Electronic Supplementary Material (ESI) for Nanoscale.

Highly Compressive and Stretchable Poly(Ethylene Glycol) Based Hydrogels Synthesised Using pH-Responsive Nanogels Without Free-Radical Chemistry.

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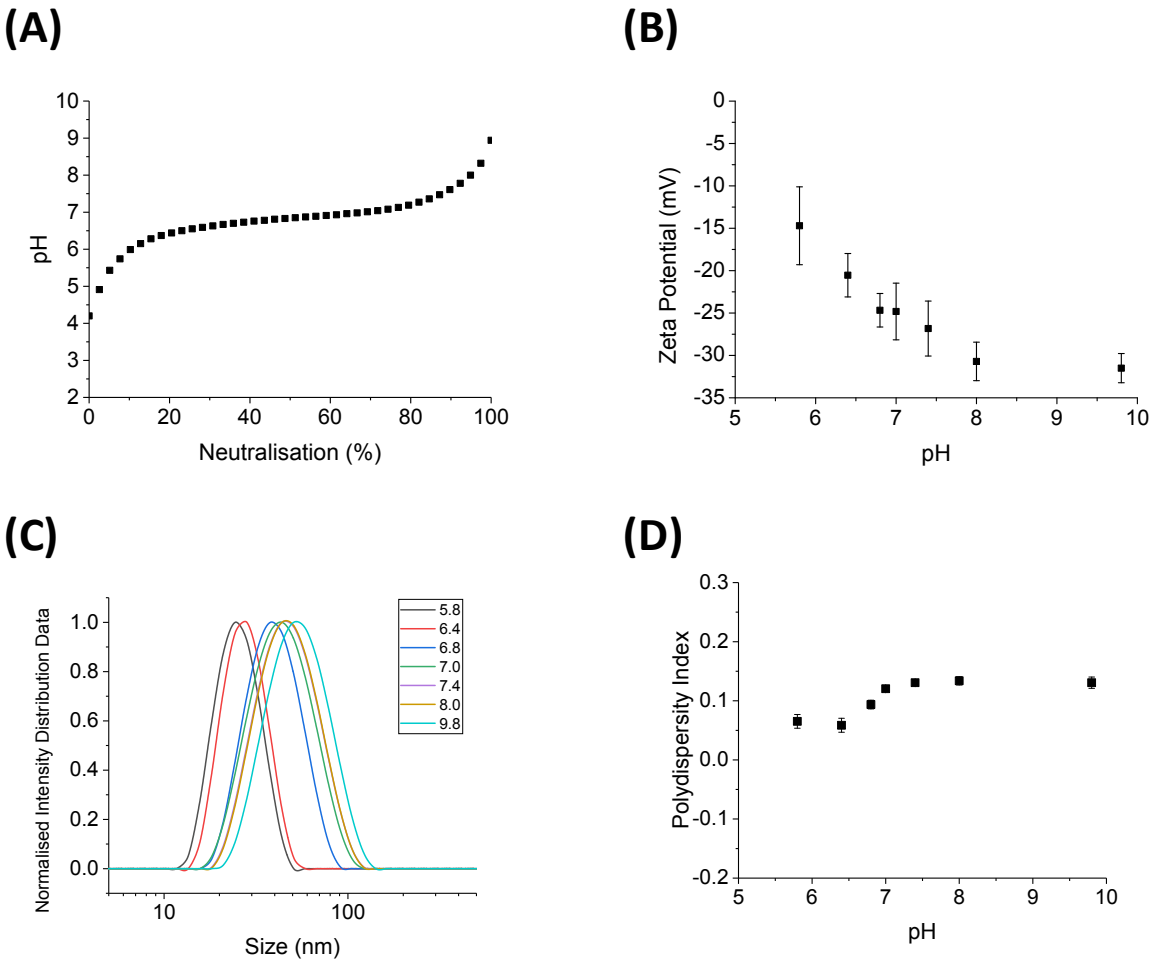

Figure S1. (A) Potentiometric titration data for the nanogels (NGs). (B) Variation of zeta potential with pH. (C) Dynamic light scattering (DLS) size distribution. (D) Polydispersity Index from DLS.

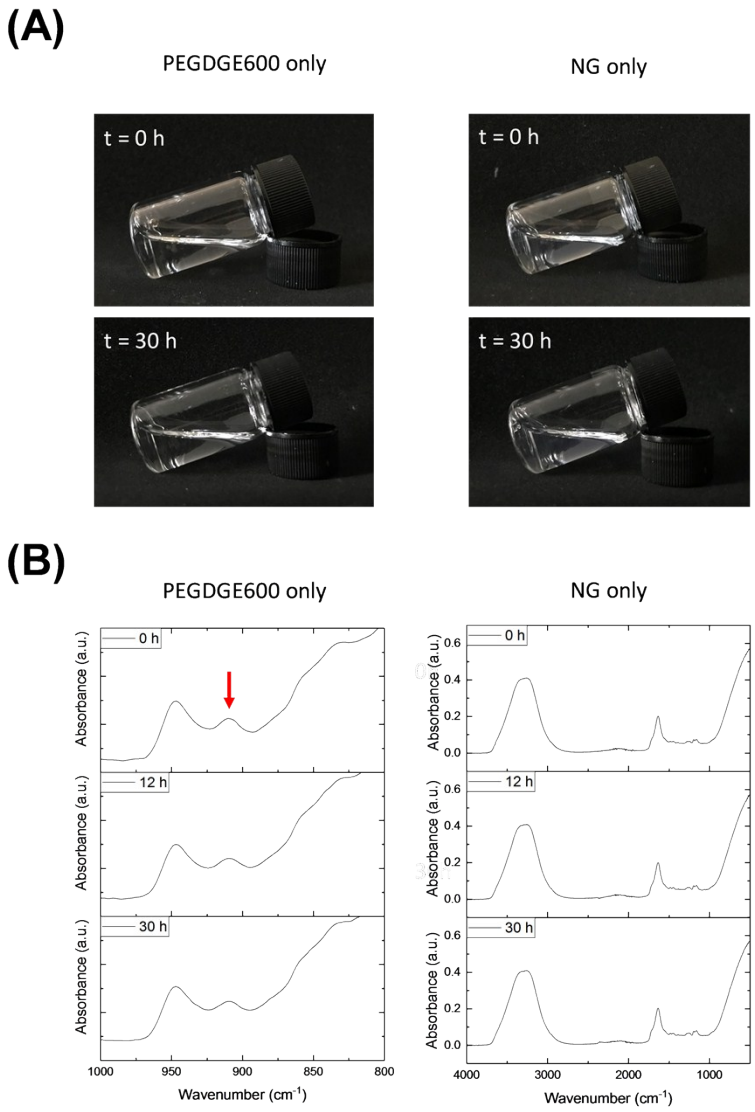

Figure S2. (A) Digital photographs of the inversed vial test. The tube containing either NG or PEGDGE600 did not formed a gel. (B) FTIR study on the kinetic of the formation of PEGDGE600-based nanocomposite hydrogel at time t = 0, 12 and 30 hour for solutions of (Left) PEGDGE600 only, red arrow indicates the epoxide band; (Right) NG only. There are no significant change with different time intervals.

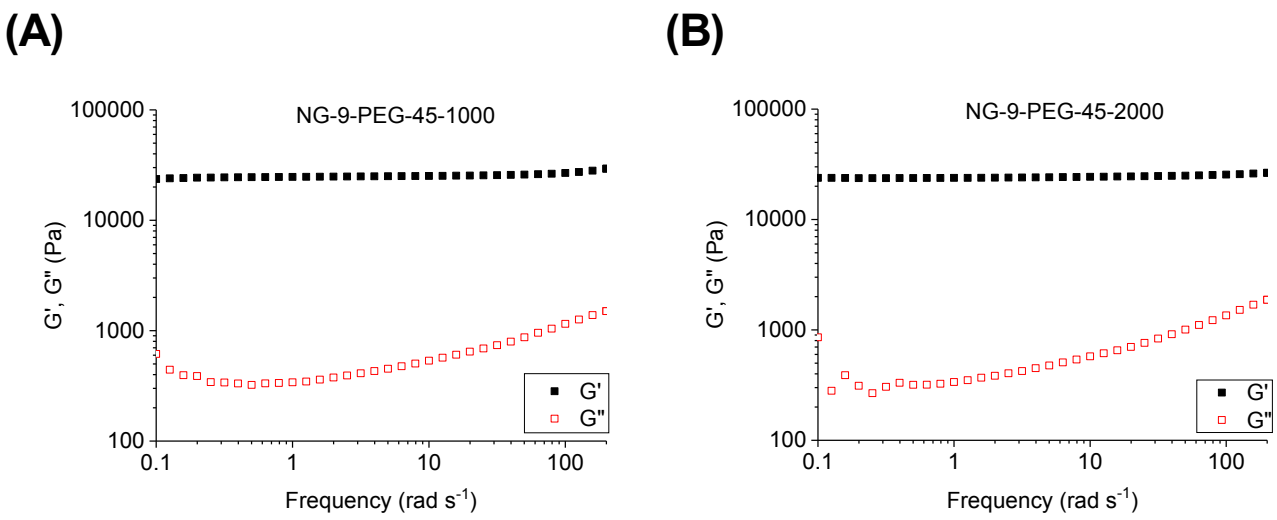

Figure S3. Frequency sweep rheology data for (A) NG-9-PEG-45-1000 gel and (B) NG-9-PEG-45-2000 gel.

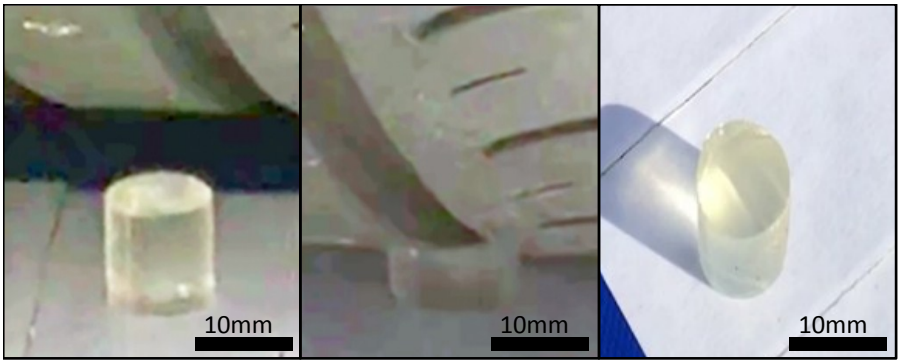

Figure S4. Crush experiment where the NG-13-PEG-20-6000 gel was run over by a rear tyre of a 1.0 tonne car (see Video S1, ESI†). Images are captured from Video S1. All hydrogels were prepared under same conditions for 72 h at 37°C with a constant initial solid content of the NG of 20.0 wt.%.

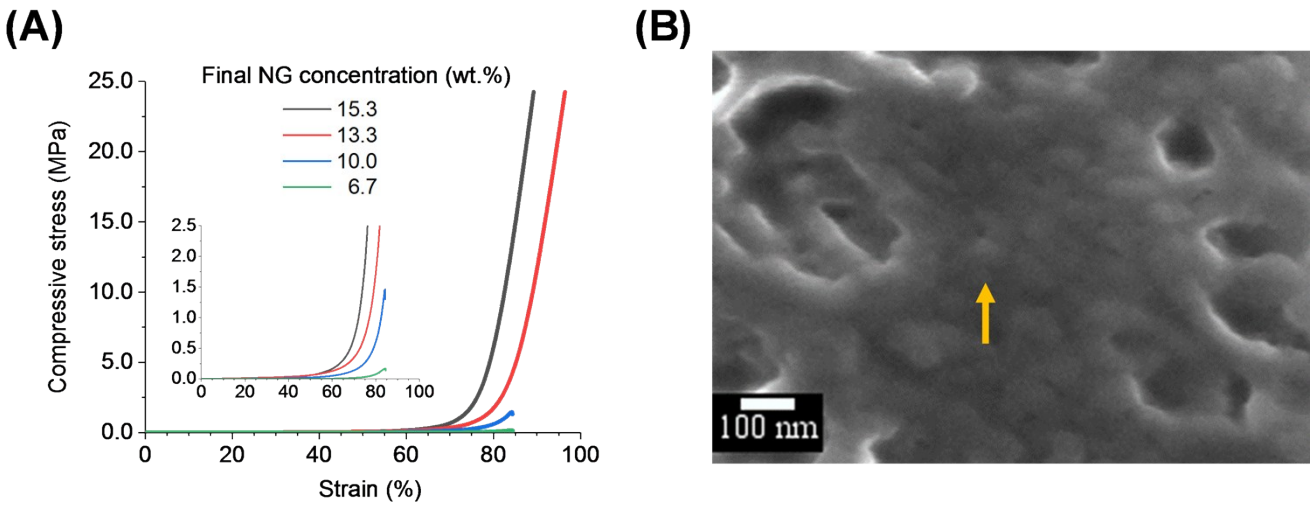

Figure S5. (A) Compressive stress vs. strain data for the NG-x-PEG-20-6000 gels with different final NG concentration ratio (x = 6.7 -15.3 wt.%). (B) SEM image for NG-13-PEG-20-6000 gel. Yellow arrow indicates the NG particle.

SAXS data analysis

A solution of PEG6000 was subtracted as a background prior to fitting the pre-gel sample, whilst data from the hydrogel were fitted as collected. Plots were first converted to 2θ vs I×q^2 to correct for instrumental geometry and structure factor peaks were fit to Lorentzian peaks. The *q*-position at which the principle scattering peak maximum occurred was used to calculate the average centre-to-centre distances between NGs ($D = 2\pi/q_{max}$).

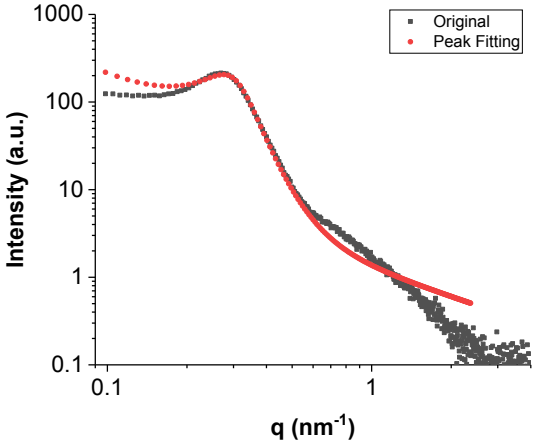

Figure S6. Example of Lorentzian peak fitting in SAXS data, conducted in Igor Pro software for the pre-gel mixture for NG-13-PEG-20-6000 gel.

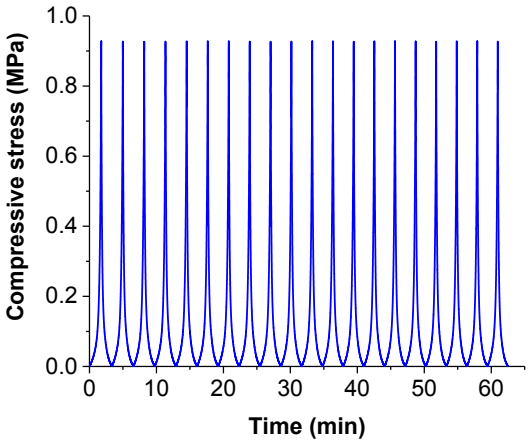

Figure S7. Compressive stress vs. time curves. Repetitive loading and unloading compressive cycles for the NG-13-PEG-20-6000 gel.

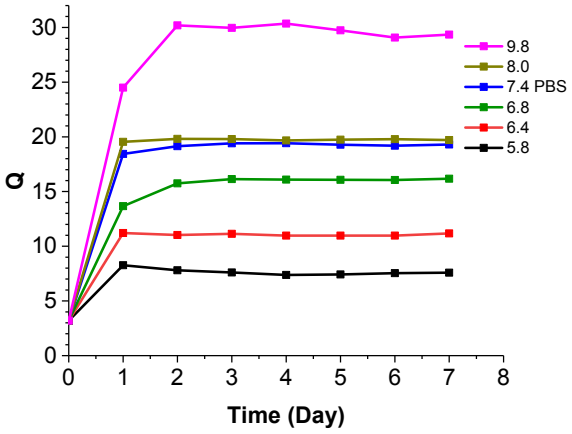

Figure S8. Variation of volume swelling ratio (Q) at different pH conditions for the NG-13-PEG-20-6000 gel.

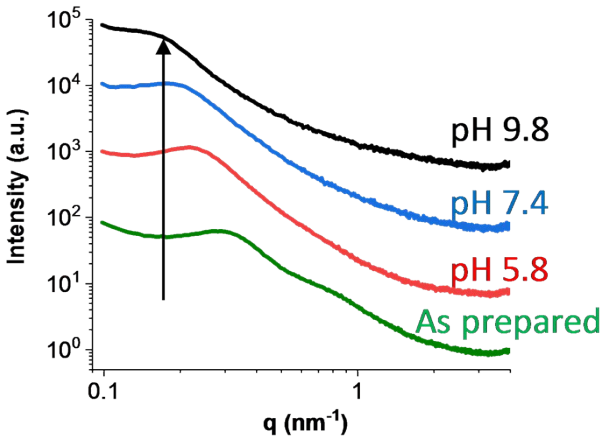

Figure S9. SAXS data for the NG-13-PEG-20-6000 gel as prepared and after swelling in different pH conditions for 24 hour. The arrow indicates the principle scattering peak.

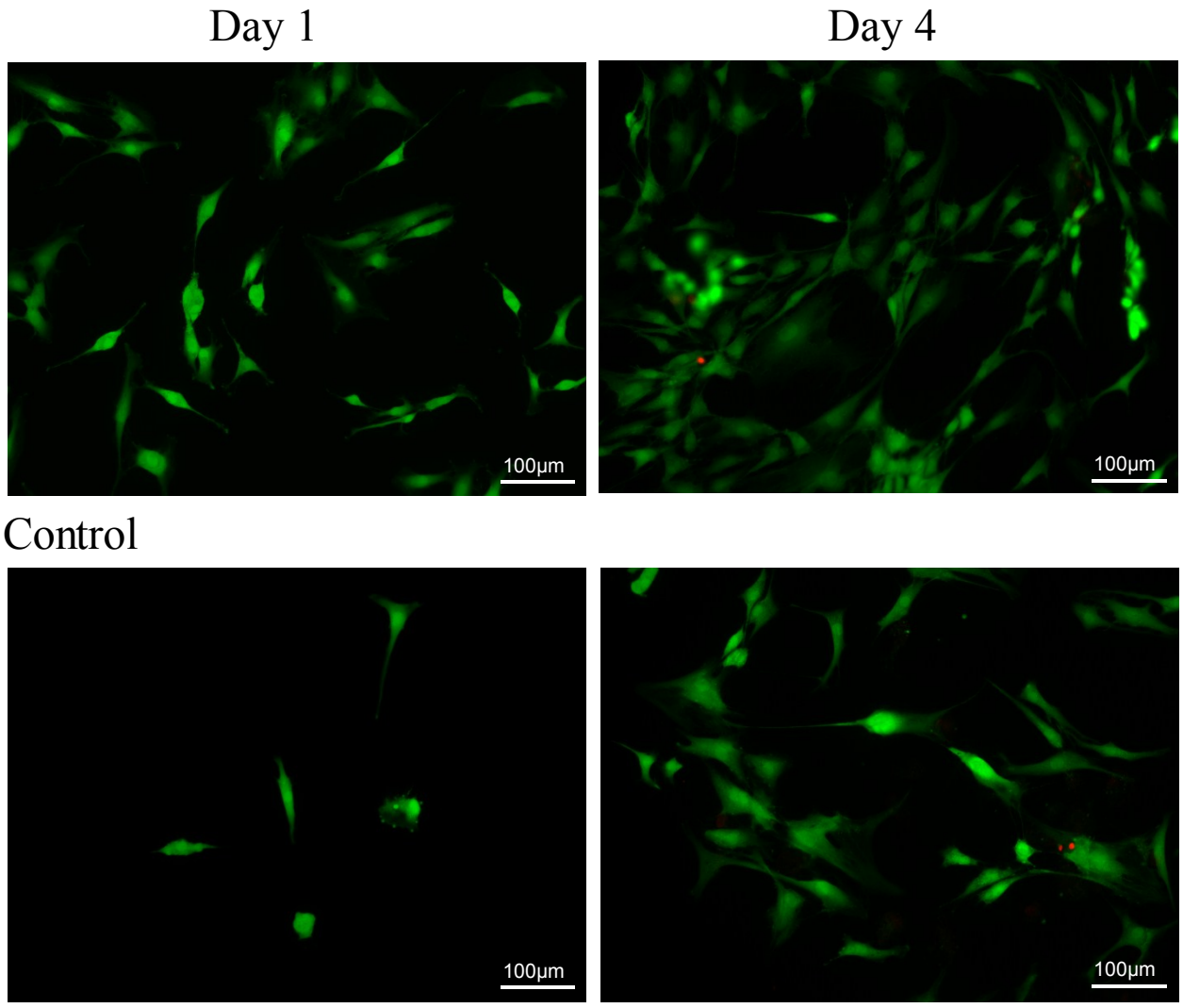

Fig. S10. Cell challenge data for the NG-13-PEG-20-6000 gel using human nucleus pulposus cell.

Table S1. Conditions, compositions and compressive mechanical properties for the NG-x-PEG-y-z gels. [a]

x: (wt.%)	y: (wt.%)	z: (g mol^{-1})	Time (day)	Modulus (KPa)	Fracture strain (%)	Compressive stress (KPa)	Fracture energy density (MJ m^{-3})	The molar ratio [COOH]/ [Epoxide]
9.1	45.5	600	1	195 ± 5.8	27.4 ± 0.1	69 ± 2	-	0.3
9.1	45.5	1000	1	71 ± 6.9	36.5 ± 5.2	49 ± 7	-	0.4
9.1	45.5	2000	1	55 ± 0.7	43.1 ± 4.6	45 ± 2	-	0.8
9.1	45.5	6000	1	15 + 1.7	92.0 ± 3.3	4068 ± 1150	-	2.6
9.1	45.5	6000	3	78 ± 6.6	87.7 ± 3.2	4320 ± 792	0.35 ± 0.006	-
10.5	36.8	6000	3	91 ± 12.7	89.9 ± 1.5	9110 ± 455	0.62 ± 0.160	-
11.8	29.4	6000	3	79 ± 1.7	99.5 ± 0.1	23130 ± 1540	1.97 ± 0.128	-
13.3	20.0	6000	3	50 ± 6.4	> 97.7 ± 1.8	24200 ± 7	1.88 ± 0.105	-
15.3	20.0	6000	3	46 ± 2.4	94.2 ± 5.2	23381 ± 1127	1.65 ± 0.044	-
10.0	20.0	6000	3	22 ± 0.2	85.9 ± 2.3	1374 ± 124	0.09 ± 0.002	-
6.7	20.0	6000	3	0.8 ± 0.1	81.6 ± 3.9	111 ± 69	0.01 ± 0.004	-

a) *x* and *y* are the final solid content in the formulation of NG and PEGDGE, respectively. *z* is the molecular weight of PEGDGE.

Table S2. Values obtained from fitting SAXS data for the NG-13-PEG-20-6000 mixture/gel.

Condition	*q* value of peak maximum (nm^{-1})	Mean distance by SAXS (nm)
NG only	0.294 ± 0.001	21.4 ± 0.04
Pre-gel mixture (NG + PEGDGE6000)	0.296 ± 0.001	21.2 ± 0.05
NG-13-PEG-20-6000 (as prepared)	0.322 ± 0.002	19.5 ± 0.15