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Supporting Information

Highly Stretchable and Highly Resilient Polymer–Clay Nanocomposite Hydrogels with Low Hysteresis

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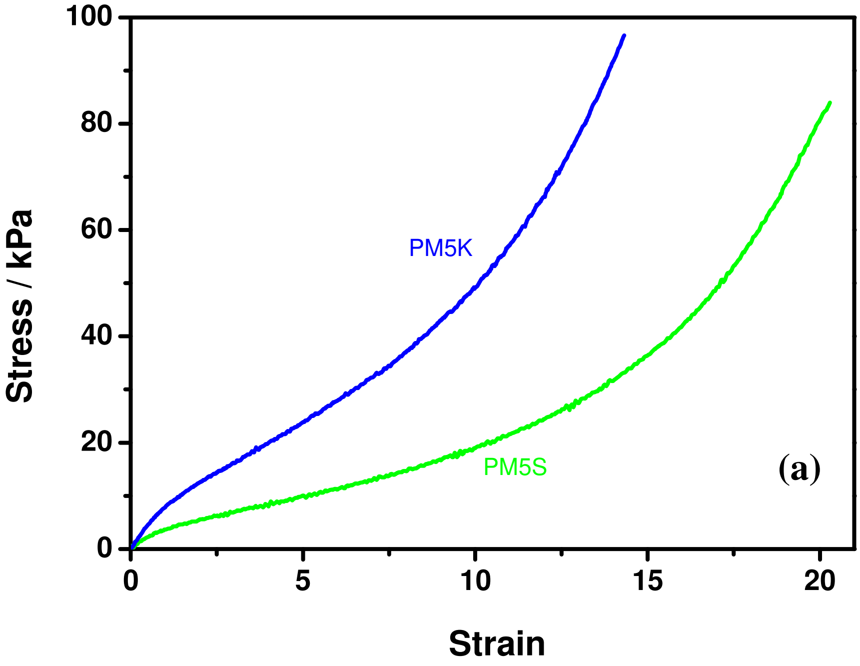
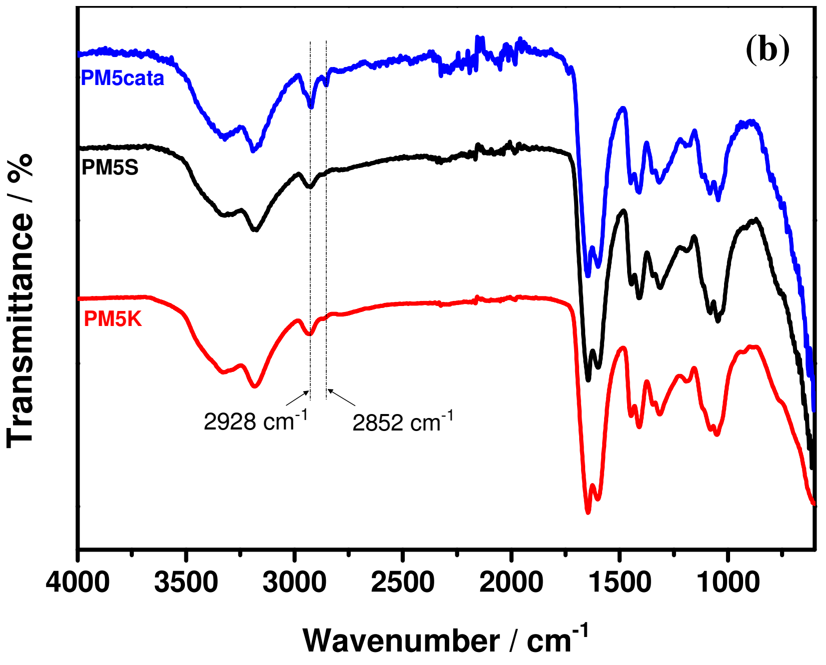
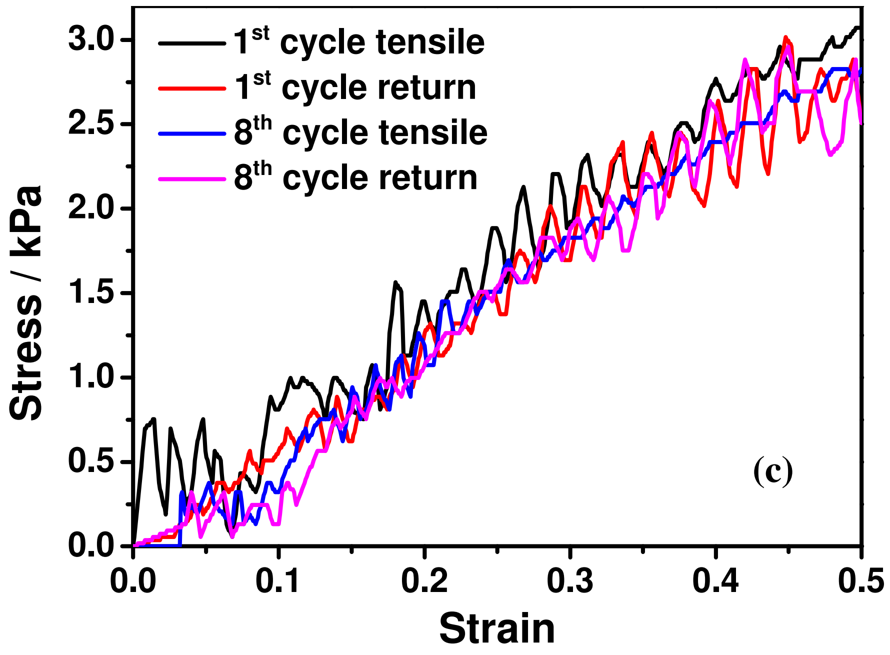
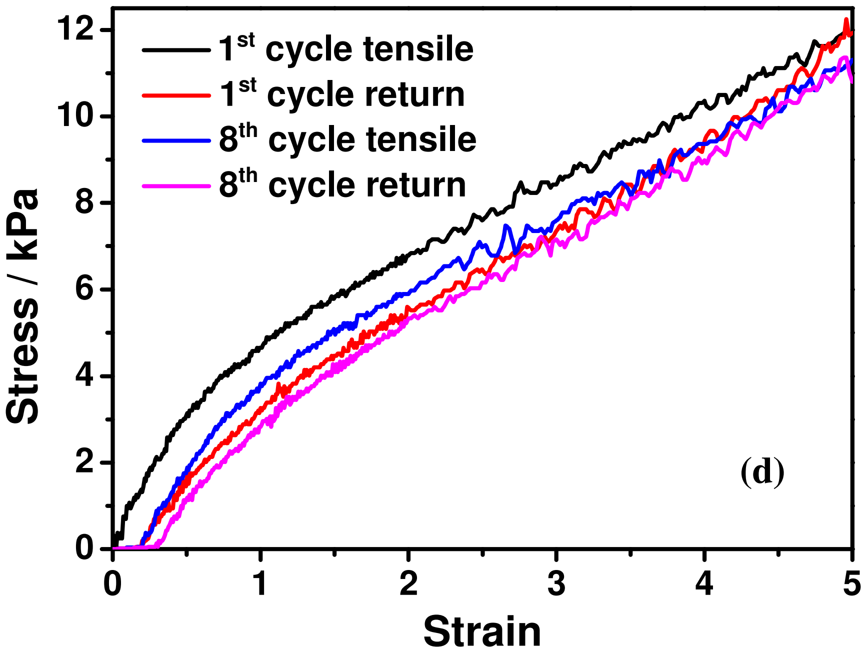
Strengthening and toughening effects by grafting acrylamide onto other polysaccharides such as starch and *k*-carrageenan

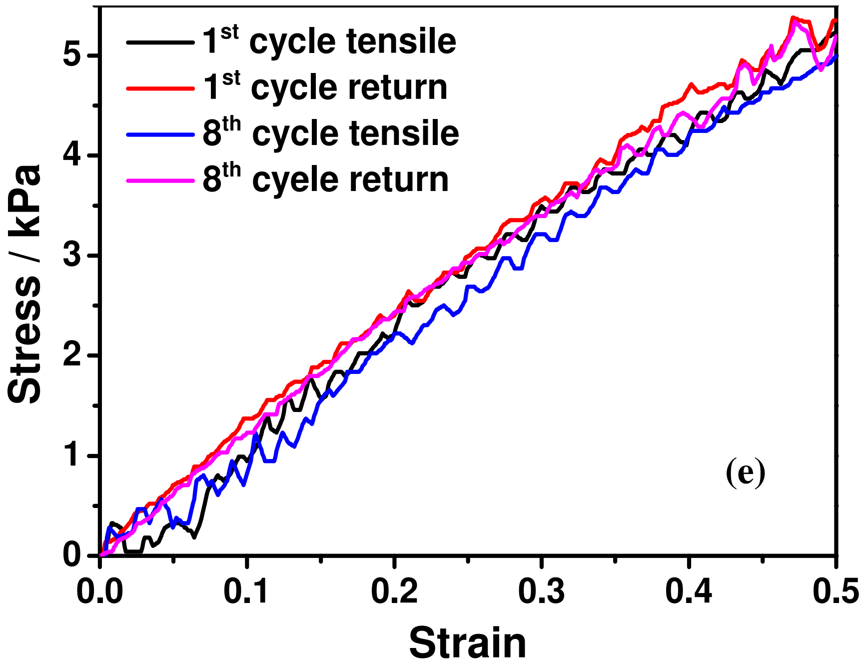
In order to understand the effect of grafting acrylamide (AM) onto polysaccharides, neutral starch and negatively charged *k*-carrageenan were also used to make nanocomposite hydrogels denoted as PM5S for polyacrylamide (PAM)–starch–montmorillonite (MMT) nanocomposite hydrogel, and PM5K for PAM–*k*-carrageenan–MMT nanocomposite hydrogel. They were synthesized following the same method and material ratio as for making PAM–chitosan–MMT nanocomposite hydrogel (PM5CHI), and were structurally characterized, tensile tested and cyclic tensile tested in the same way. The results were summarized in Figure S1, Table S1 and Table S2.




(b)
PM5cata
PM5S
PM5K
2928 cm-1
2852 cm-1
Transmittance / %
Wavenumber / cm-1
4000
3500
3000
2500
2000
1500
1000


1st cycle tensile
1st cycle return
8th cycle tensile
8th cycle return
(c)
Stress / kPa
Strain
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0.0
0.1
0.2
0.3
0.4
0.5


1st cycle tensile
1st cycle return
8th cycle tensile
8th cycle return
(d)
Stress / kPa
Strain
0
2
4
6
8
10
12
0
1
2
3
4
5


1st cycle tensile
1st cycle return
8th cycle tensile
8th cyele return
(e)
Stress / kPa
Strain
0
1
2
3
4
5
0.0
0.1
0.2
0.3
0.4
0.5

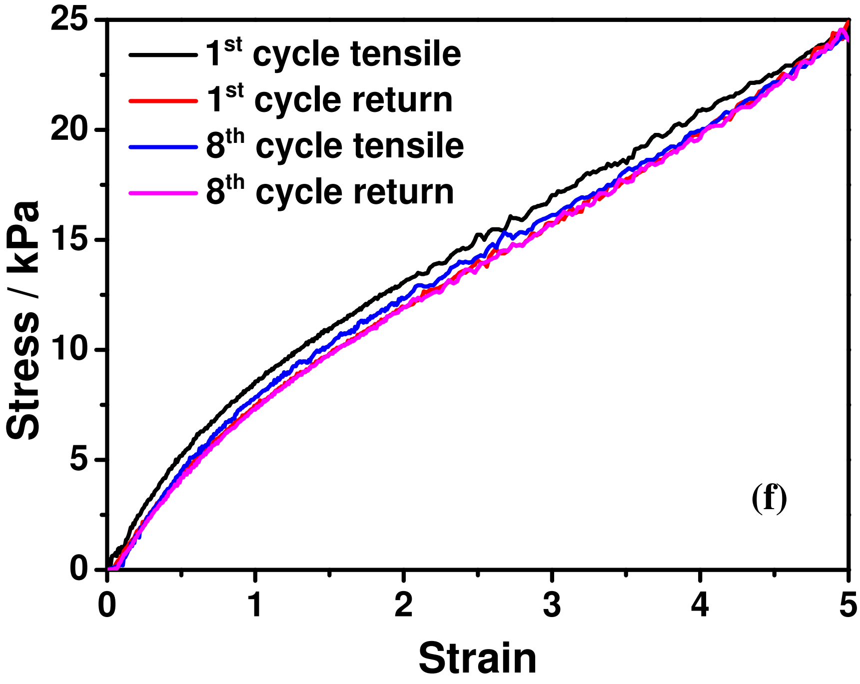


Figure S1. (a) Tensile stress–strain curves of PM5S and PM5K hydrogels; (b) FTIR spectra of PM5S, PM5K and PM5cata dry samples; and cyclic tension to (c) 50% of PM5S, (d) 500% of PM5S, (e) 50% of PM5K, and (f) 500% of PM5K hydrogels.

Table S1. Tensile properties of PM5S and PM5K hydrogels.

Samples	Young's modulus / kPa	Tensile strength / kPa	Strain at break	Energy at break / MJ m^{-3}
PM5S	6.3 ± 0.4	89.2 ± 4.9	20.9 ± 0.8	0.67 ± 0.04
PM5K	9.1 ± 0.1	92.0 ± 4.3	14.2 ± 0.2	0.52 ± 0.02

Table S2. Hysteresis ratios of PM5S and PM5K hydrogels.

		PM5S	PM5K
Strain	Cycle	Hysteresis Ratio	
0.5	1st Cycle	0.12	−0.07
0.5	8th Cycle	0.02	−0.1
5	1st Cycle	0.15	0.06
5	8th Cycle	0.08	0.02

Due to the structural similarity to chitosan, it was possible to graft AM onto the backbones of starch and *k*-carrageenan by etherification as described in the manuscript. From Figure S1 (a) and Table S1, the incorporation of the two polysaccharides enhanced the tensile strength, strain at break and fracture energy compared to those of PAM−MMT nanocomposite hydrogel (PM5), confirming the effective load transfer from PAM matrix to polysaccharide backbones during stretching because of strong covalent grafting. Compared to these two neutral and negatively charged polysaccharides, positively charged PM5CHI displayed the best mechanical properties which confirmed the formation of strong chitosan−MMT electrostatic bonding, much stronger than the hydrogen bonding in starch−MMT or *k*-carrageenan−MMT nanocomposite hydrogels. From FTIR spectra (Figure S1 (b)), it could be determined that PAM branching existed in both PM5S and PM5K by comparing the two peaks at 2928 cm^{-1} and 2852 cm^{-1} occurred for PM5cata.

As for cyclic tensile results shown in Figure S1 (c−f), PM5S displayed similar hysteresis ratios compared to PM5CHI, indicating the ample hydrogen bonds between neutral starch macromolecules and MMT platelets in PM5S. However, in terms of cyclic tension to 50%, PM5S showed a different pattern from that of PM5CHI despite the similar hysteresis ratios. The more zigzags for PM5S implied the starch macromolecules slipped along the MMT platelets with the starch−MMT hydrogen bonding breaking and rebuilding quickly when deformed, unlike the unzipping process between chitosan and MMT platelets. When it came to PM5K, the cyclic tensile properties were more like PM5, indicating that *k*-carrageenan macromolecules did not interact with MMT platelets like chitosan or starch as both *k*-carrageenan and MMT platelets were negatively charged. The mechanical properties of PM5K were dominated by PAM−MMT hydrogen bonding and PAM−*k*-carrageenan covalent grafting, rather than polysaccharide−MMT interaction in the case of chitosan or starch.

Tensile tests of a wet soft poly(vinyl alcohol) sample

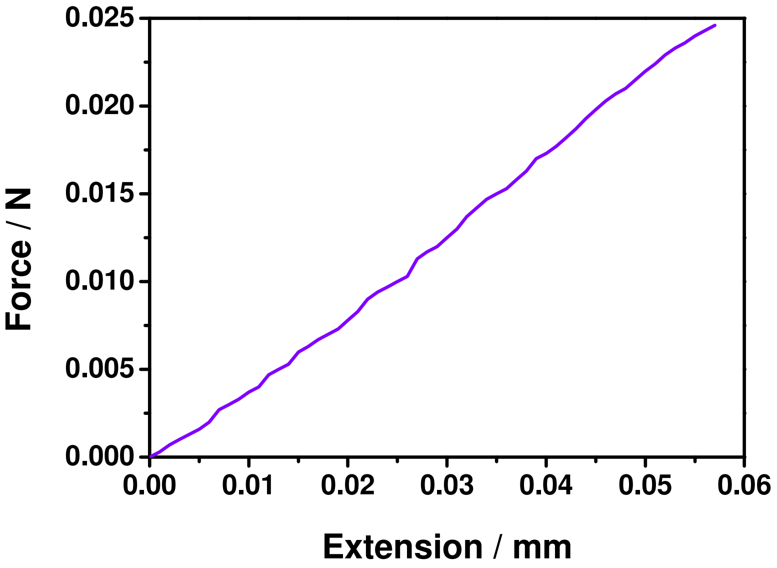


Figure S2. Tensile test to 0.025 N of a wet PVA sample.

The poly(vinyl alcohol) (PVA) sample was cut from a dry PVA film and then immersed in distilled water for a week to enable a full swelling. The dimension of this sample was 10 mm × 1 mm × 1 mm. The sample was tensile tested to a small load of 0.025 N which was similar to the maximum load of cyclic tension to 50% test of PM5 and PM5CHI. As seen in Figure S2, despite the similar number of data points, PVA sample displayed much smoother curve than those of PM5 and PM5CHI, which confirmed that the zigzag of the curves from cyclic tensile tests on PM5 and PM5CHI was mainly due to the intrinsic properties of the samples instead of the noise from the machine.

Shape–recovery of PM5 and PM5CHI hydrogels

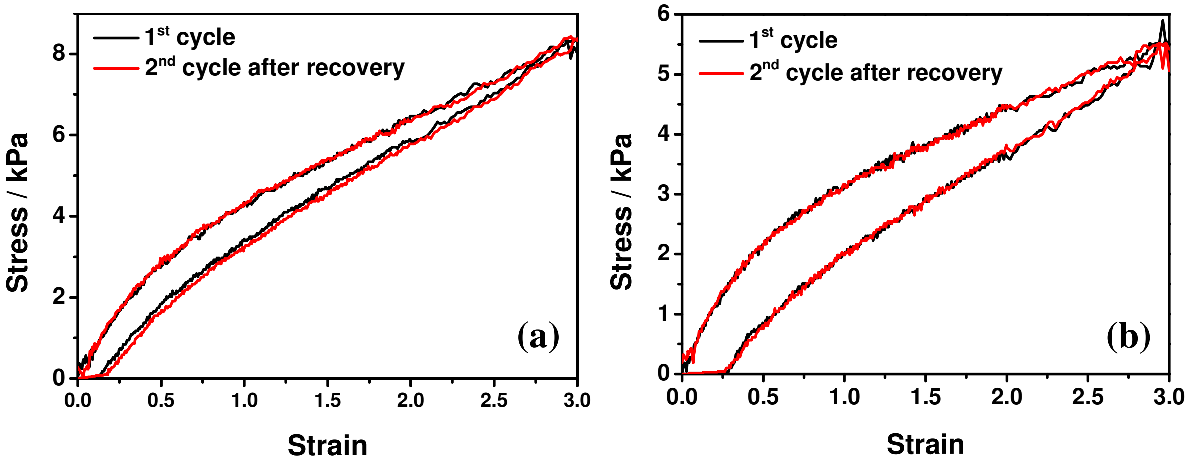
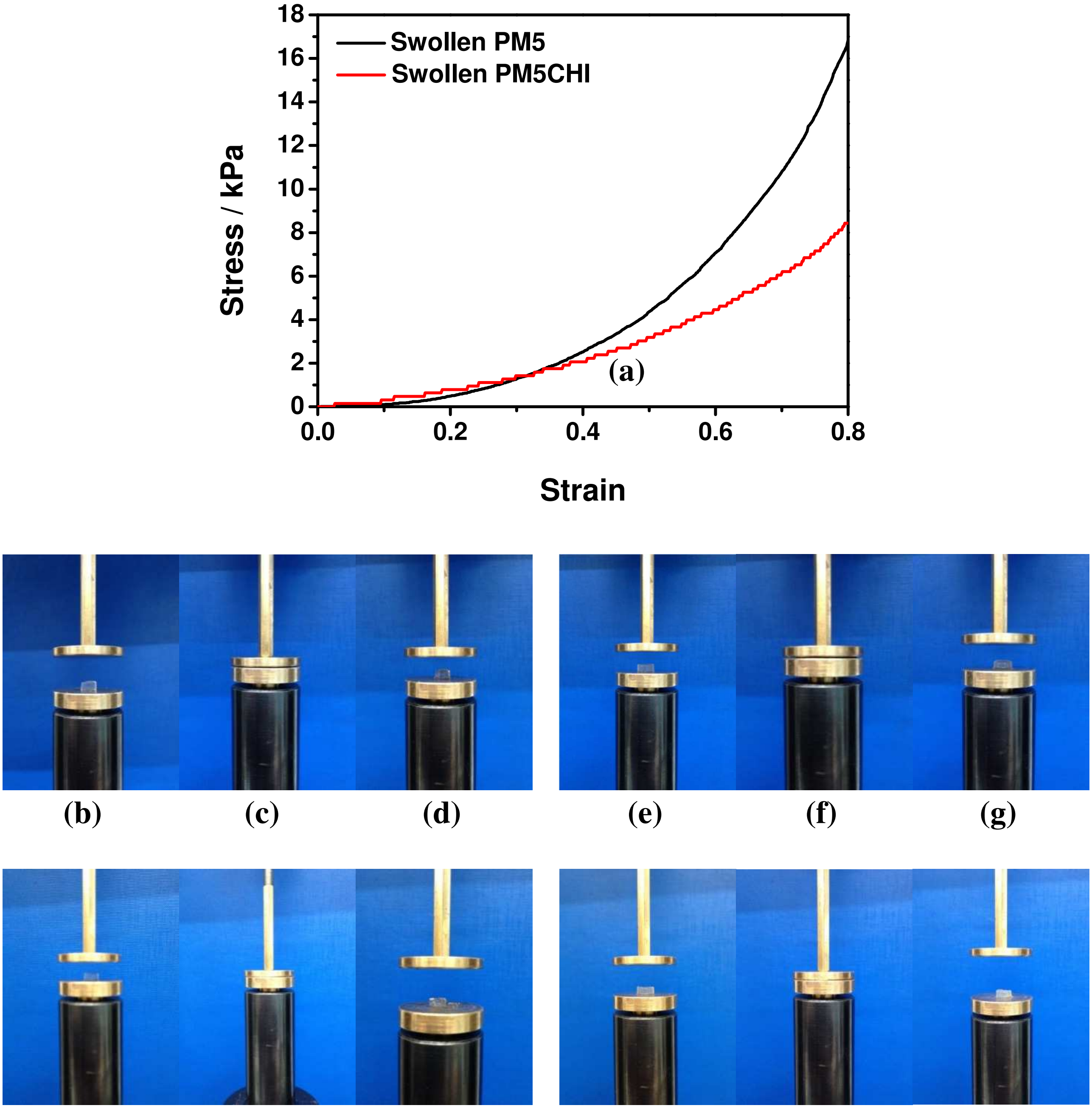


Figure S3. Shape–recovery of (a) PM5 and (b) PM5CHI hydrogels in 1 minute following cyclic tensile test to 300%.

As seen from Figure S3, both PM5 and PM5CHI hydrogels were able to recover their original state within 1 minute even under a strain of 300%.

Compression tests on the fully swollen hydrogels



(b) (c) (d) (e) (f) (g)

(h) (i) (j) (k) (l) (m)

Figure S4. (a) Compression tests to 80% on the fully swollen nanocomposite hydrogels: before, during and after compression of (b, c, d) PM5 and (e, f, g) PM5CHI; compression tests to a load of 1 kN on the fully swollen (h, i, j) PM5 and (k, l, m) PM5CHI.

As shown in Figure S4 (a), like many other nanocomposite hydrogels, both of the swollen PM5 and PM5CHI did not break and recovered instantly after the compression test to a maximum strain of 80%. Unlike chemically crosslinked hydrogels, these nanocomposite hydrogels were able to withstand a large extent of compressive deformation. This was attributed to the uniform distribution of stress brought by the low crosslinking density and uniform distribution of inter-crosslinking chain length.[1]

The compression test to a load of 1 kN was also performed. As can be seen from Figure S4 (b−m), the fully swollen PM5 was broken while the fully swollen PM5CHI still kept intact. On one hand, the difference in the equilibrium swelling ratio of the two hydrogels affected the compressive properties. On the other hand, the strong electrostatic bonds between chitosan and MMT platelets were able to withstand higher stress than the hydrogen bonding between PAM and MMT platelets.[2−3]

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