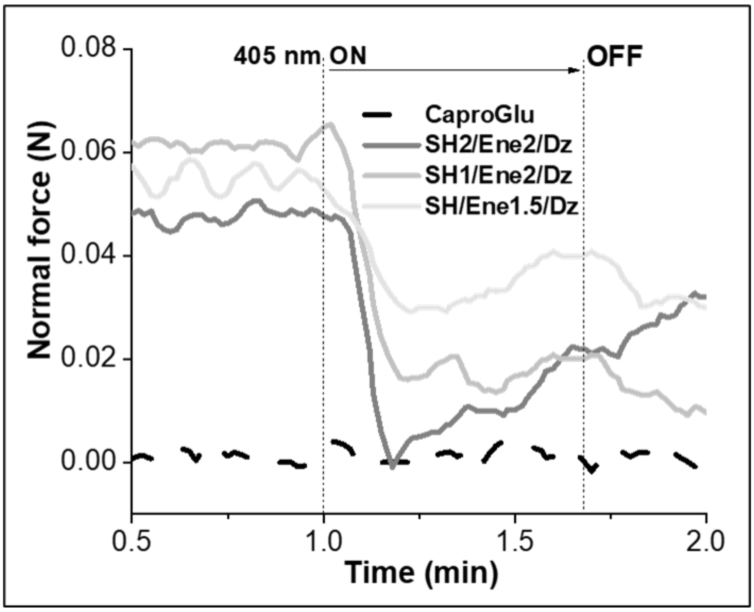
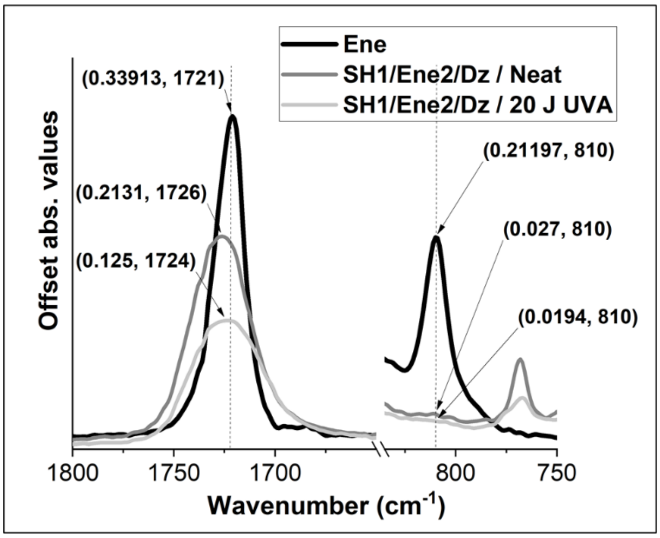


Figure S7. Magnified region of normal force vs light activation time (405 nm; the full range is displayed in **Figure 3D** in main text); the thiol-acrylate (SH-Ene) crosslinking causes polymer volume shrinking as evident from drop in normal force, in comparison to pure CaproGlu (control-1).



$$DC(\%) = \left(1 - \frac{A^{Neat/UVA}}{A^{Ene}}\right) \text{x } 100$$

$$A^{Ene} = \frac{R^{810}}{R^{1721}} = \frac{0.21197}{0.33913} = 0.625$$

$$A^{Neat} = \frac{R^{810}}{R^{1721}} = \frac{0.027}{0.2131} = 0.127$$

$$DC^{Neat}(\%) = \left(1 - \frac{0.127}{0.625}\right) \text{x } 100 = 79.7\%$$

Figure S8. Degree of alkene conversion (DC %) calculated from absorbance value at 810 cm^{-1} normalized to carbonyl peak of PEGDA (Ene; 1721 cm^{-1}): (Left) FTIR representative spectral region with data readings (R) used to calculate absorbances (A) normalized to carbonyl peaks; (Right) DC (%) calculated for SH1/Ene2/Dz after mixing and exposure to ambient light for 24 h (mark as “Neat” – without UVA activation).

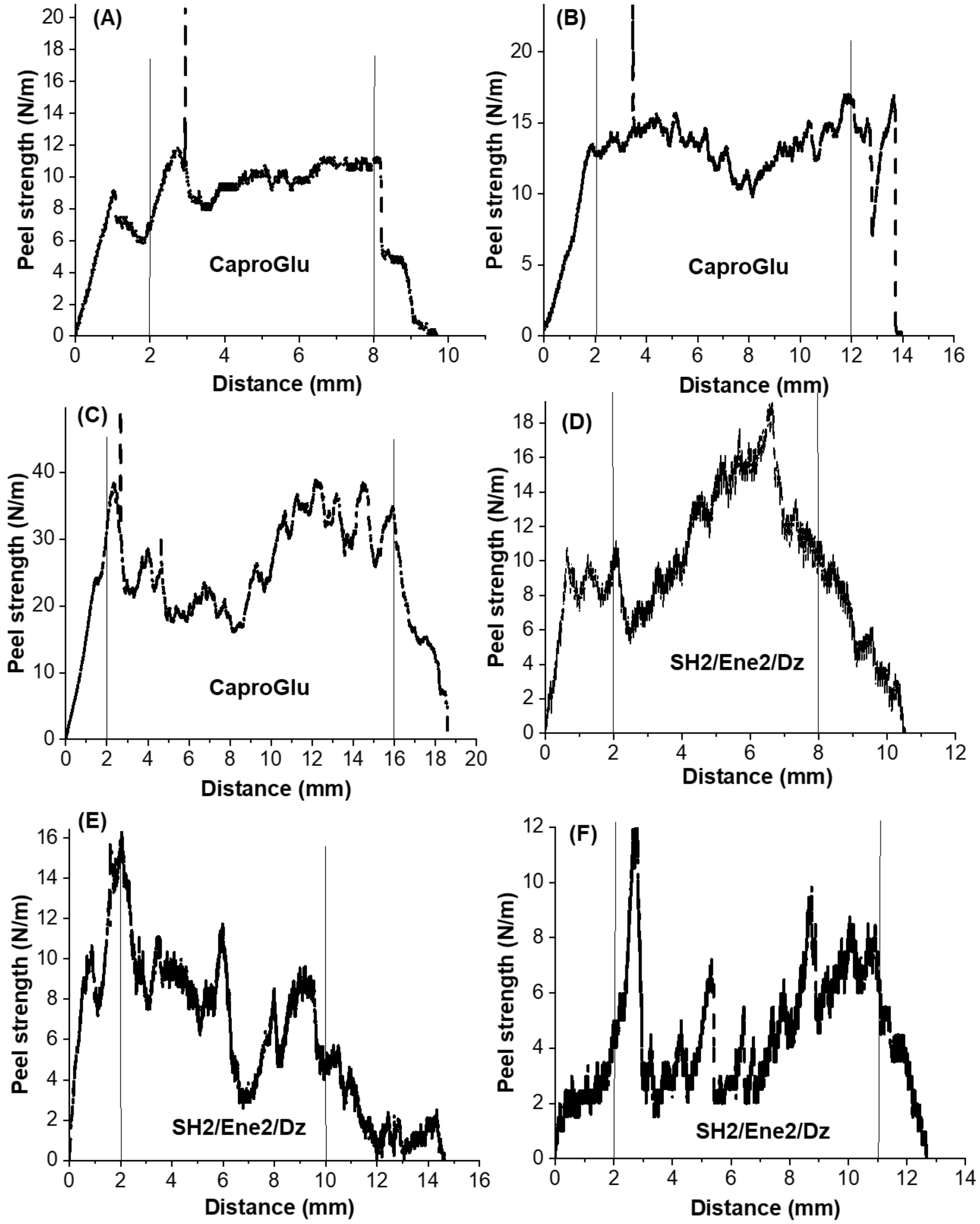


Figure S9. Peel strength vs displacement curves of CaproGlu (control; n = 3) and HPN (n = 3) samples after activation with UVA light (20 J.cm^{-2}): (A-C) CaproGlu; (D-F): SH2/Ene2/Dz. Vertical lines indicate the peel strength data range used to calculate the average values for each sample.

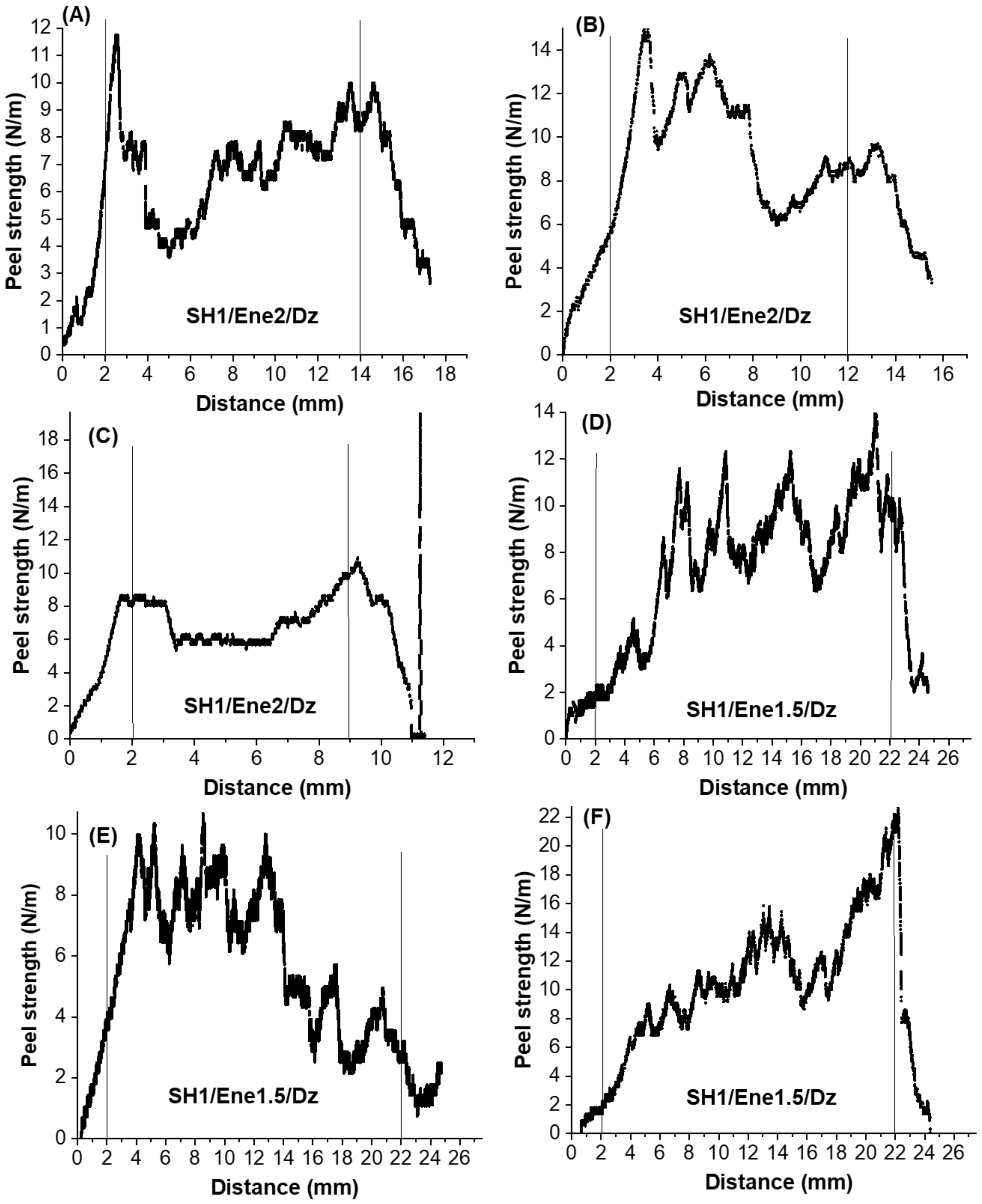


Figure S10. Peel strength vs displacement curves of HPN (n = 3) samples after activation with UVA light (20 J.cm^{-2}): (A-C) SH1/Ene2/Dz; (D-F): SH1/Ene1.5/Dz. Vertical lines indicate the peel strength data range used to calculate the average values for each sample.

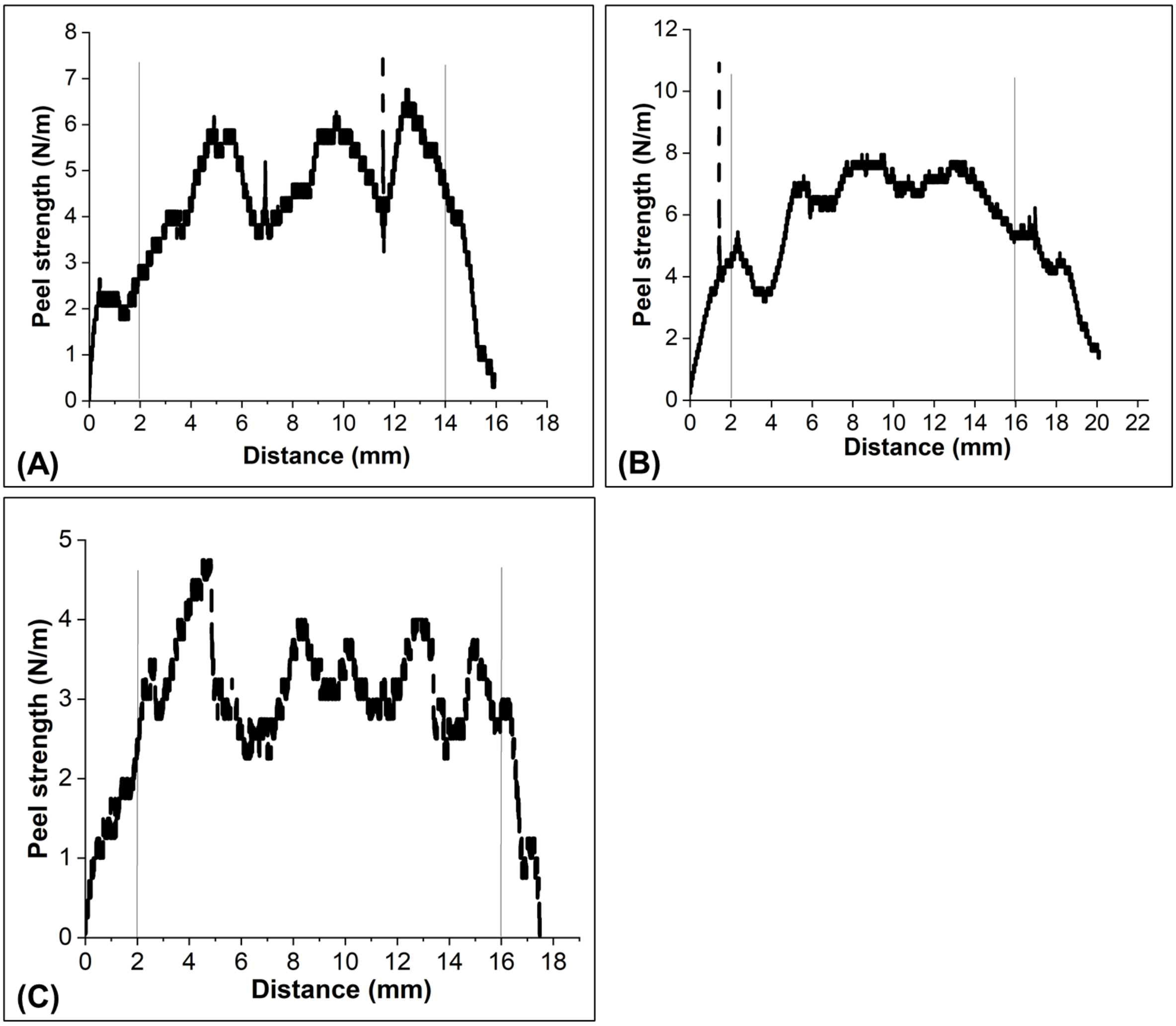
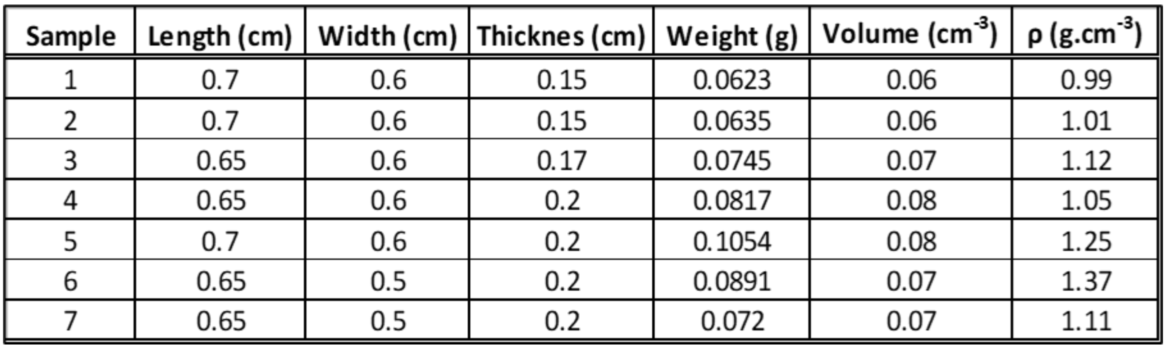


Figure S11. Peel strength vs displacement curves of HPN (n = 3) samples without UVA activation: (A-C) SH1/Ene2/Dz. Vertical lines indicate the peel strength data range used to calculate the average values for each sample.

Table S2. 3-component thiol/alkene/CaproGlu hybrid network SH1/Ene2/Dz (**Table 1**) composition – 7 samples measured prior to UVA activation and lap shear adhesion experiment; the density is calculated from sample weight and dimensions: ρ = (1.1 ± 0.1) g.cm^{-3}.



Sample	Length (cm)	Width (cm)	Thicknes (cm)	Weight (g)	Volume (cm^{-3})	ρ (g.cm^{-3})
1	0.7	0.6	0.15	0.0623	0.06	0.99
2	0.7	0.6	0.15	0.0635	0.06	1.01
3	0.65	0.6	0.17	0.0745	0.07	1.12
4	0.65	0.6	0.2	0.0817	0.08	1.05
5	0.7	0.6	0.2	0.1054	0.08	1.25
6	0.65	0.5	0.2	0.0891	0.07	1.37
7	0.65	0.5	0.2	0.072	0.07	1.11

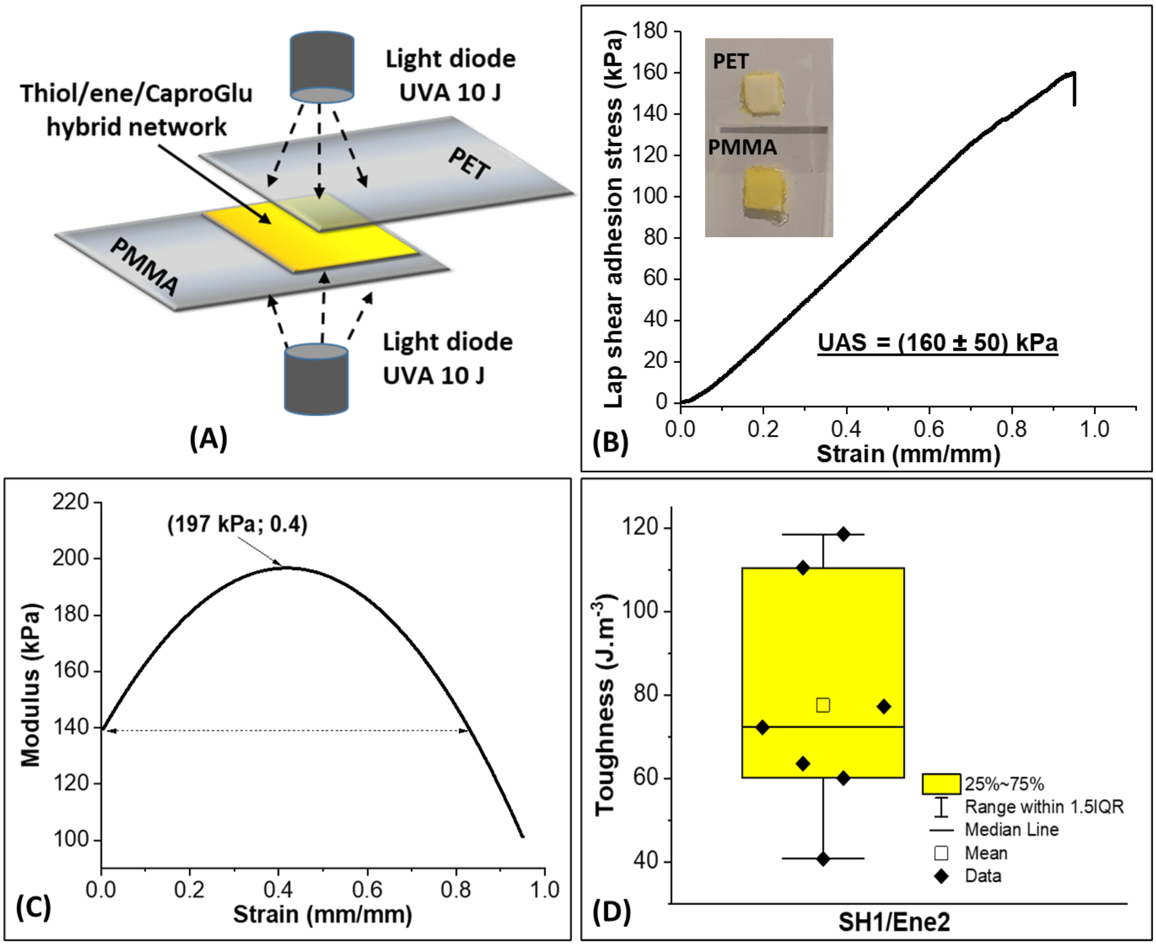


Figure S12. Lap shear adhesion test and representative mechanical profile of 3-component thiol/ene/CaproGlu hybrid network – SH1/Ene2/Dz (n = 7): (A) experimental design for crosslinking of SH1/Ene2/Dz sample in PMMA/hybrid network/PET sandwich structure by crosslinking the network from 2 sides through light-transparent substrates (PMMA-bottom; PET-top) by using 2 UVA diodes – each side of SH1/Ene2/Dz sample absorbed the UVE energy = 10 $J.cm^{-2}$ (total absorbed dose = 20 $J.cm^{-2}$); (B) representative lap shear adhesion stress vs strain data recorded for SH1/Ene2/Dz (inset showing cohesive failure of SH1/Ene2/Dz at yield point); (C) modulus vs strain with indicated maximum value at 197 kPa (dashed arrow indicates the modulus drop to initial value at 140 kPa); (D) modulus of toughness calculated as area under stress vs strain curves (n = 7; individual curves for each measured sample are shown in Supporting Information; ANOVA; interquartile range (IQR): 25th to the 75th percentile).

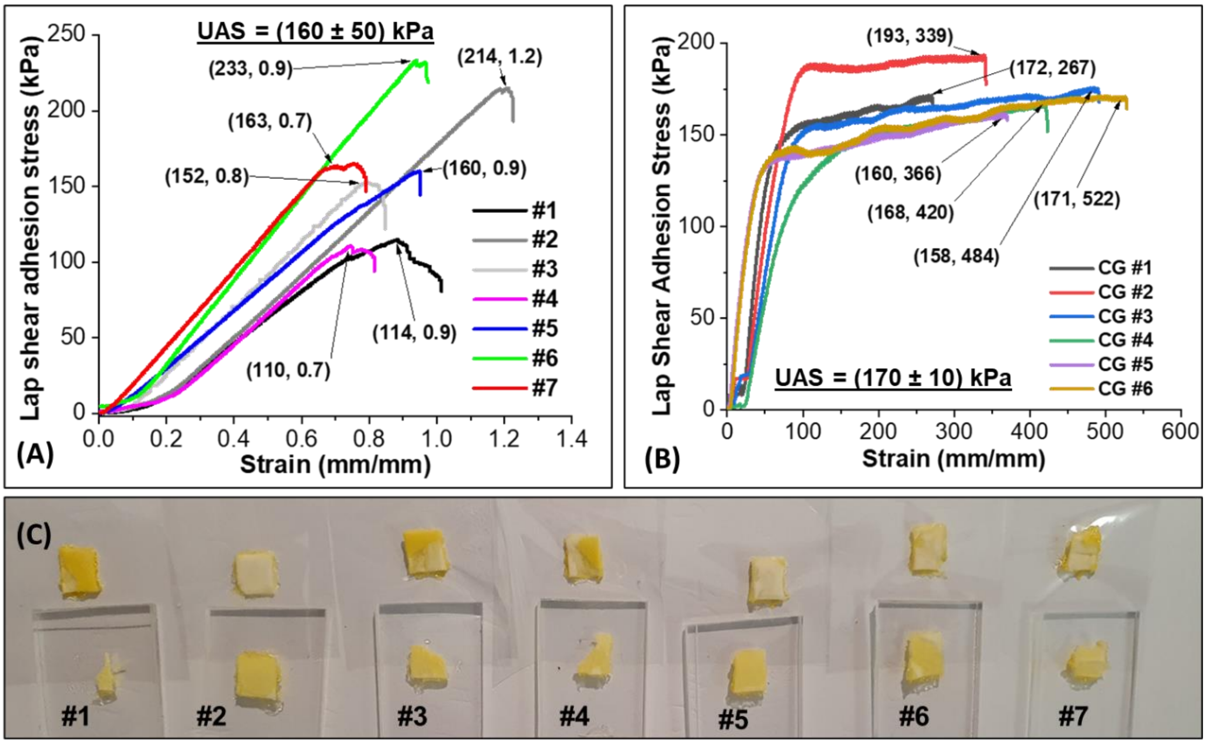


Figure S13. Lap shear adhesion stress vs strain profile measured for PMMA-hybrid network (SH1/Ene2/Dz)-PET sandwich structure: (A) data collected for 7 samples and average value of ultimate adhesion strength for SH1/Ene2/Dz; (B) pure CaproGlu (CG; control-1) data collected from 6 samples measuring lap shear adhesion stress vs strain PMMA-CaproGlu-PET structure and average value of ultimate adhesion strength; (C) photography of measured samples after mechanical lap shear failure demonstrating cohesive adhesion.