Supporting Information

Polyacryloyl Hydrazide Incorporation in Ionic Hydrogels Improves Toughness, Elasticity, Self-Healability, Adhesive & Strain Sensing Properties

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Synthesis of Polyacryloyl hydrazide (PAHz)

PAHz was synthesized as reported earlier¹. First polymethylacrylate (PMA) was synthesized using free radical polymerization of MA (34.4 g, 400 mmol) in presence of potassium bromate (0.16 g, 0.96 mmol) and sodium hydrogen sulfite solution (0.48 g, 4.6 mmol). The polymerization was quenched in 600 mL of sodium chloride solution (176.0 g, 300 mmol) and resulting polymer was purified using water washing. Subsequently, the above PMA (14.0 g) was reacted at 60 °C with hydrazine hydrate (54.3 g, 1.1 mol) in presence of TBAB (14.0 g, 43.4 mmol) in THF to synthesize PAHz. Yield: 12.6 g, 90%. ¹H NMR (500 MHz, D₂O) δ (ppm): 1.2 (m, 1H, -C**H**-CO-), 2.0 (m, 2H, -C**H**₂-CH-), 3.1 (br, 2H, -N**H**₂). FT-IR (in cm⁻¹): 3275 (br, N-H), 2895 (m, C-H), 1705 (s, C=O), 1010 (m, C-N). M_n = 15000 g/mol, PDI = 1.9 (The M_n of PMA was determined from SEC analysis using THF as the eluent and the value was assigned to corresponding PAHz since the chain length and molecular weight remains unaltered during the functional group transformation process as reported earlier).¹

Hydrogel Sample Code	PAHz* (mmol)	Cross Linker (mmol)	AMPS (mmol)	Initiator (α-ketoglutaric acid) (mmol)
PAMS-PAH-MBA	2.8	MBA	17.0	0.17
		0.17		
PAMS-PAH-PEG	2.8	PEGDA	17.0	0.17
		0.85		
PAMS-MBA	N.A.	MBA	17.0	0.17
		0.17		

Table S1: Formulations of different PAHz based PAMPS hydrogels

* the molar amounts are with respect to the repeating unit.



Figure S1: Anisotropic swelling of PAMS-PAH-MBA sample (A) Schematic representation of swelling pattern of PAMS-PAH-MBA hydrogel sample, (B1 & B2) microscopic measurement of thickness of dry and swelled film of PAMS-PAH-MBA.

Fracture Energy Calculation

To determine the fracture energy (*G*) of hydrogels, tearing test was performed with H5KL universal tensile machine (Tinius Olsen). The sheet like hydrogel samples (width 5 mm, thickness 5 mm and length 30 mm) were cut into the shape shown in **Figure S2**, with initial notch length of 20 mm. The two legs of the sample were wrapped with plastic adhesive cello-tape (Premier Stationery Industries, India) and clamped up to the notch. The upper leg was pulled upward at a constant velocity of 5 mm/min. The average tearing force F was recorded and G was calculated by using the equation; $G = F_{avg}/2w$, where F_{avg} is the average force and "w" is the width of the hydrogel.²



Figure S2: (A) Force versus strain plots of different hydrogels during tearing test, (B) test setup for tearing test to determine fracture energy.

For example, for a typical PAMS-PAH-PEG hydrogel sample of length 30 mm and width 5 mm, the F_{avg} was recorded to be 12.1 N. The *G* value was calculated to be 1210 J/m². Similarly, *G* values for different systems were calculated from the maximum average force (using force vs. strain plot **Figure S2- A**) obtained from tearing test for different hydrogels.



Figure S3: Schematics for the lap shear tensile tests of hydrogels sandwiched between different substrates.



Figure S4: Circuit design for strain sensing application of hydrogel.



Figure S5: Sensing performance of PAMS-PAH-PEG hydrogel as motion sensor towards

the cyclic movements of human finger.



Figure S6: The digital photographs showing the change in appearance of PAMS-PAH-MBA hydrogel sample during various stages of gelation process.



Figure S7: FTIR spectra of AMPS, PAHz and ionic complex of PAHz and AMPS.



Scheme S1: Dye labelling of PAHz polymer by dansyl chloride in PAMS-PAH-MBA hydrogel matrix.



Figure S8: (A) DLS traces of aqueous PAHz (2 wt% solution) and effect of incremental addition of AMPS to it, (B) FESEM image of solvent cast film of PAHz. A 2 wt% solution of PAHz in water was drop cast on to a silica substrate for this purpose.



Figure S9: (A) Top surface of a typical dry PAMS-PAH-MBA hydrogel, (B) top surface of "A" after 10 min of swelling in distilled water.



Figure S10: Images showing the brittleness of control PAMS-MBA hydrogel under compression.



Figure S11: Hysteresis traces of PAMS-MBA hydrogel.



Figure S12: FESEM images of freeze-dried samples of (A) PAMS-PAH-MBA and (B) PAMS-PAH-PEG.



Figure S13: (A1) A piece of latex rubber tubing in THF, (A2) A1 after 2 days, (A3) A1 after 10 days, (B1) a piece of PAMS-PAH-MBA hydrogel sample (water content 70wt%) in THF, (B2) B1 after 10 days, (B3) the hydrogel removed from THF after 10 days and (B4) compressed B3. The elasticity of sample is least affected by the exposure to THF.



Figure S14: Comparison of mechanical properties of hydrogels prepared under sunlight and under UV radiation (365 nm).





Figure S15: Digital photographs of PAMS-PAH-MBA synthesized using (A) 1.0, (B) 0.5, (C) 0.1, (D) 0.07 and (E) 0.05 mol% of MBA, (F) Stress versus Elongation plots of PAMS-PAH-MBA samples prepared using different amounts of MBA.

Measurement of ionic conductivity of hydrogels

Ionic conductivity of the hydrogels was measured by Four probe setup (Model DFP-02, SES Instruments Pvt. Ltd., Roorkee) (**Figure S16**). Hydrogel sheet was kept beneath the probes and resistivity (ρ) was calculated using the following formulas³ and from the reciprocal of resistivity, the conductivity of hydrogel was calculated.

 $\rho = (V/I) x 2\pi S$, where V is voltage, I is current, S is the distance between two probes.

Corrected resistivity, $\rho 0 = \frac{\rho}{G(\frac{w}{S})}$, where w is height of the sample, G (w/s) is the correction factor collected from standard table. The conductivity is subsequently determined as follow; C = 1/ $\rho 0$.



Figure S16: Ionic conductivity testing setup (A) circuit diagram, (B) Four probe testing setup

Hydrogel sample	Adhered material surface	Adhesive Strength (MPa)	
PAMS-PAH-PEG	Glass	0.11	2.84 (Dry)
	Aluminum	0.09	2.13 (Dry)
	Stainless Steel	0.06	0.81 (Dry)
	HDPE	0.04	-
PAMS-PAH-MBA	Glass	0.06	0.70 (Dry)

 Table S2: Adhesive strength of different hydrogels



Figure S17: Tensile hysteresis loop of five consecutive cycles of PAMS-PAH-PEG hydrogel.

Tack Test for adhesive strength measurement

Tack test was performed in H5KL (Tinius Olsen) machine with 100 N load cell. Hydrogel samples were cut into disc shape with 10 mm diameter and 3 mm height. The sample was attached with upper stage clamp of machine by super glue (Fevi kwik, Pidilite Industies Pvt. Ltd.) before 6 h prior to test (**Figure S18**) and kept in a close container to resist water evaporation from specimen.



Figure S18: (A) Experimental setup for tack test, (B) Force vs. time plots with different hydrogel samples during tack test, (C) Force vs. time plot for PAMS-PAH-PEG hydrogels with different adhering substrates in tack test, (D) Adhesive strength of PAMS-PAH-PEG hydrogel towards different materials.

The adhering materials like glass sheet, steel, aluminum, HDPE sheet was also fixed strongly with the lower stage of the machine by super glue adhesive tape before 24 h prior to test. Adhering material sheet (e.g. glass) was cleaned with water and acetone before use. The upper stage of the machine containing hydrogel sheet was subjected to compress with 10 μ m/s speed until it reached the preset force value of 1 N during contact with the adhering material with a contact time of 10 s. Then the upper stage was pull back with 10 μ m/s speed until debonding occur. The force and time data (**Figure S18**) was recorded and the adhesive strength was calculated from the ratio of debonding peak force to surface area of the hydrogel sample⁴.



Figure S19: Compressive stress (σ) in MPa versus strain (λ) in % plots of different hydrogel samples (water content \approx ca. 70 wt%).

Determination of Toughness

Toughness, U_{max} (MJ/m³) of hydrogels were calculated from area under curve of compressive stress vs. strain plots of different hydrogels. Origin Pro 8.5 software was used to calculate the U values using the *integration* function. For PAMS-PAH-MBA hydrogel sample it is calculated as 1.74 MJ/m³ from the area shown by gray colored shade in **Figure S20**. Similarly, U_{max} values were calculated for other hydrogels.



Figure S20: Compressive stress vs. strain plot of PAMS-PAH-MBA hydrogel. Origin pro 8.5 software was used to figure out the area under curve which gives the toughness value.

Supporting Movies

Movie S1 shows a PAMS-PAH-MBA hydrogel sample sustains multiple impacts by a hammer and the shape remains least affected by the process.

Movie S2 demonstrates the resilience of PAMS-PAH-MBA (water content ca. 70 wt%) after being run over by a car (average weight of 1.3 ton) repeatedly.

Movie S3 as synthesized PAMS-PAH-MBA hydrogel resisted repeated attempts to cutting using a blunt kitchen knife.

Movie S4 shows self-healing ability of PAMS-PAH-PEG hydrogel. A PAMS-PAH-PEG sample cut into two pieces autonomously joins within 5 min and withstands extension.

Movie S5 shows the strain sensing property of hydrogel. A typical PAMS-PAH-PEG hydrogel (50wt% water) sheet is connected with a circuit comprising a DC power source and LED light indicator. During stretching the resistance goes up and simultaneously LED light intensity decreases and vice-versa.

References

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