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Electronic Supplementary Information

Super-tough and thermo-healable hydrogel – promising for shape-memory absorbent fiber

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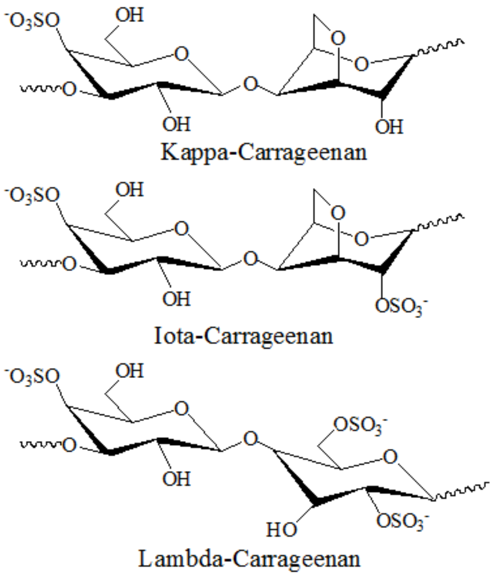

Fig. S1. The typical repeating units for carrageenans.

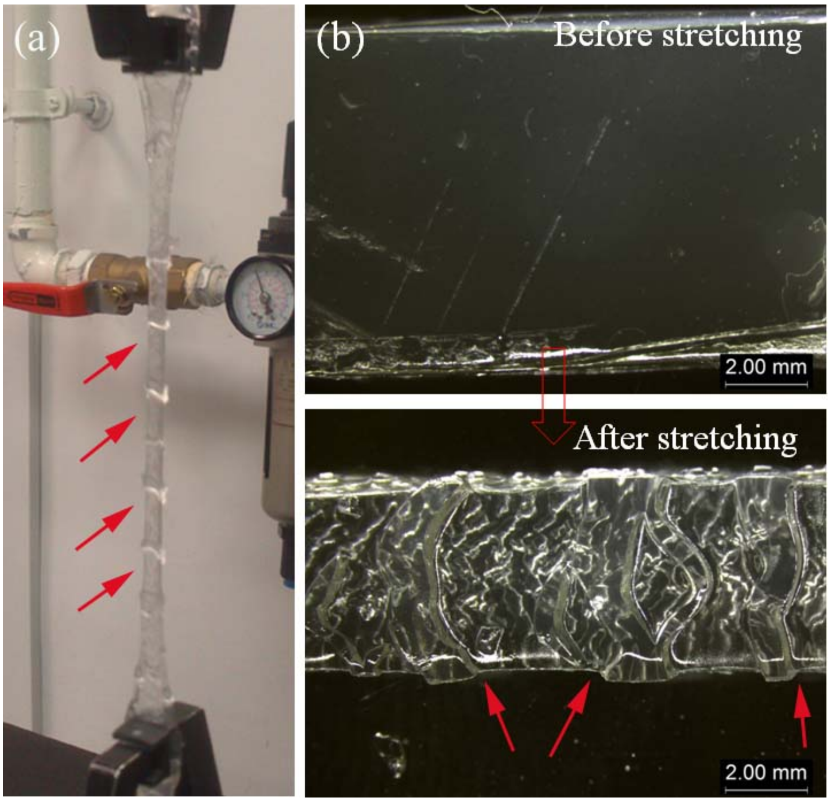

Fig. S2. The stable cracks during stretch progress of the DN gel in composition of 66.7 wt% PAAm: (a) digital photo; (b) optical microscope images before and after stretching. (arrows point the cracks or necking sections)

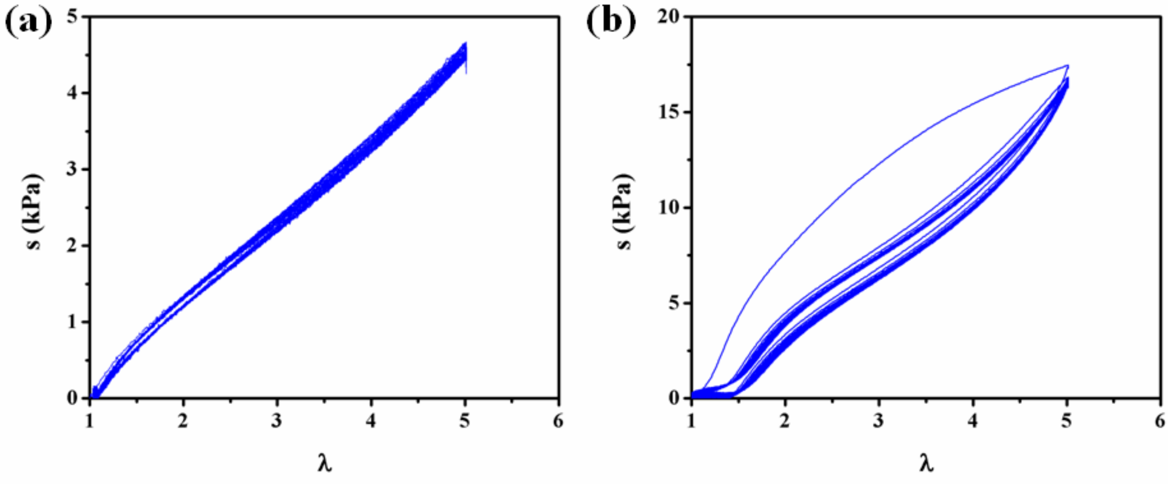

Fig. S3. Twenty successive loading / unloading cycles of PAAm (a) and IC / PAAm DN gel (b) with maximum stretch λ = 5.

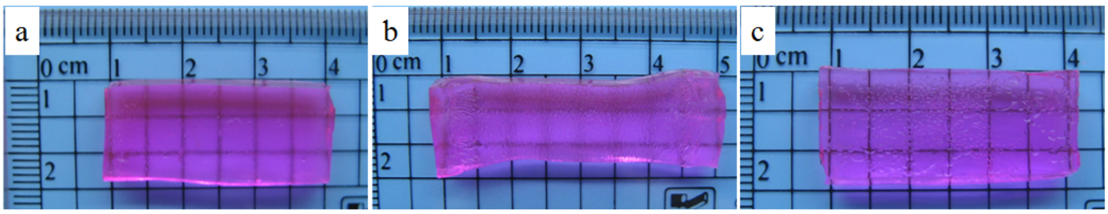

Fig. S4. Recovery of stretched IC / PAAm DN gel: a) original gel; b) relaxed gel after a stretch up to 15 x; c) thermally healed gel at 70 ˚C for 8 h.

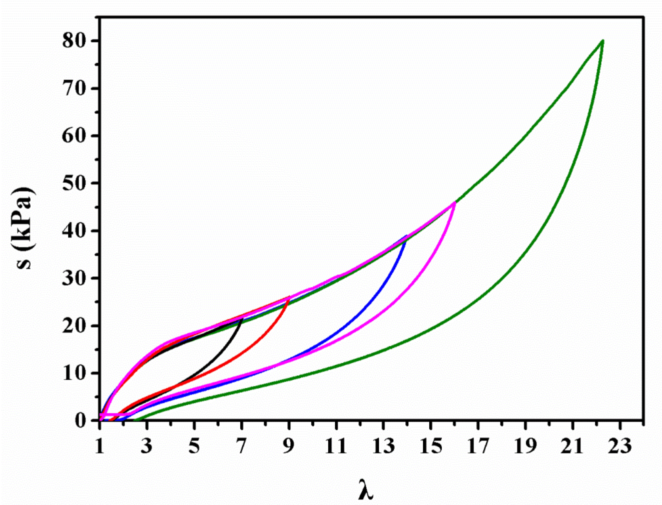

Fig. S5. Loading and unloading cycles of a typical IC / PAAm DN gel at various maximum stretches.

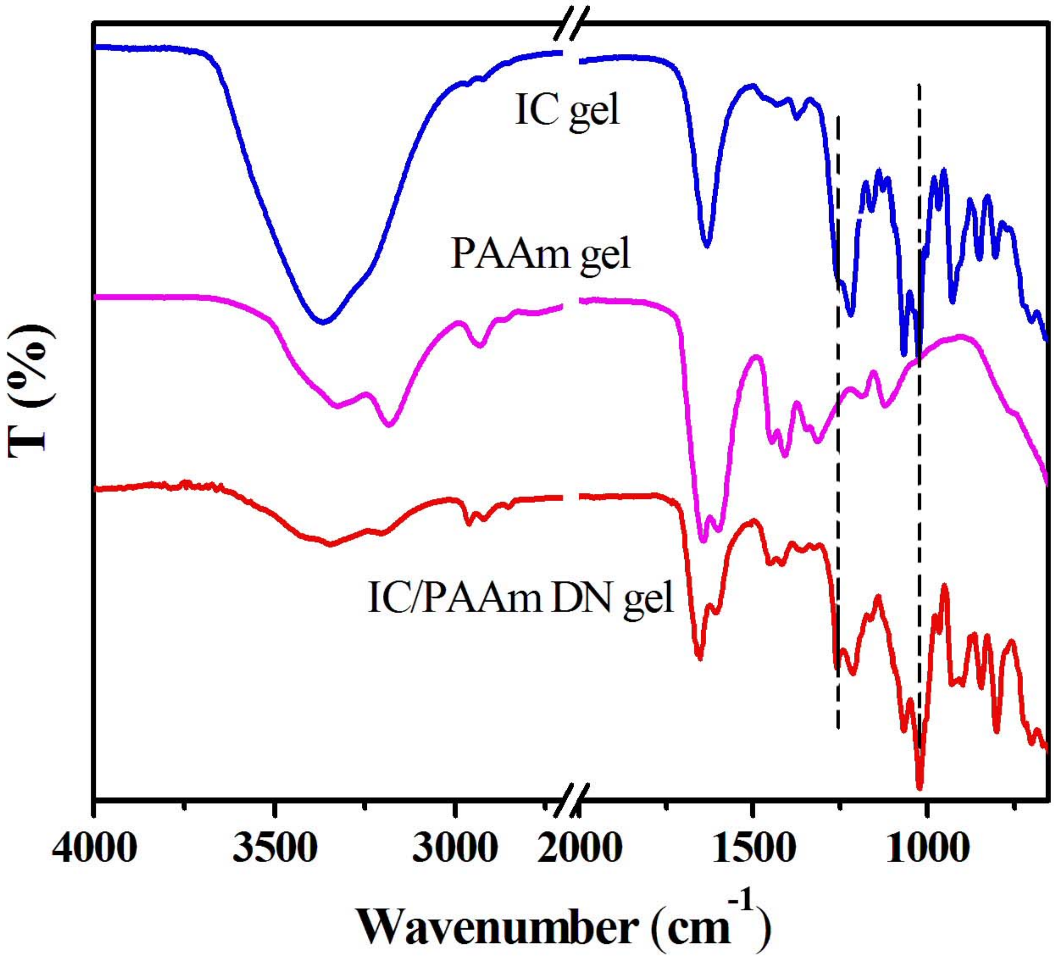

Fig. S6. FT-IR spectra of dried samples of IC, PAAm, and IC / PAAm DN gels.

The spectra of three dried gels are shown in Fig. S6. IC shows a broad peak at 3365 cm^{-1} for O-H stretching, and a sharp peak at 1633 cm^{-1} for O-H deformation.[1] The four important bands at 849, 928, 1024 and 1218 cm^{-1} are attributed to D-galactose-4-sulfate, 3, 6-anhydro-D -galactose, glucosidic linkage and sulfate ester stretching of IC backbone, respectively.[2] The PAAm gel exhibits bands at 3325 and 3183 cm^{-1}, corresponding to a stretching vibration of N-H, and 1642 cm^{-1} for C=O stretching. The bands at 1602 cm^{-1} for N-H deformation of primary amine, 1446 cm^{-1} for CH_2 in-plane scissoring, 1409 cm^{-1} for C-N stretching of primary amide, 1314 cm^{-1} for C-H deformation, and 1119 cm^{-1} for NH_2 in-plane rocking are also observed clearly.[3]

Previous studies reported that vinyl monomers could be easily grafted onto carrageenan during their polymerization.[2, 4-7] The group –OH on IC can be induced to form free radicals by chemical initiators. The free radicals then react with the double bond of AAm, resulting in a graft of PAAm onto carrageenan. In the spectrum of the IC / PAAm DN gel, the peaks at 1258 and 1024 cm^{-1} for C-O stretching are evidently intensified due to the grafting structure. And the intensities of O-H stretching peak at 3349 cm^{-1} and CH-OH structure at 1072 cm^{-1} are decreased obviously. This result indicates the grafting structure of PAAm on IC chains.

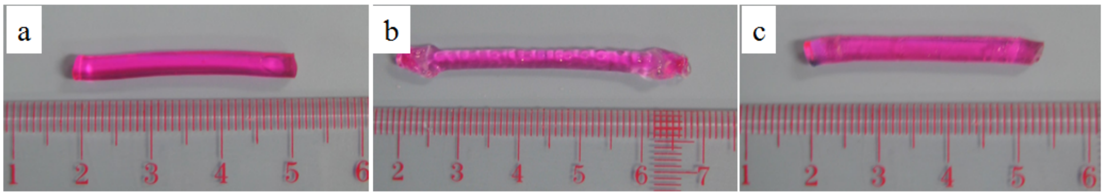

Fig. S7. Ideal recovery of a gel fiber being strained, dried, and rewetted: a) original gel fiber; b) gel fiber recovered by wetting after drying at a stretch of 15 x; c) gel fiber healed at 70 ˚C for 8 h in seal.

Table S1. Tensile properties of PAAm gel, IC/PAAm gels at different conditions.

	Factors	Tensile strain at Break (%)	Tensile stress at Break (kPa)	Young's Modulus (kPa)	Fracture Energy (J/m^2)
Effect of carrageenan network	PAAm	1512±68	26±1	2.4±0.1	1320±60
	IC/PAAm	2518±75	106±3	7.2±0.2	9500±280
	KC/PAAm	1316±59	75±3	40.8±1.8	7570±340
Effect of crosslinker MBA content (wt.% based on AAm)	0.03	3020±76	56±1	5.2±0.1	890±220
	0.06	2518±75	106±3	7.2±0.2	9500±280
	0.12	2086±83	96±3	7.5±0.3	7020±280
	0.25	1450±58	106±4	10.9±0.4	6860±270
	0.425	1182±47	125±5	14.1±0.6	6120±240
Effect of IC / AAm mass ratio	1:2	2096±73	96±3	14.6±0.5	8310±290
	1:4	2203±77	101±3	10.0±0.4	8900±310
	1:8	2518±75	106±3	7.2±0.2	9500±280
	1:10	2755±82	77±2	5.1±0.2	7910±230
Effect of strain rate (mm/min)	50	2518±75	106±3	7.2±0.2	9500±280
	250	2574±90	105±3	7.1±0.2	9430±310
	500	2522±80	104±3	7.1±0.2	9400±290
70 ^{o}C test	PAAm gel	1475±66	14±1	1.5±0.1	1150±50
	IC/PAAm gel	1710±77	48±2	6.0±0.3	4210±190

Table S2. Tensile properties of the absorbent fibers dried from the DN gel.

Sample	Tensile strain at Break/ %	Tensile stress at Break/ MPa	Young's Modulus/ MPa
Fiber dried in relax	2.3±0.2	45±2	2400±120
Fiber dried under tension	27.5±1.4	147±6	3000±130
Fiber dried under tension & post annealed	11.6±0.6	399±20	5440±260

References

1 M. D. Oza, K. Prasad, A.K. Siddhanta, *Carbohyd. Res*. 2012, 357, 23.

2 A. Pourjavadi, A. M. Harzandi, H. Hosseinzadeh, *Eur. Polym. J.* 2004, 40, 1363.

3 J. Y. Sun , X. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak, Z. Suo, *Nature* 2012, 489 , 133;

4 N. Rasool, T. Yasin , J. Y. Y. Heng , Z. Akhter, *Polymer* 2010, 51, 1687.

5 M. M. Mishra, M. Yadav, A. Sand, J. Tripathy, K. Behari, *Carbohyd. Polym*. 2010, 80, 235.

6 W. Sukhlaaied, Sa-A. Riyajan, *Carbohyd. Polym.* 2013, 98, 677.

7 S.K.Verma , V. S.Pandey, M.Yadav, K. Behari, *Carbohyd. Polym.* 2014, 102, 590.