Supplementary Information

Injectable, shear-thinning, photocrosslinkable, and tissue-adhesive hydrogels composed of diazirine-modified hyaluronan and dendritic polyethyleneimine

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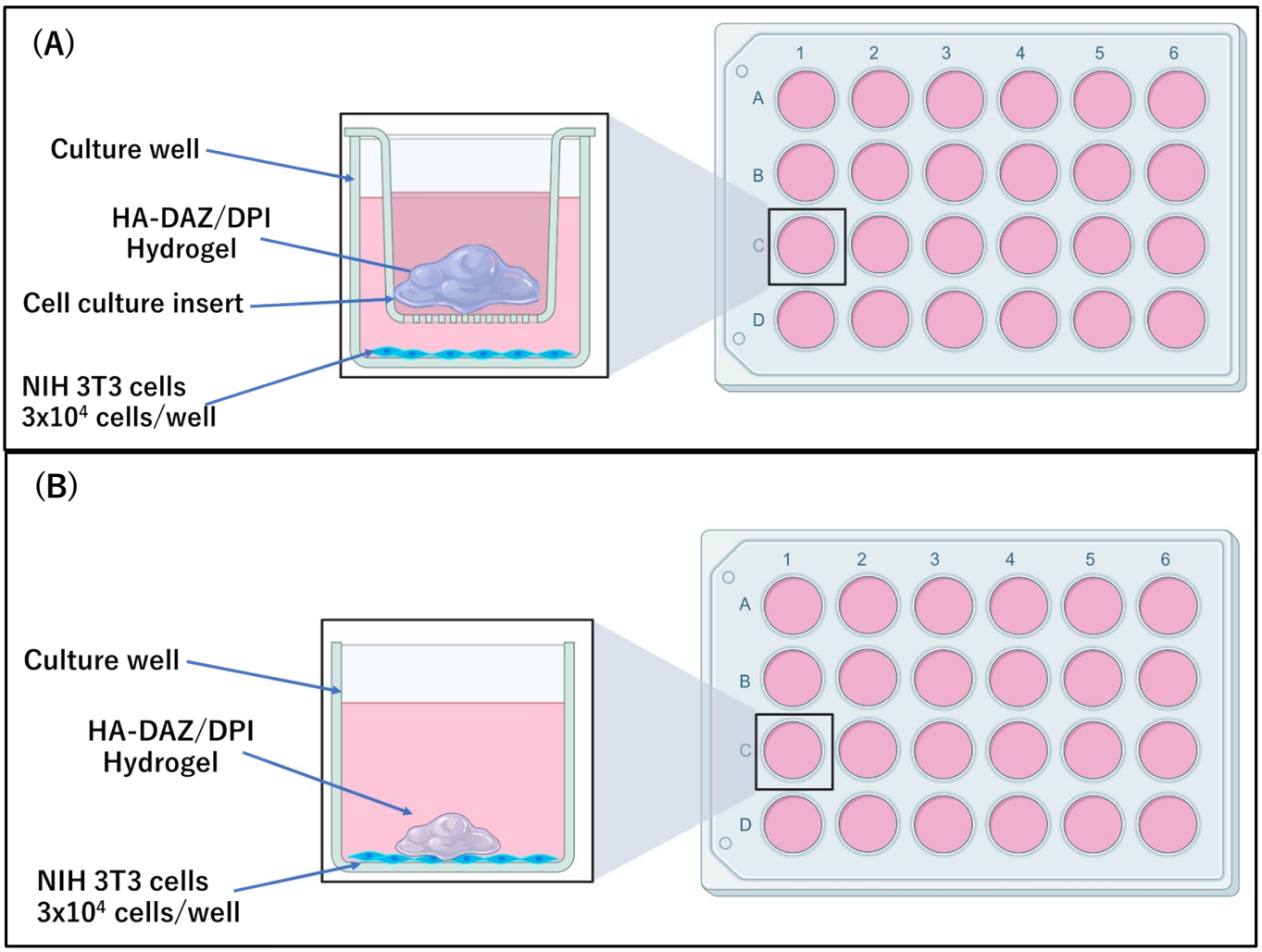


Fig. S1. Schematic illustration of the cytocompatibility experiment. Shown are (A) separation of the hydrogel and cells using a cell culture insert and (B) direct placement of the hydrogel on cells.

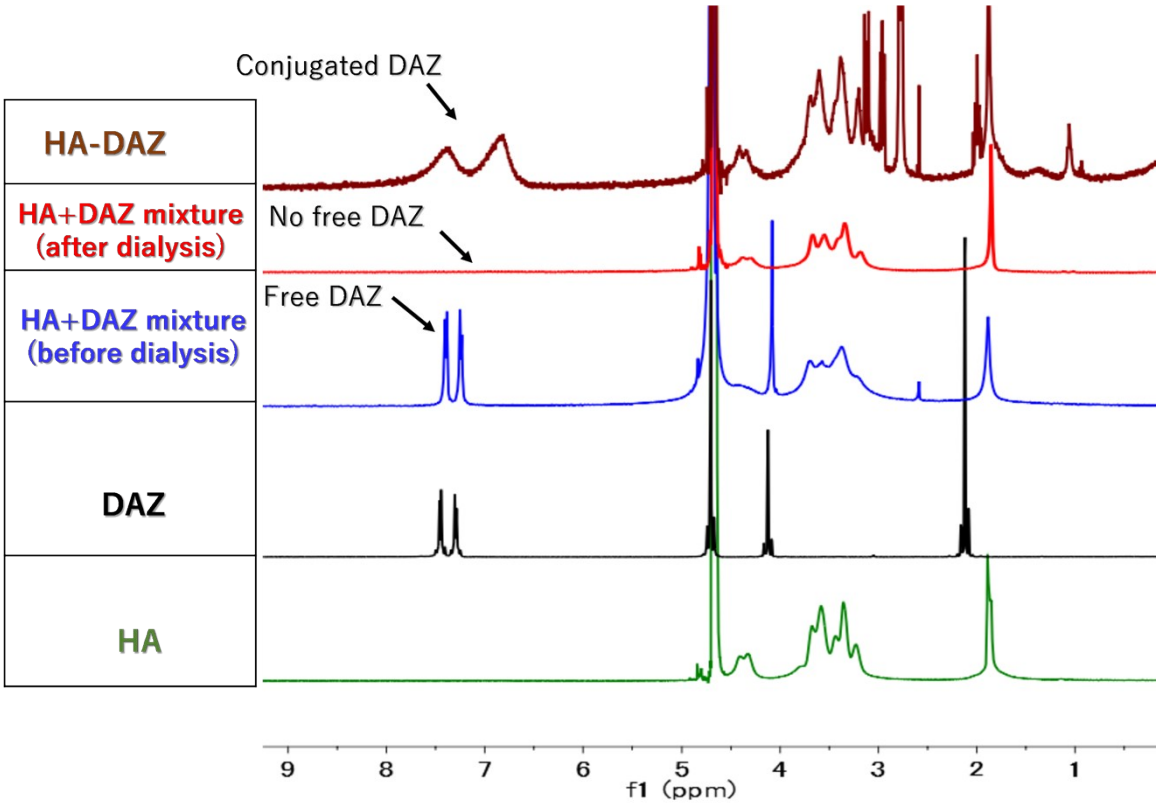
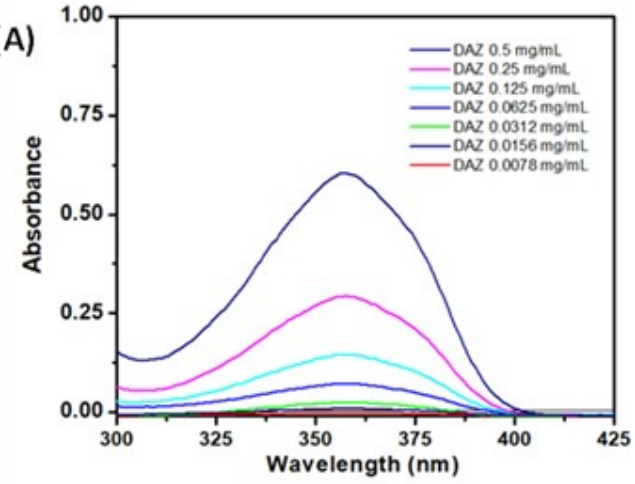


Fig. S2 ^{1}H NMR spectra of the HA and DAZ mixture before and after dialysis. Peaks associated with DAZ disappeared after the dialysis, indicating successful purification.

(A)



(B)

Concentration (mg/mL)	Absorbance
0.0156	0.009
0.0312	0.025
0.0625	0.072
0.125	0.145
0.25	0.293
0.5	0.602

(C)

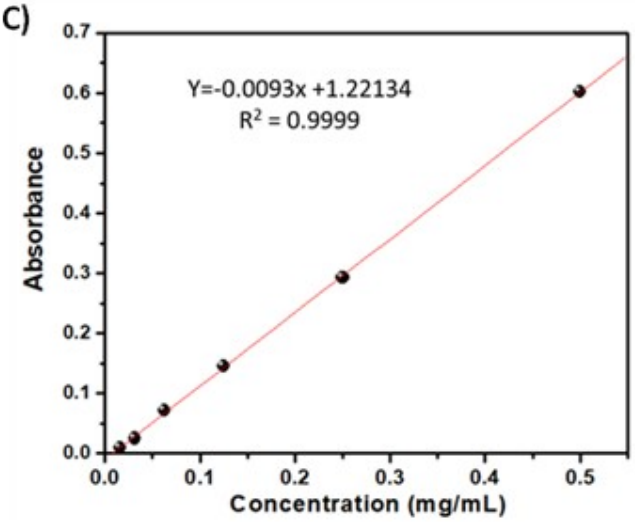


Fig. S3. (A) UV-vis spectra and (B) absorbance value at 348 nm of diazirine of the different concentrations in DMSO. (C) Calibration line between absorbance at 348 nm and diazirine concentration.

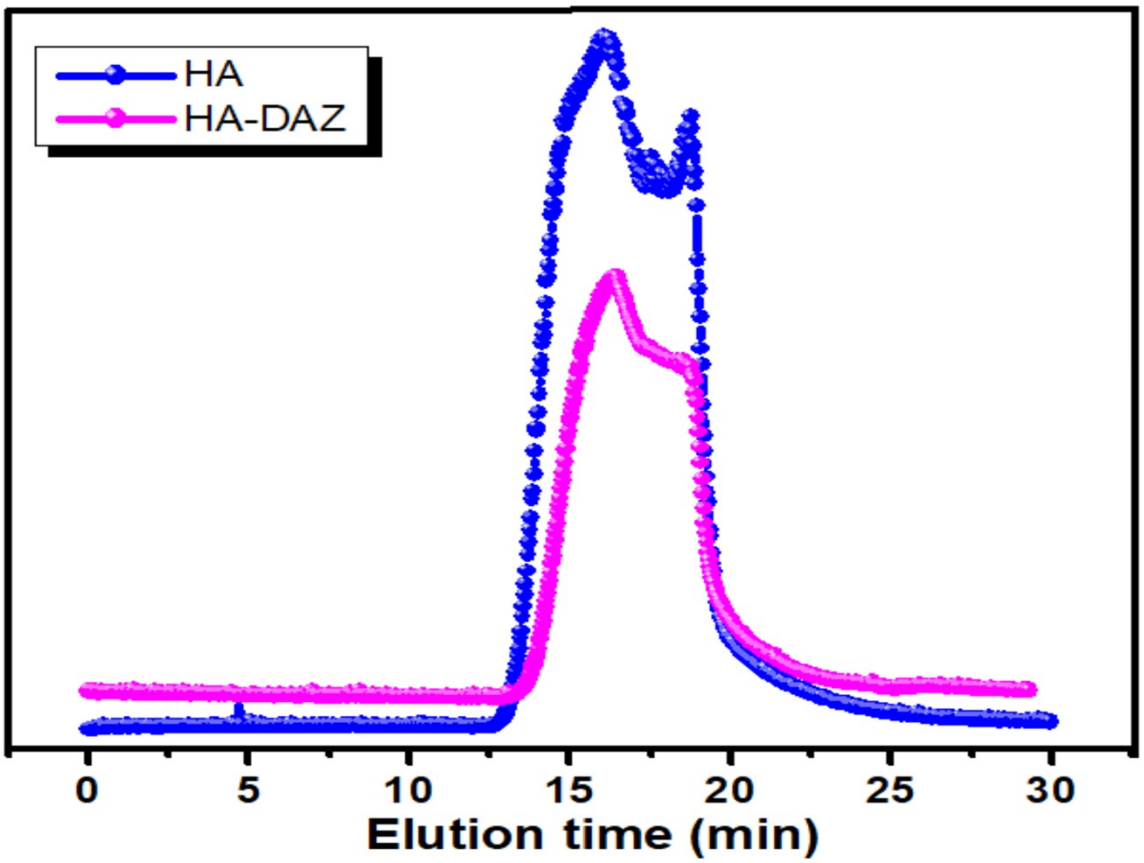


Fig. S4. GPC elution curves for HA and HA-DAZ

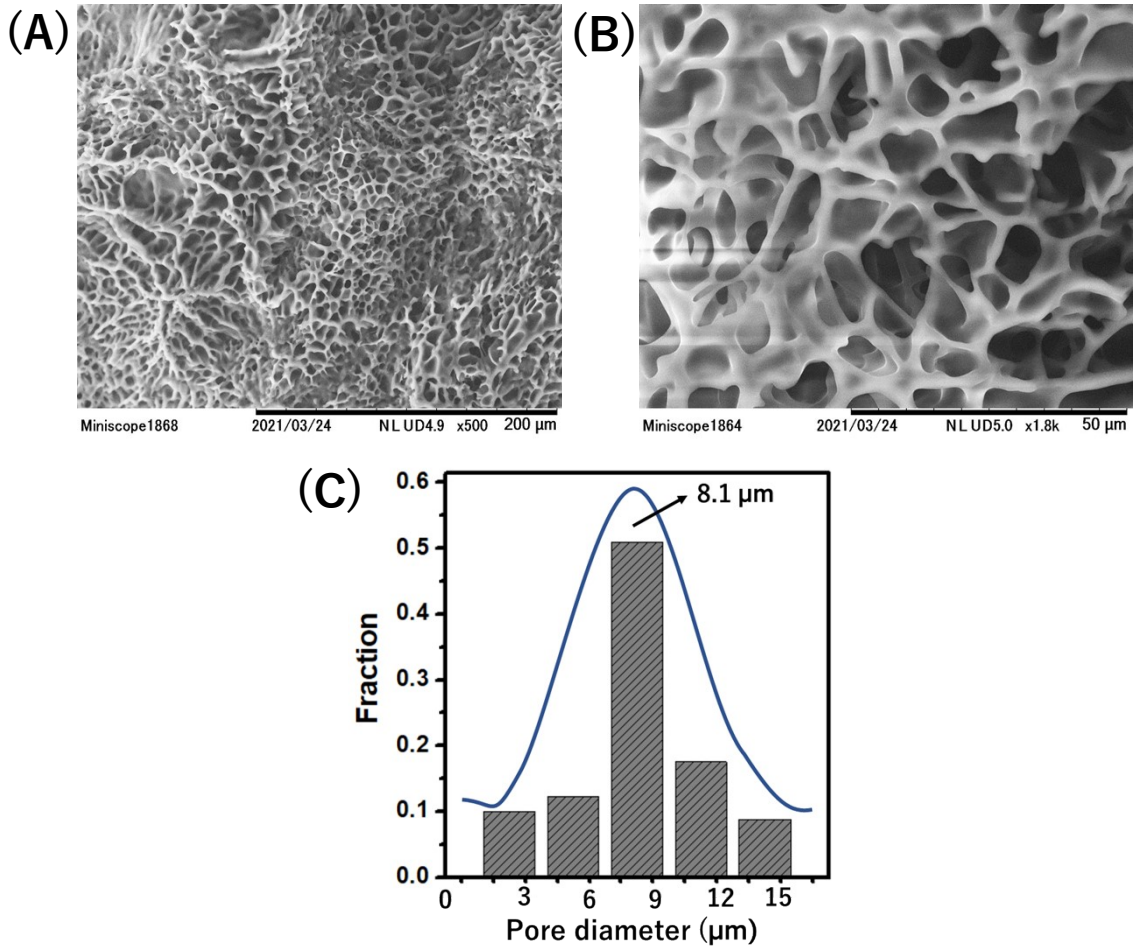


Fig. S5. Pore-size estimation of the photo-crosslinked HA-DAZ hydrogels. (A-B) show cross-sections of the HA-DAZ/DPI hydrogel and (C) shows the pore-size distribution of the DAZ/DPI crosslinked hydrogel. The average pore size of the photocrosslinked HA-DAZ/DPI hydrogel was calculated using SEM images.

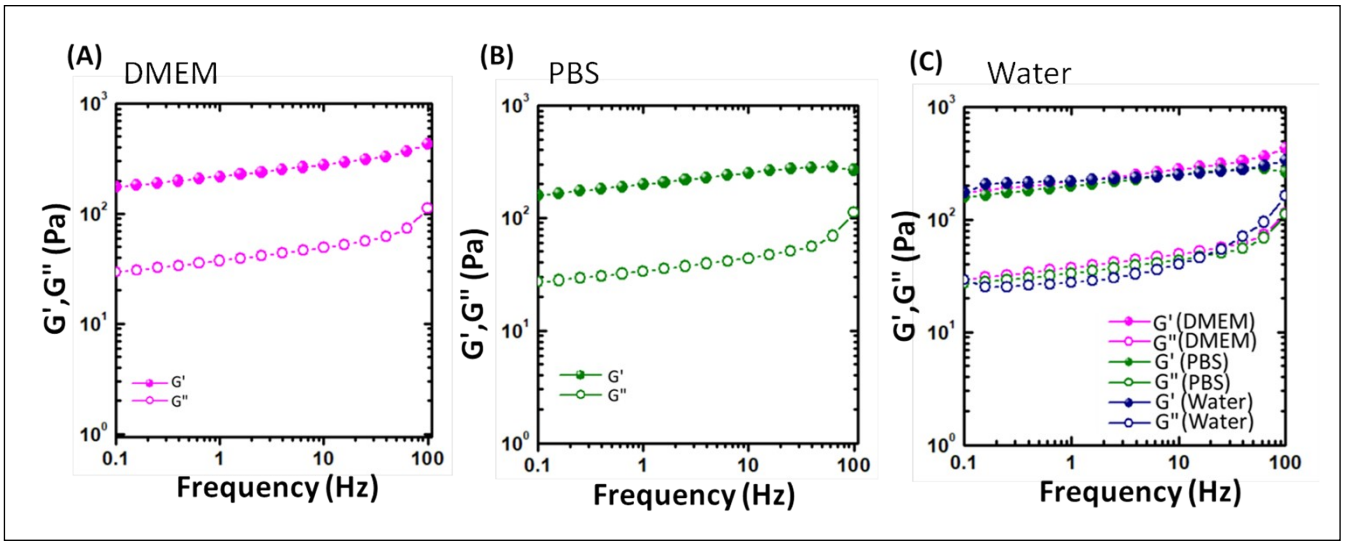


Fig. S6. Frequency sweep test of HA-DAZ/DPI hydrogels prepared with (A) DMEM and (B) PBS (adjusted to pH 7.4). Data for HA-DAZ/DPI hydrogels prepared with water (described in the main text) is also shown in (C) Water for comparison.

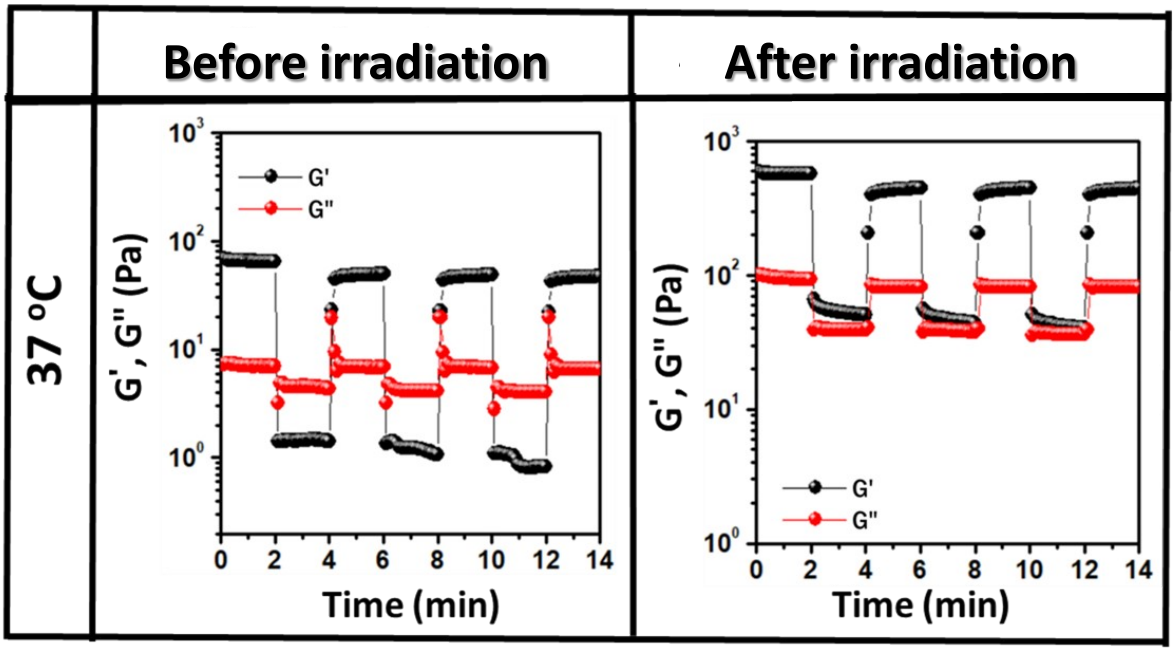


Fig. S7. Self-healing properties of HA-DAZ/DPI as examined by alternative strain sweep before and after photocrosslinking at 37°C

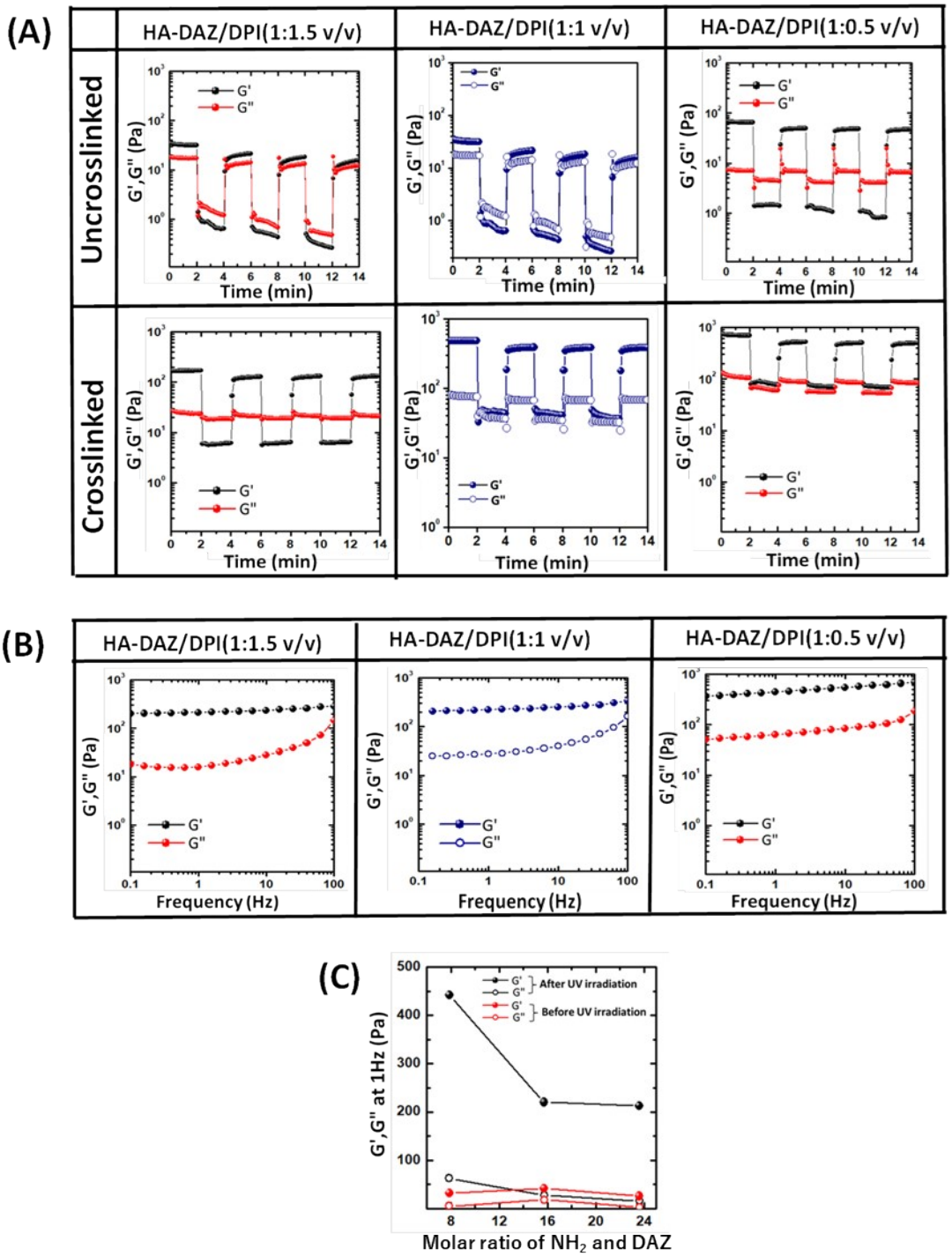


Fig. S8. Alternative strain sweep test and frequency sweep test of HA-DAZ/DPI hydrogels prepared using three different mixing volume ratios of HA-DAZ solution to DPI solution (i.e., 1.0:1.5, 1.0:1.0, and 1.0:0.5 vol/vol). The concentrations of the HA-DAZ and DPI precursor polymer solutions were 1.0 and 3.3 wt%, respectively. (A) Time course of G' and G" of uncrosslinked and crosslinked HA-DAZ/DPI with alternative strain sweep (B) Dependency of G' and G" on frequency of crosslinked HA-DAZ/DPI. (C) The relationship between the molar ratios of NH_2 of DPI to DAZ of HA-DAZ and G' and G" at a frequency of 1 Hz shown in (B).

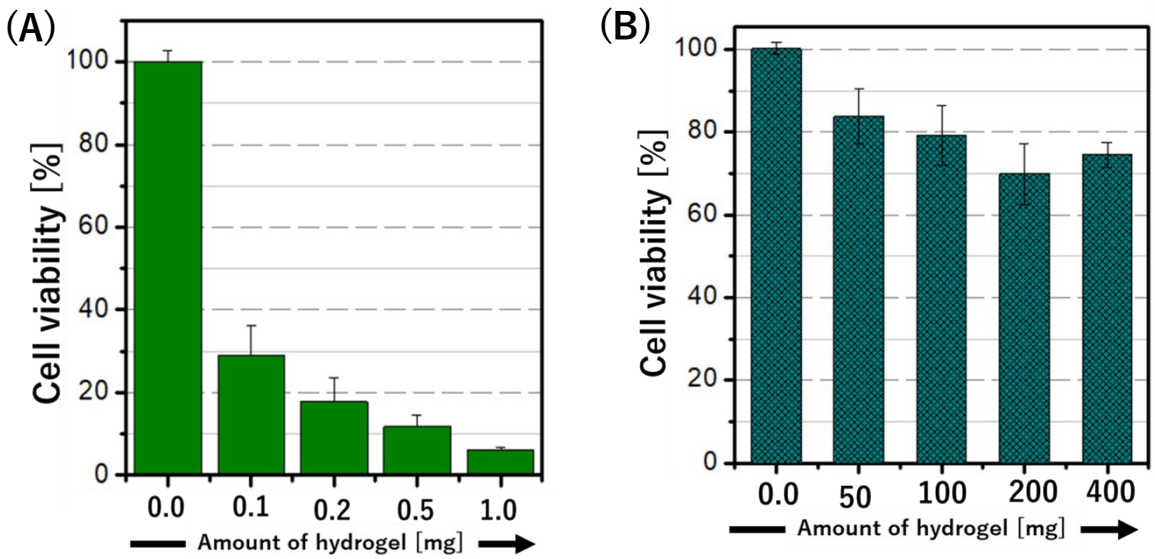


Fig. S9. (A) Cell viability of NIH-3T3 cells incubated with different concentrations of DPI for 48h. (B) Cell viability of NIH3T3 cells in direct contact with different amounts of HA-DAZ/DPI hydrogels.

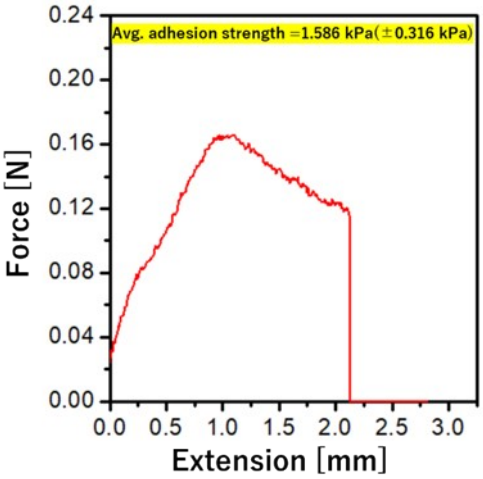


Fig. S10. The lap-shear adhesion test between the HA-DAZ solution after photocrosslinking and porcine esophagus mucosa samples.

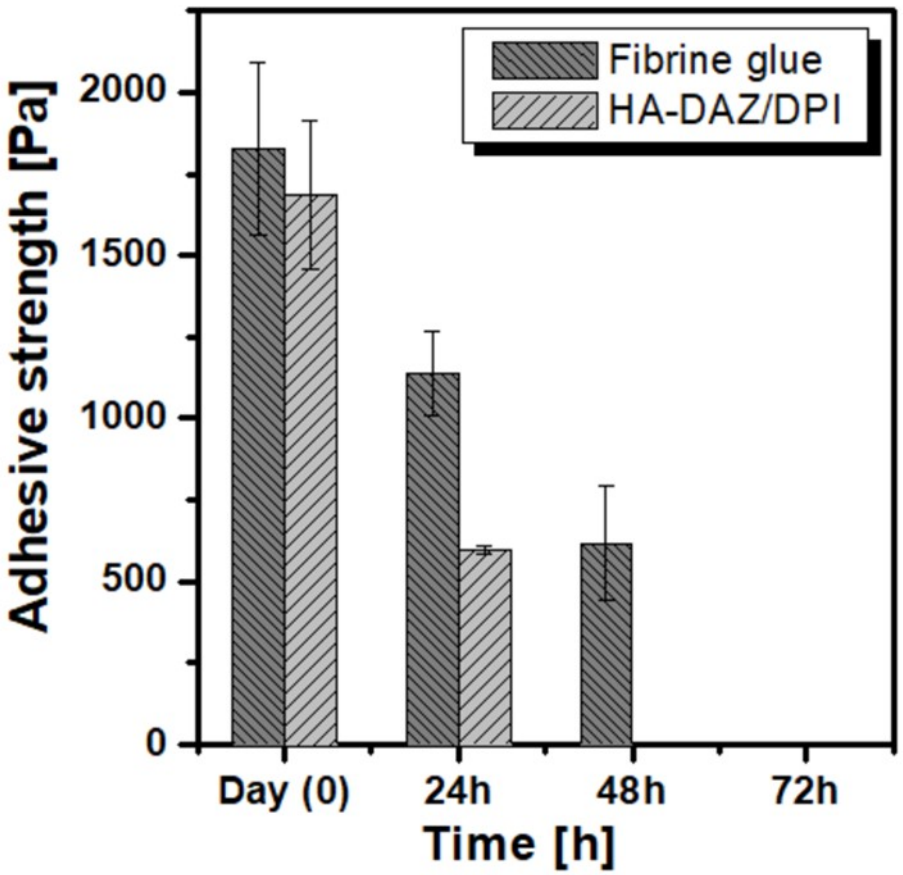


Fig. S11 The time-dependent adhesion strength of HA-DAZ/DPI hydrogel and fibrin glue using porcine esophageal mucosa as a substrate under immersion in phosphate buffer solution. A lap-shear test was performed to measure the adhesion strength at each incubation time point after adhesion of the materials to the mucosa.

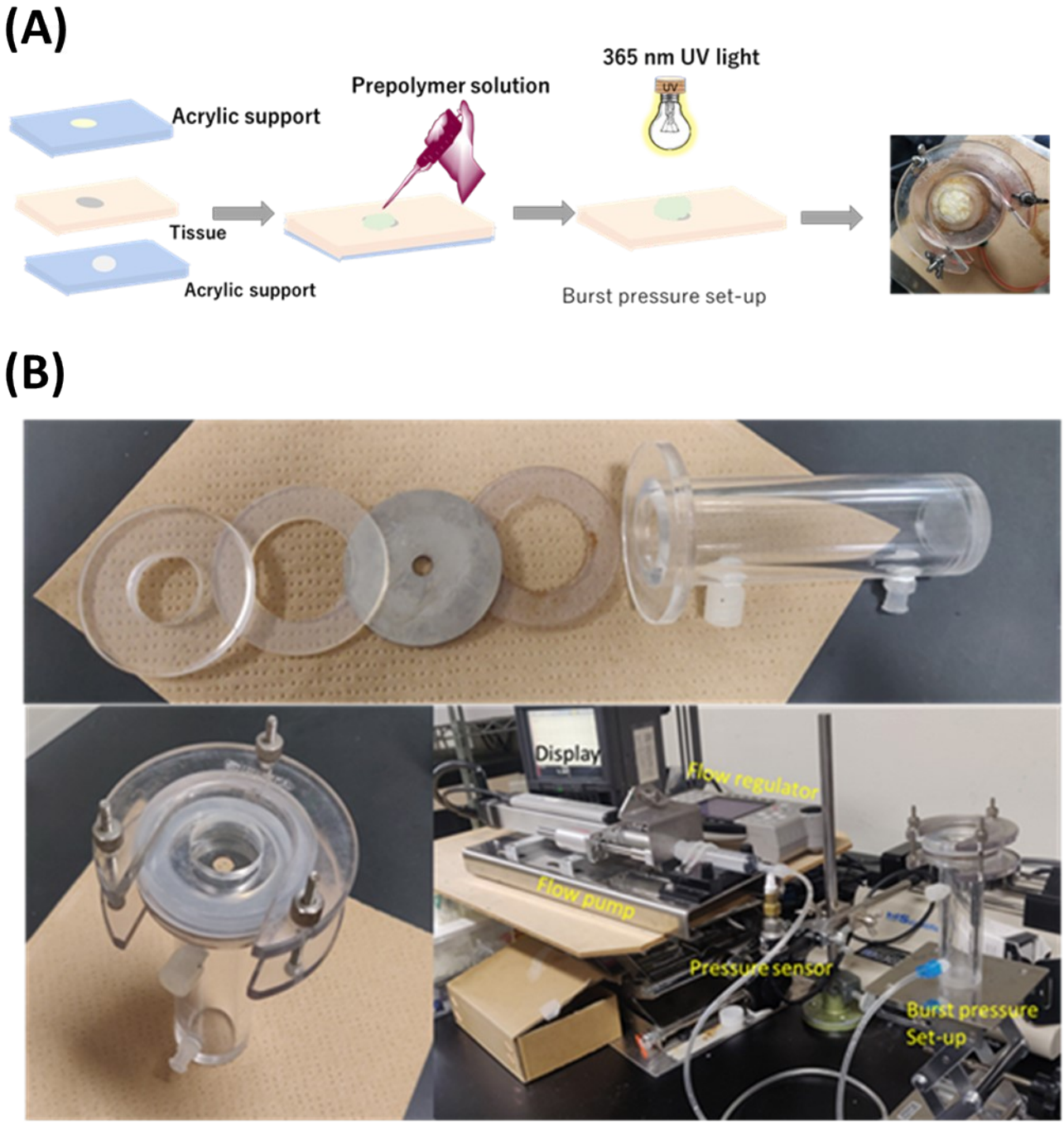


Fig. S12. (A) Experimental procedure and apparatus used for the burst pressure test using porcine esophagus mucosa. The upper panel shows a schematic illustration, while the lower panel shows (B) images of the actual custom-designed and fabricated burst pressure setup.

Supplementary Information

Table S1: Comparison of exposed UV light intensity, exposure duration, and adhesion strength of previously reported diazine-based hydrogels.

Polymer	UV Power $mW/cm^{-2.}$	Exposure Time	Adhesion Substrate	Adhesion strength	Reference
PLGA-g-diazirine	0.5	10 min	Porcine aorta	4.5 kPa	Terry W. J. Steele Macromolecular Bioscience, 14(4), pp.478-484.
(PAMAM-g-diazirine)	21.3	5 min	Cardiovascular tissue	40 kPa	Terry W. J. Steele Macromolecular bioscience 16, no. 7 (2016): 1072-1082
PAMAM-g-diazirine	100.0		Collagen film	40 kPa	Terry W. J. Steele Biomacromolecules,2018 19(5), 1425-1434.
PHEMA-diazirine	17.3	3 min	Bovine meniscus tissue	38 kPa	Terry W. J. Steele, and Harm-Anton Klok Biomacromolecules 2020, 21, 1, 240–249
PAMAM-g-diazirine	6.0	5 min	Porcine aorta	25 kPa	Junying Zhang and Terry W. J. Steele Molecules, 23(4), 796
CEC-diazirine	6.0	2 h	-	-	Jin Kim Montclare Biomacromolecules 2021, 21, 9, 3608–3619
Benzophenone methacrylamide (BPMA)	18.0	1 h	-	-	Amy E. Herr Analyst, 2021,146, 6621-6630
PAMAM-g-diazirine	8.0	2 h	-	-	Jin Kim Montclare Biomacromolecules 2021, 22, 4, 1509–1522
HA-diazirine	6.0	5 min	Porcine esophagus submucosa	2.7kPa	This paper

PLGA = poly(lactic-co-glycolic acid), **PAMAM** = polyamidoamine, **PHEMA** = Poly 2-hydroxyethyl methacrylate, **CEC** = Chromo domain-containing protein.