

Electronic Supplementary Information for:

**3D printable, thermo-responsive, self-healing, graphene oxide
containing self-assembled hydrogels formed from block copolymer
wormlike micelles.**

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Additional experimental materials and methods

Materials

Glycerol monomethacrylate (GMA) was kindly donated from GEO Specialty Chemicals (U.K.), 4-Cyano-4-(2-phenylethane sulfanylthiocarbonyl) sulfanylpentanoic acid (PETTC) was prepared in-house using previously published methods.^{1,2}

Synthesis of poly (glycerol monomethacrylate) (PGMA) via RAFT solution polymerisation

PGMA was synthesised by RAFT polymerisation in ethanol at 70 °C and has been widely reported in the literature (Figure S1).³ GMA monomer (20 g, 124 mmol) and PETTC RAFT agent (0.8476 g, 2.5 mmol) were weighed into a 250 mL round-bottomed flask and purged with N₂ for 30 min. 4,4-azobis(4-cyanovaleric acid) (ACVA) initiator (0.14 g, 0.5 mmol, PETTC/ACVA molar ratio = 5:0) and anhydrous ethanol (20 g, previously purged with N₂ for 20 min) were then added, and the resulting yellow solution was degassed for a further 15 min while stirring to form a homogeneous solution. The flask was subsequently sealed and immersed in an oil bath set at 70 °C.³ After 120 min, the polymerisation was quenched by immersion in an ice bath and opening to air. The final degree of polymerisation (DP) was 58, as determined by ¹H-NMR analysis (Figure S2) using D₂O. The polymer was purified by dialysis (MWCO = 3500 g mol⁻¹) against deionised water and freeze-dried to form a yellow powder. DMF GPC analysis indicated an M_n of 4700 g mol⁻¹ and an M_w/M_n of 1.17 (Figure S3).

Preparation of PGMA-PPMA-x% GO nanocomposite worm gels by physical mixing

The 20 % w/w G₅₈-H₁₇₀ copolymer worm gel and the GO dispersion (~15 mg ml⁻¹) were cooled to approximately 5 °C until the copolymer dispersion was in a free-flowing state. Appropriate quantities of the pre-cooled GO dispersion and/or deionised water were added to the cooled copolymer dispersion. The samples were mixed gently for 10 s in cooled water using a vortex mixer and subsequently allowed to return to room temperature (Figure S6).

¹H NMR spectroscopy. ¹H NMR spectra were recorded on a Bruker Avance III 400MHz spectrometer with 128 scans averaged per spectrum at 25 °C.

Gel permeation chromatography (GPC). 0.50 % w/w polymer solution was prepared in DMF containing DMSO (10 μL mL⁻¹) as a flow-rate marker. GPC measurements were conducted using HPLC-grade DMF eluent containing 10

mM LiBr at 60 °C at a flow rate of 1.0 mL min⁻¹. An Agilent Technologies 1260 Infinity GPC / SEC system fitted with two Polymer Laboratories PL gel 5µm Mixed C columns connected in series, and a refractive index detector was used to assess molar mass distributions using polystyrene calibration standards.

Dynamic light scattering (DLS). A Malvern Zetasizer Nano ZS instrument was used to measure particle size. The instrument is equipped with a He–Ne solid-state laser operating at 633 nm and detects back-scattered light at a scattering angle of 173°. All size measurement data were averaged over three consecutive runs comprising thirteen measurements each.

Atomic force microscopy (AFM). The GO dispersion was diluted to 0.1 % w/w and then 100 µL diluted GO dispersion were then spin coated on a newly cleaved mica sheet at 1500 rpm for 30 seconds. AFM imaging was performed on a Bruker Multimode 8 (Bruker, USA). The dispersion were scanned in room temperature in ScanAsyst (tapping) mode, using a ScanAsyst-Air probe with 70 Hz frequency and nominal spring content k, of 0.4 N m⁻¹. AFM images were acquired at 512*512 pixels resolution over scanning ranging from 2*2 to 10*10 µm. At a scan frequency of 1 Hz and analysed with Gwyddion software.

Raman spectroscopy. Raman spectroscopy was been performed using a Horiba Scientific LabRAM HR Evolution instrument using a He-Ne laser (wavelength 633 nm) with an edge filter, and a grid of 600 gr/mm. Samples were cast and flattened on cleaned glass slides, and a 50x long working distance objective was used to focus the laser on the samples with a laser power of 0.29 mW.

Supporting data tables

Table S1. Oscillatory rheology information of the GO containing composite worm gel.

Entry	Composition of GO containing composite worm gel	G' of LVR (kPa) ^a	CGT ^b		G' after temperature change cycle (kPa)	Recovery efficiency (%) ^c
			Cooling (°C)	Heating (°C)		
1	15% PGMA-PHPMA-2% GO	3.1 ± 0.6	6	9	2.8 ± 0.8	80.2
2	15% PGMA-PHPMA-4% GO	6.1 ± 0.3	4	7	4.6 ± 1.3	87.6
3	15% PGMA-PHPMA-6% GO	3.5 ± 0.4	6	8	2.4 ± 1.4	83.2
4	20% PGMA-PHPMA-2% GO	7.3 ± 0.8	3	2	7.3 ± 0.6	92.5
5	20% PGMA-PHPMA-4% GO	20.5±1.9	N/A	2	20.5 ± 2.5	96.8
6	20% PGMA-PHPMA-6% GO	3.7 ± 0.4	2	5	3.4 ± 1.6	96.5
7	25% PGMA-PHPMA-2% GO	33.1±3.5	N/A	N/A	32.6 ± 5.4	98.1
8	25% PGMA-PHPMA-4% GO	11.6±2.0	N/A	N/A	15.3 ± 3.8	98.3
9	25% PGMA-PHPMA-6% GO	9.7±1.1	N/A	N/A	9.5 ± 2.2	97.5

^a LVR: Linear viscoelastic region

^b CGT: Critical gelation temperature

^c Recovery efficiency: Dividing the G' of the last low strain (0.2%) by the G' of the original low strain obtained by the rheology shear-thinning recovery test.

Table S2. Tensile test information of the GO containing composite worm gel.

Entry	Composition of GO containing composite worm gel	Young's modulus / KPa	Fracture strain / %	Toughness / KJ/mm ³	Healing efficiency (%) ^a
1	15% PGMA-PHPMA-2% GO	41.5±4.9	1.3±0.2	21.9±6.7	55.2
	After healing	30.3±8.4	1.1±0.4	12.1±2.2	
2	15% PGMA-PHPMA-4% GO	95.55±9.4	3.5±0.2	486.2±48.2	63.2
	After healing	75.9±14.5	3.1±0.6	307.3±22.4	
3	15% PGMA-PHPMA-6% GO	56.15±13.2	1.5±0.3	47.9±10.8	39.2
	After healing	35.5±17.5	1.2±0.7	18.8±4.9	
4	20% PGMA-PHPMA-2% GO	105.3±7.2	4.2±1.4	844.1±86.4	96.1
	After healing	93.7±12.4	4.2±1.1	811.5±96.7	
5	20% PGMA-PHPMA-4% GO	356.4±22.2	7.5±1.3	10760.5±205	97.7
	After healing	345.7±29.6	7.5±1.8	10510.3±279	
6	20% PGMA-PHPMA-6% GO	54.5±13.1	2.1±0.5	125.2±18.4	90.8
	After healing	48.7±15.2	2.1±0.5	113.7±19.1	
7	25% PGMA-PHPMA-2% GO	446.7±14.4	13.4±4.8	41956.2±304	106.9
	After healing	195.5±34.15	15.2±3.2	44861±254	
8	25% PGMA-PHPMA-4% GO	232.6±27.8	9.4±1.5	11855.9±460	123.3
	After healing	149.5±44.5	10.6±2.7	14614±601	
9	25% PGMA-PHPMA-6% GO	185.5±10.4	8.6±1.1	6990.4±371	122.8
	After healing	128.9±37.4	9.8±0.9	8585.5±268	

^a Healing efficiency: Dividing the toughness of healed samples by the toughness of the original samples.

Supporting Figures

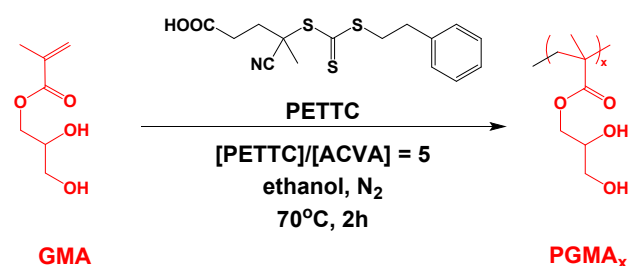


Figure S1. Synthesis of PGMA_x macromolecular chain-transfer agent (macro-CTA) *via* RAFT solution polymerisation in ethanol at 70 °C.

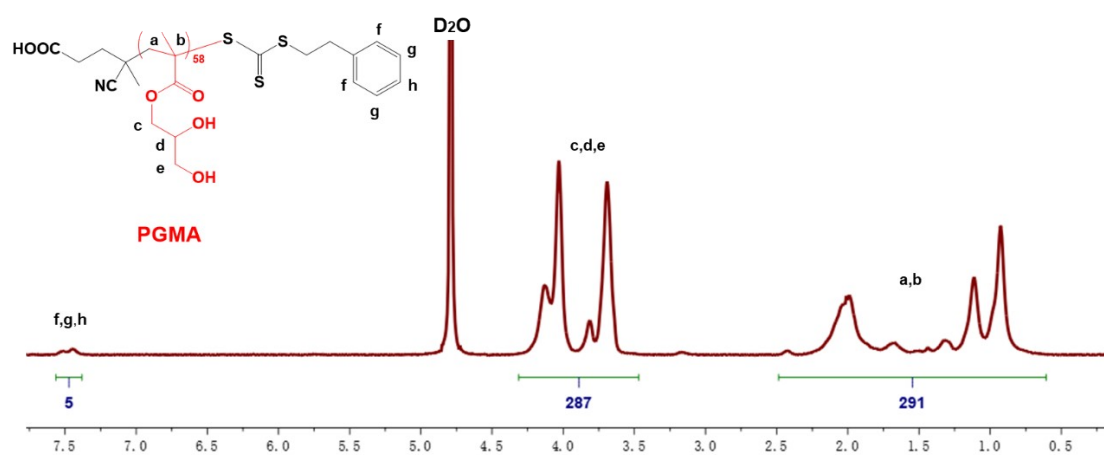


Figure S2. Assigned NMR spectra of PGMA₅₈ macro-CTA in D₂O.

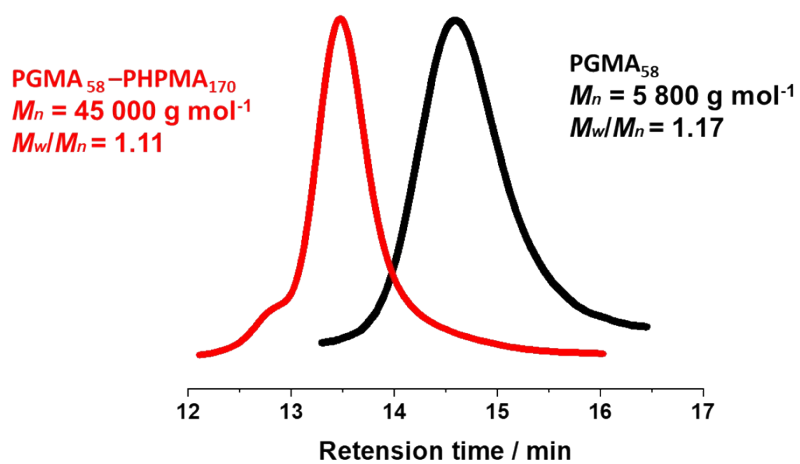


Figure S3. DMF GPC data recorded for PGMA₅₈ macro-CTA and PGMA₅₈-PPHMA₁₇₀. M_n and M_w/M_n values were determined using polystyrene calibration standards.

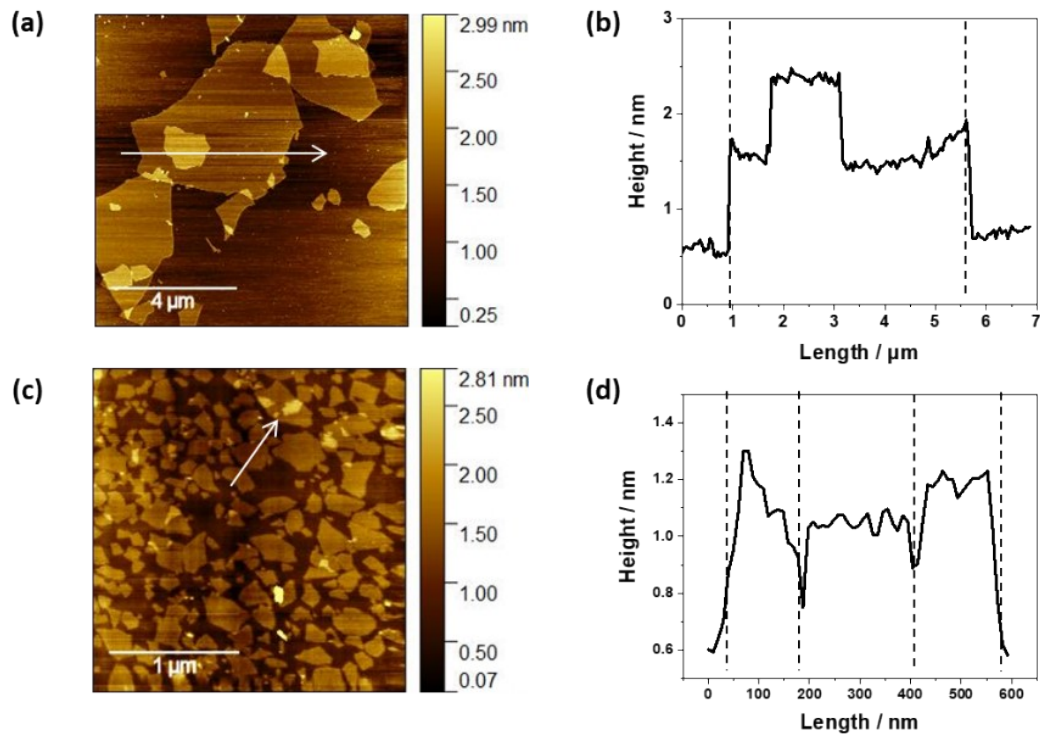


Figure S4. AFM images for (a) GO sheets after bath sonication; (b) GO sheets after probe sonication. (a) and (b) height profiles corresponding to the large GO sheets and small GO sheets respectively. Samples were diluted to 0.1 % w/w before being deposited at room temperature.

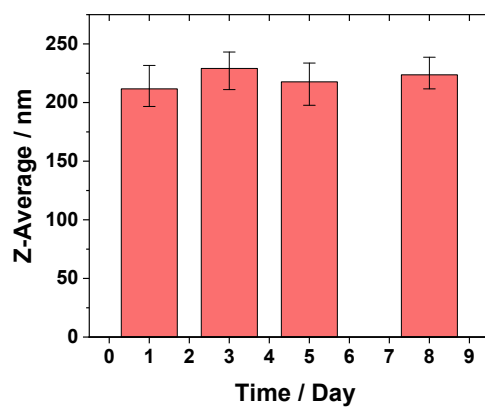


Figure S5. Dynamic light scattering studies for 0.1 % w/w GO dispersions after probe sonication. The GO flake equivalent diameter (Z-average) recorded at 25 °C after day 1, day 3, day 5 and day 8.

0.7% GO 1.5% GO 1.7% GO 2% GO 2.5% GO



Figure S6. Photograph taken at room temperature of 15% G_{58} - H_{170} -x% GO composite gels prepared *via* physical mixing copolymer with GO at low temperature.

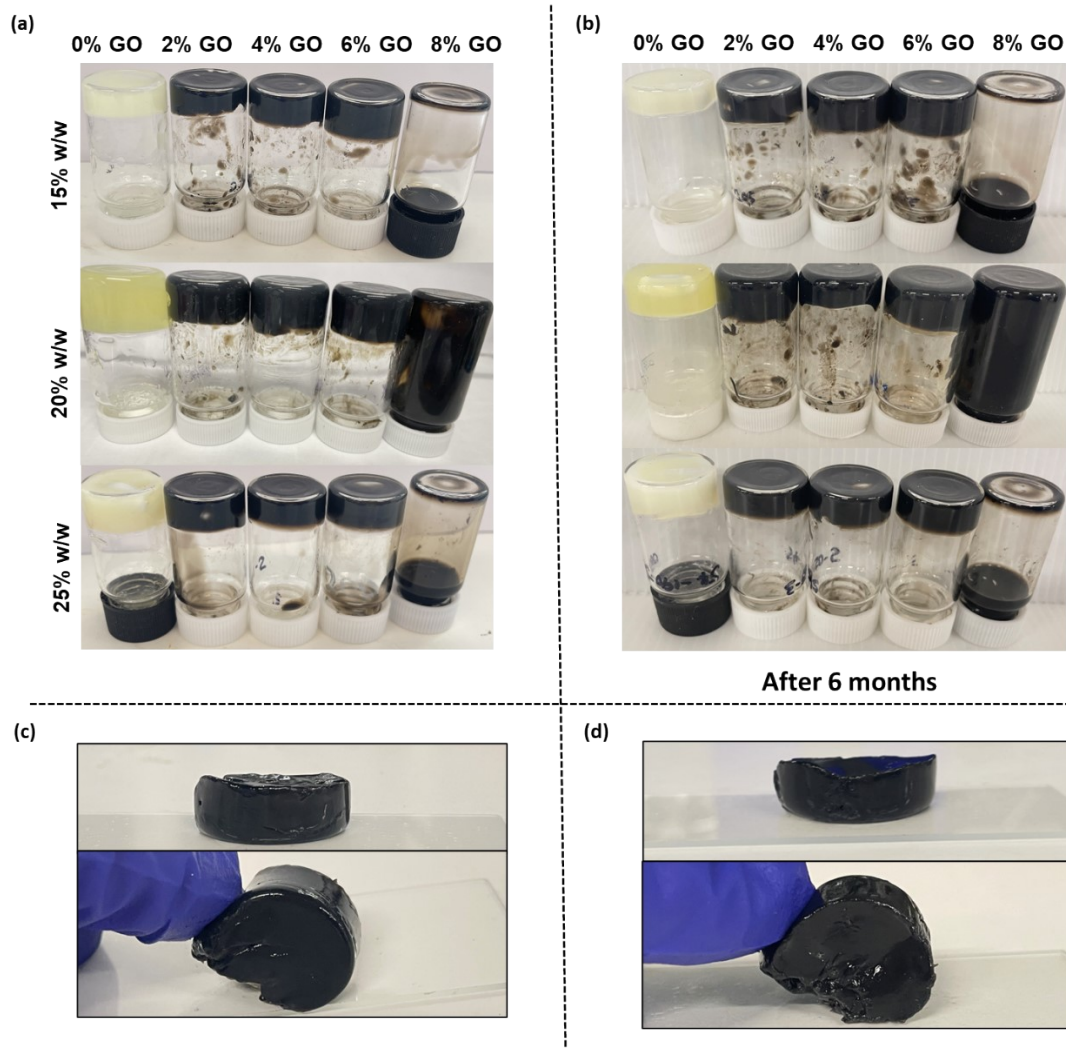


Figure S7. Photographs taken at room temperature of (a) n% G_{58} - H_{170} -x% GO composite gels prepared *via* RAFT *in situ* polymerisation (a and c) shortly after preparation, (b and d) after 6 months storage at room temperature.

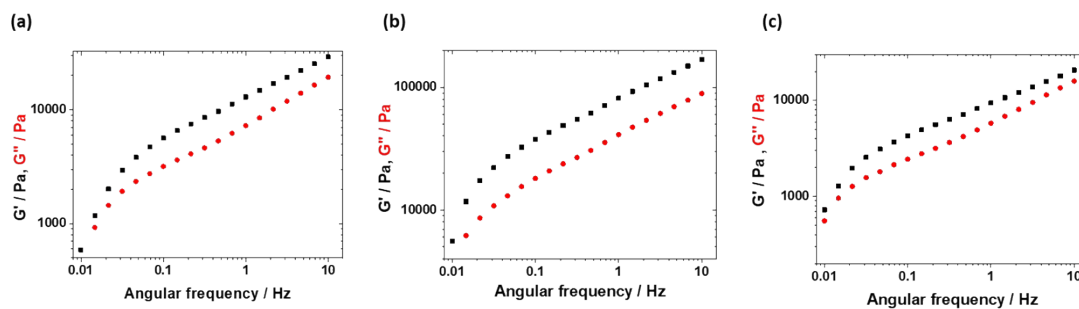


Figure S8. Angular frequency dependent storage modulus (G') and loss modulus (G'') for (a) 15% w/w G-H-4% GO, (b) 20% w/w G-H-4% GO and (c) 25% w/w G-H-4% GO based on copolymer. Measurements were recorded between 0.01 and 10 Hz at 0.2 % strain and 25 °C.

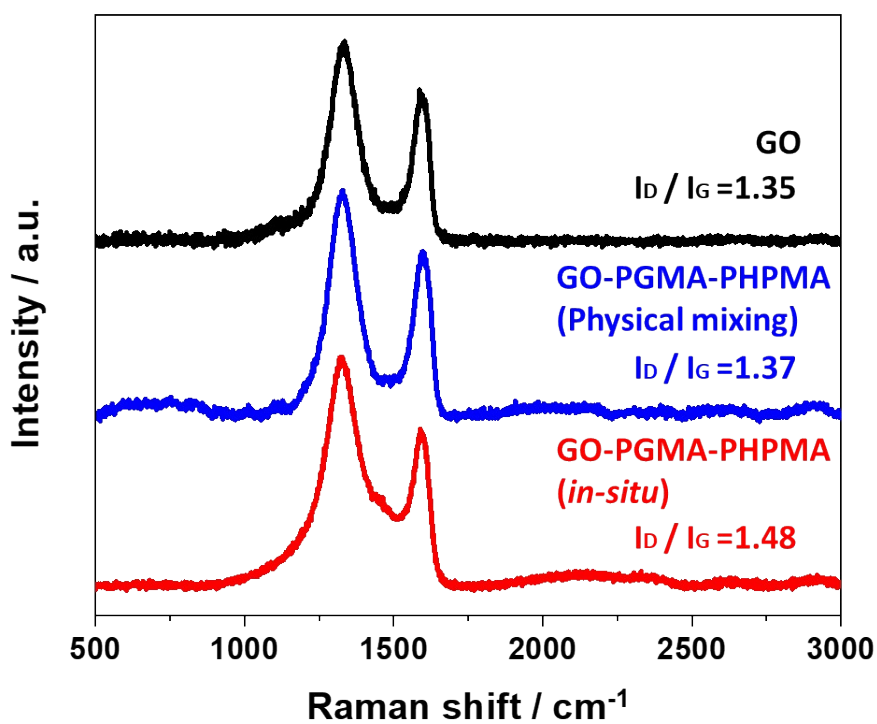


Figure S9. Raman spectra of GO, GO-PGMA-PHPMA prepared by physical mixing and GO-PGMA-PHPMA prepared by *in situ* polymerisation.

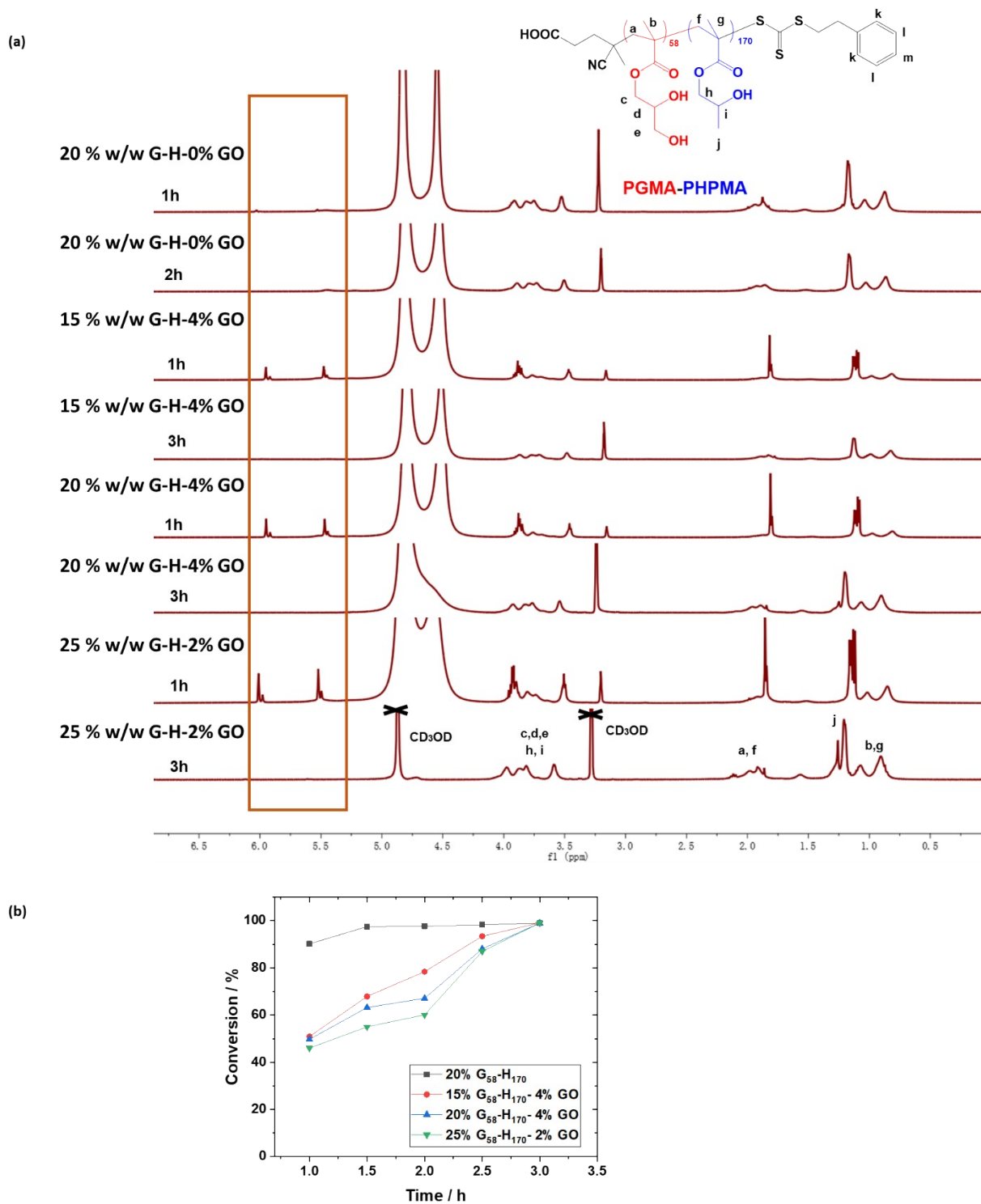


Figure S10. (a) Assigned NMR spectra recorded in CD₃OD for samples extracted during *in situ* polymerisation for a PGMA₅₈-PPHMA₁₇₀ copolymer (sampling times 1h and 2h) and 15% G₅₈-H₁₇₀-4%GO, 20% G₅₈-H₁₇₀-4%GO and 25% G₅₈-H₁₇₀-2%GO nanocomposite gels (sampling times 1h and 3h). (b) HPMA monomer conversion as a function of time for these *in situ* RAFT polymerisations.

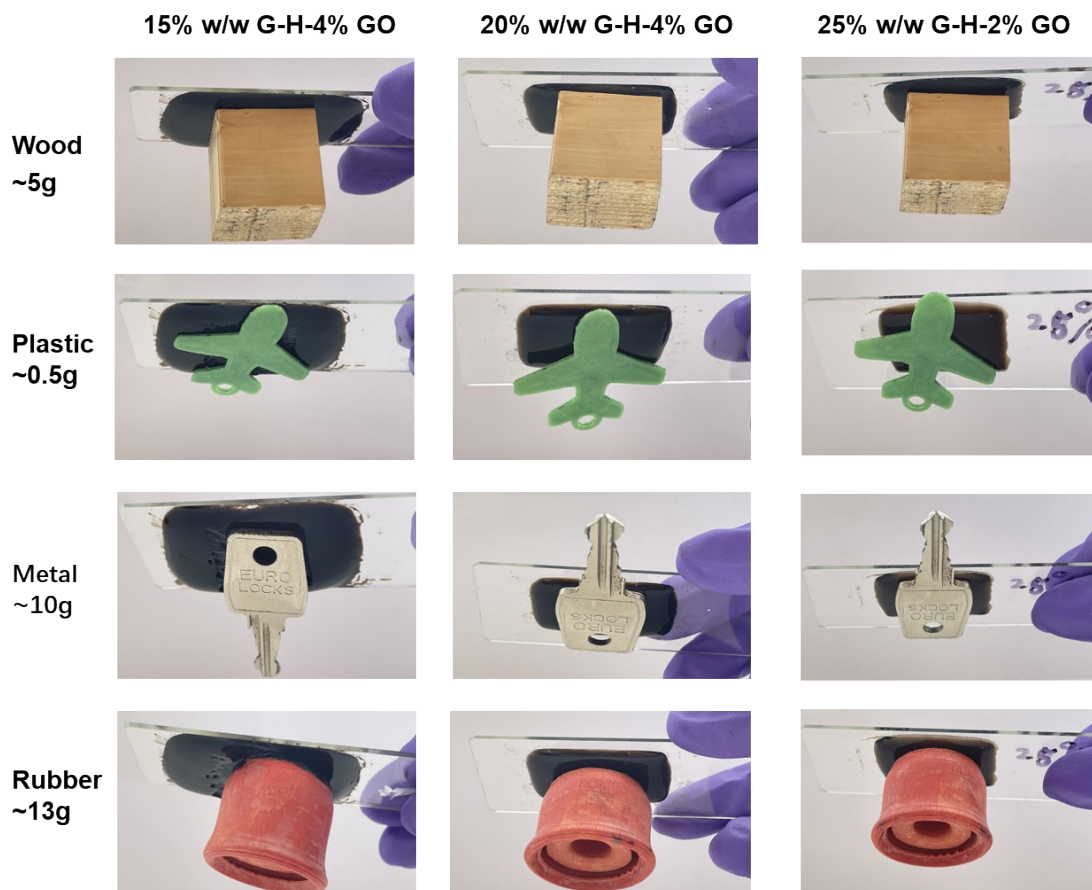


Figure S11. 15% w/w G-H-4% GO, 20% w/w G-H-4% GO and 25% w/w G-H-2% GO after self-healing adheres to various materials including glass, wood, plastic, metal and rubber.

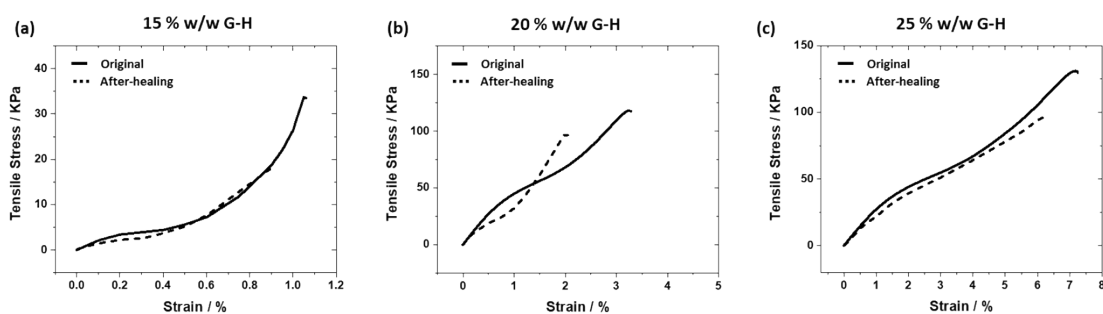


Figure S12. Tensile testing data for (a) 15 % (b) 20% and (c) 25% w/w G_{58} - H_{170} copolymer worm gels (straight line: original and dashed line: after self-healing) at room temperature.

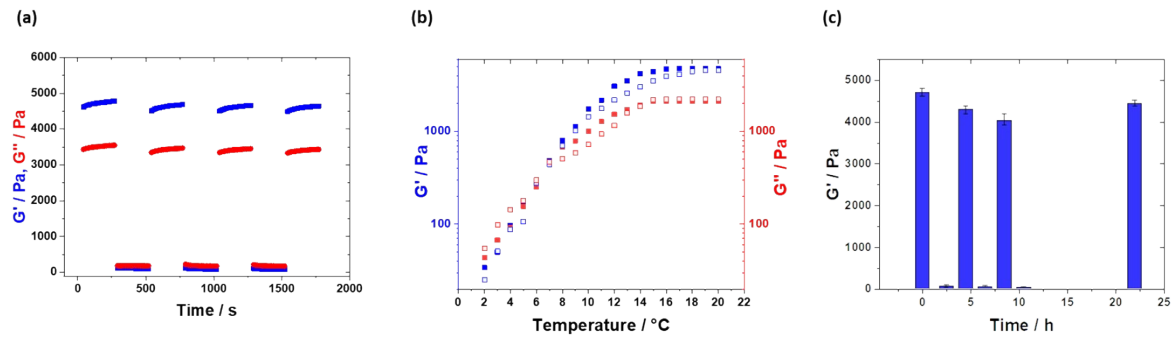


Figure S13. Rheology data for 15% G_{58} - H_{170} -2.0% GO composite gels prepared by low-temperature physical mixing of copolymer and GO. (a) Shearing-thinning recovery experiments. G' and G'' were recorded continuously with alternating small ($\gamma = 0.2\%$) and large ($\gamma = 100\%$) strain at $25\text{ }^\circ\text{C}$ with an angular frequency of 10 rad s^{-1} . (b) Temperature-dependent oscillatory rheology studies. The temperature was varied from $25\text{ }^\circ\text{C}$ to $2\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$ in $1\text{ }^\circ\text{C}$ steps with 3 minutes equilibration at each step. (c) Temperature-dependent oscillatory rheology studies obtained for storage modulus (G'). The temperature was varied from $20\text{ }^\circ\text{C}$ to $2\text{ }^\circ\text{C}$ to $20\text{ }^\circ\text{C}$ s with 2 h equilibration at each step. The final step with 12h equilibration at $20\text{ }^\circ\text{C}$. Measurements were conducted at an angular frequency of 10 rad s^{-1} and applied strain amplitude of 1.0% .

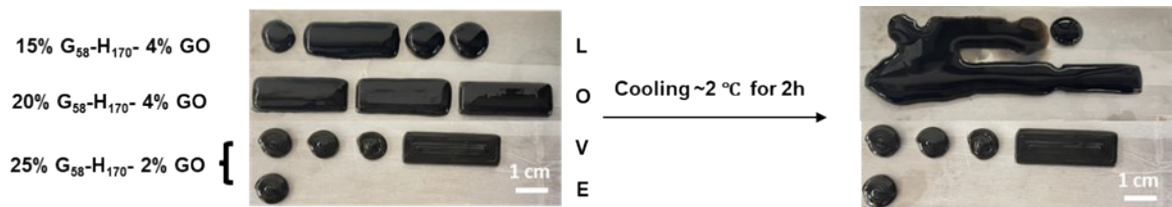


Figure S14. 3D printed international morse code (spelling 'LOVE') of 15%, 20% and 25% w/w copolymer nanocomposite worm gels after printing (left) and showing information loss for the 15% and 20% gels after cooling for 2 h (right).

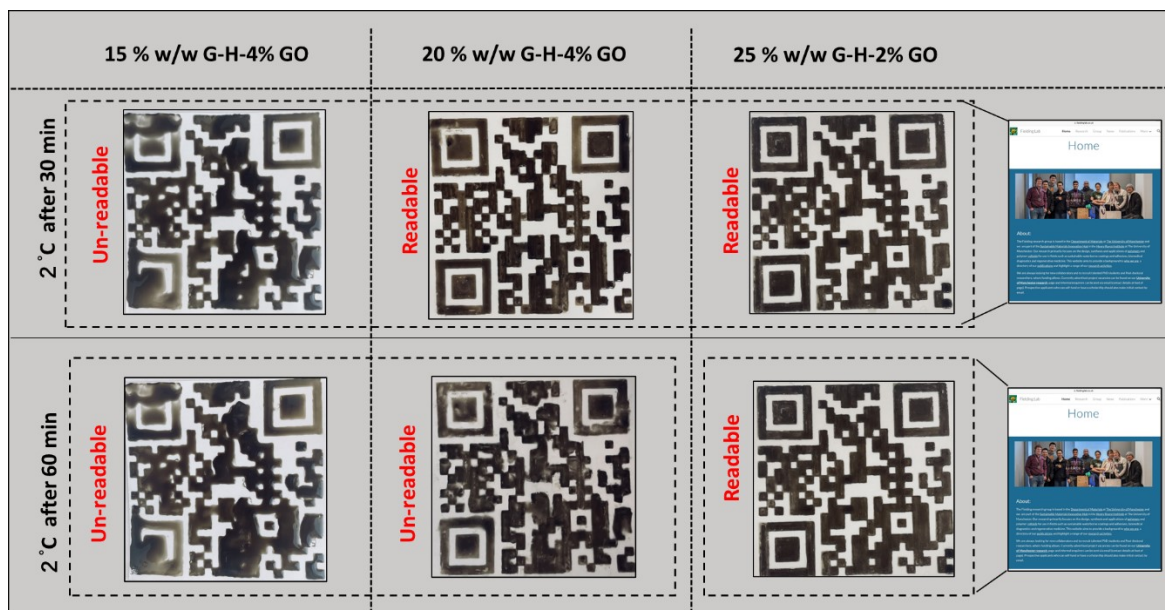


Figure S15. 3D printed QR codes using 15 % w/w $G_{58}\text{-}H_{170}\text{-}4\%$ GO; 20% w/w $G_{58}\text{-}H_{170}\text{-}4\%$ GO and 25% $G_{58}\text{-}H_{170}\text{-}2\%$ GO nanocomposite worm gels. Top row: images of QR codes after being held at 2 °C for 30 min. Bottom row: images of QR codes being held at 2 °C for 60 min.

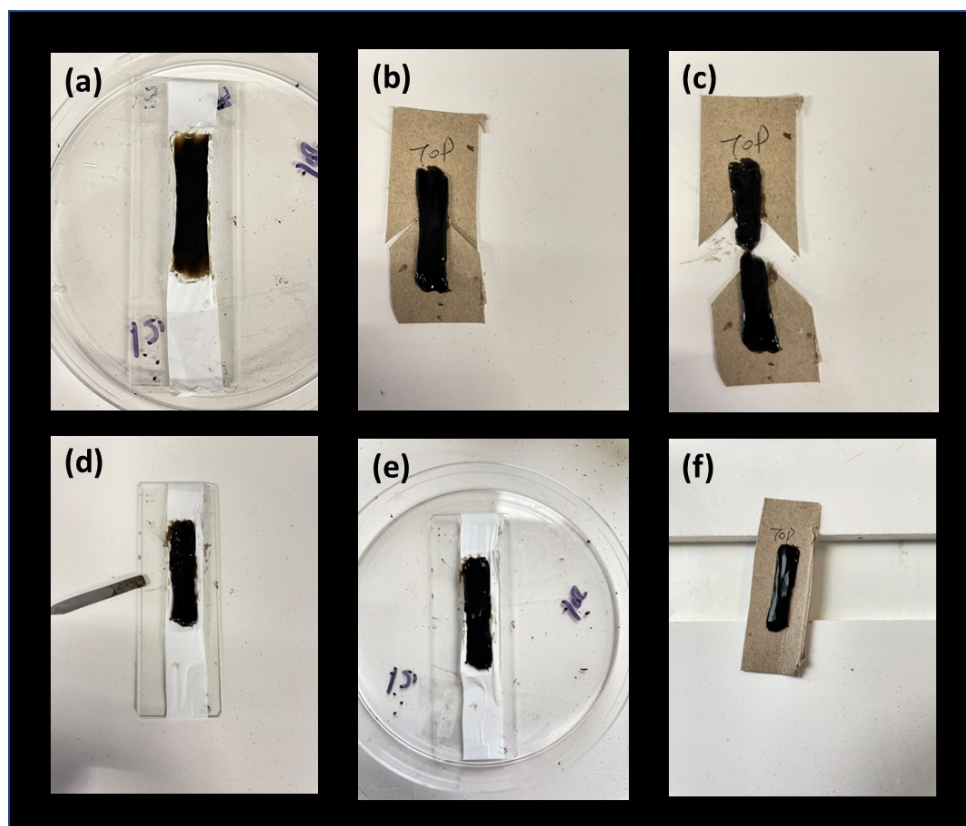


Figure S16. Digital photographs showing tensile testing sample preparation: (a) gel cast onto PTFE tape set into a silicone mould; (b) gel transferred to testing card; (c) after gel fracture; (d) fractured gel transferred to mould; (e) gel after being left at room temperature for 6 h; (f) healed gel transferred to testing card.

References

1. Semsarilar, M.; Ladmira, V.; Blanz, A.; Armes, S., Anionic polyelectrolyte-stabilized nanoparticles via RAFT aqueous dispersion polymerization. *Langmuir* **2012**, *28* (1), 914-922.
2. Wen, S.-P.; Saunders, J. G.; Fielding, L. A., Investigating the influence of solvent quality on RAFT-mediated PISA of sulfonate-functional diblock copolymer nanoparticles. *Polymer Chemistry* **2020**, *11* (20), 3416-3426.
3. Warren, N. J.; Derry, M. J.; Mykhaylyk, O. O.; Lovett, J. R.; Ratcliffe, L. P.; Ladmira, V.; Blanz, A.; Fielding, L. A.; Armes, S. P., Critical dependence of molecular weight on thermoresponsive behavior of diblock copolymer worm gels in aqueous solution. *Macromolecules* **2018**, *51* (21), 8357-8371.