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Electronic Supplementary Information

High-strength double network polydopamine nanocomposite hydrogel for adhesion under seawater

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Table S1. The Ratio of Components in Different Hydrogels.

Hydrogel	Am (wt%)	Alg-Na (wt%)	m_{DA} / m_{Am} (%)	m_{MBAm} / m_{Am} (%)	m_{APS} / m_{Am} (%)
PAM	12	—	—	0.8	10
PAM-PDA	12	—	0.6	0.8	10
PAM-Alg	12	1.5	—	0.8	10
PAM_x- Alg_y-PDA_z	x	y	z	0.8	10

Table S2. Components of Artificial Seawater (pH=8.0).

Inorganic salt	Concentration (g/L)
NaCl	25.5
KCl	0.67
$MgCl_2$•$6H_2O$	4.7
$MgSO_4$	6.3
$CaCl_2$	1.35
$NaHCO_3$	0.18

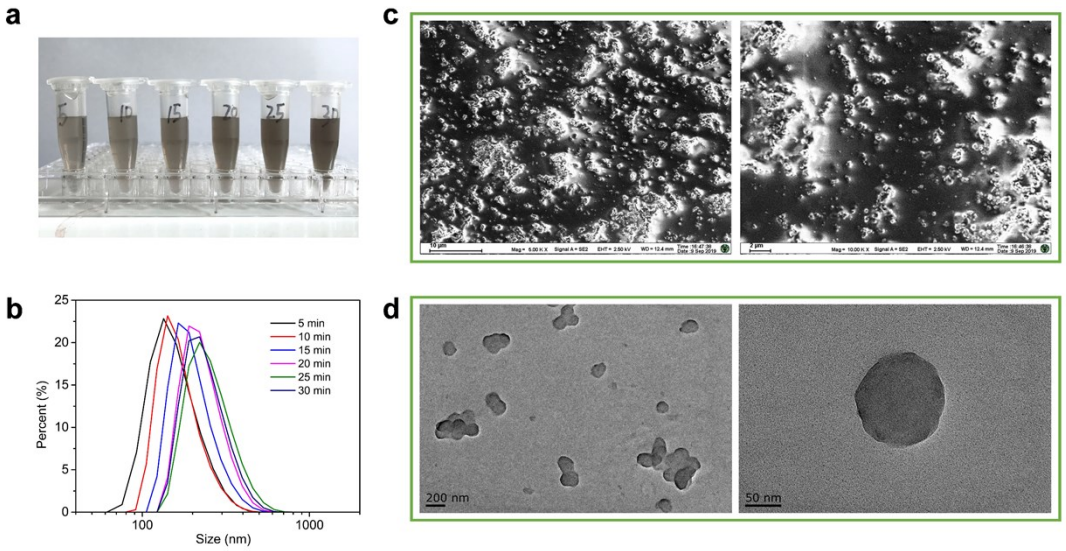

Figure S1. (a) The optical images of PDA/TEA solution (0.72 mg/mL) (TEA buffer solution: 0.2 M, pH = 9.8) with different oxidation time (5 min, 10 min, 15 min, 20 min, 25 min, 30 min); (b) The size of PDA nanoparticle measured by dynamic light scattering (Zetasizer Nano ZS90, Malvern, UK) with different oxidation time; (c) The SEM images of PDA nanoparticle formed after 20 min of oxidation; (d) The transmission electron microscope (JEM-2100, JEOL, Japan) images of PDA nanoparticle formed after 20 min of oxidation.

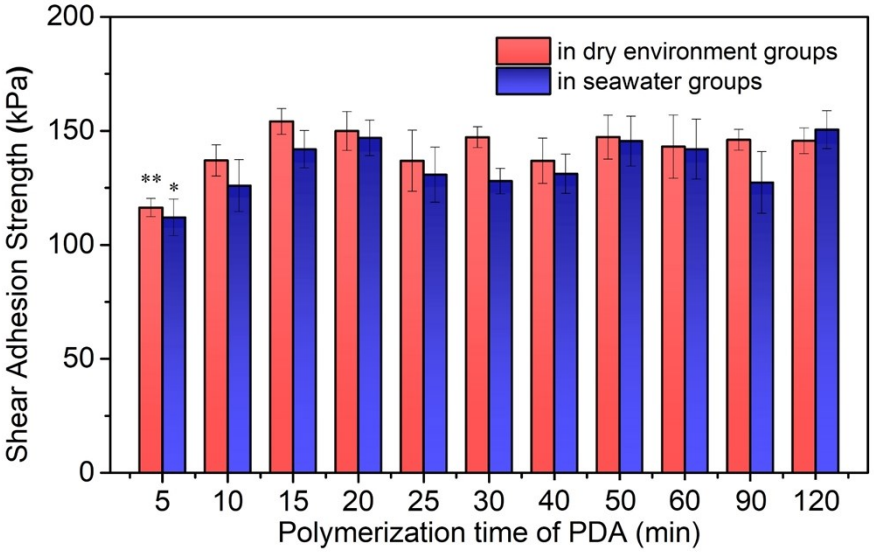

Figure S2. The shear adhesion strength of PAM_{12}-$Alg_{1.5}$-$PDA_{0.6}$ hydrogel on glass with different polymerization time of PDA ($^{*}p < 0.05$, $^{**}p < 0.01$, vs. the maximum adhesion strength in the same test environment).

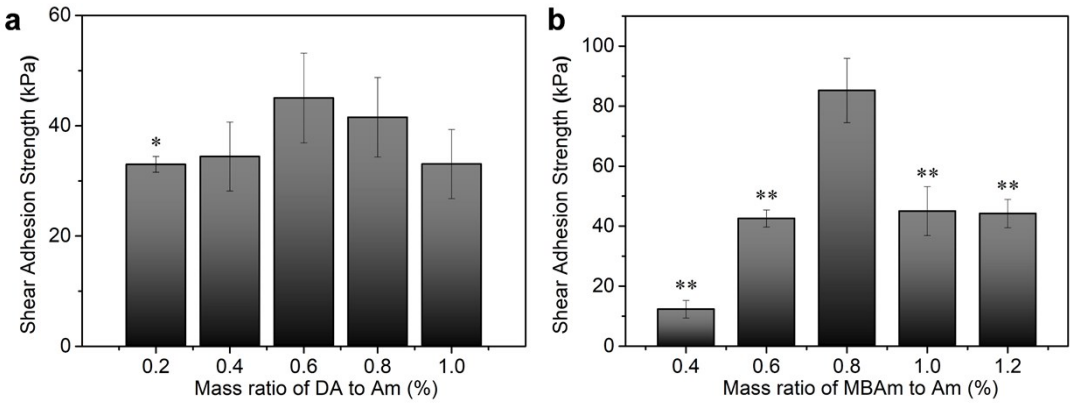

Figure S3. The shear adhesion strength of PAM-PDA hydrogel on glass in dry environment with different concentration of (a) DA and (b) MBAm ($^{*}p < 0.05$, $^{**}p < 0.01$, vs. the maximum adhesion strength in the same test environment).

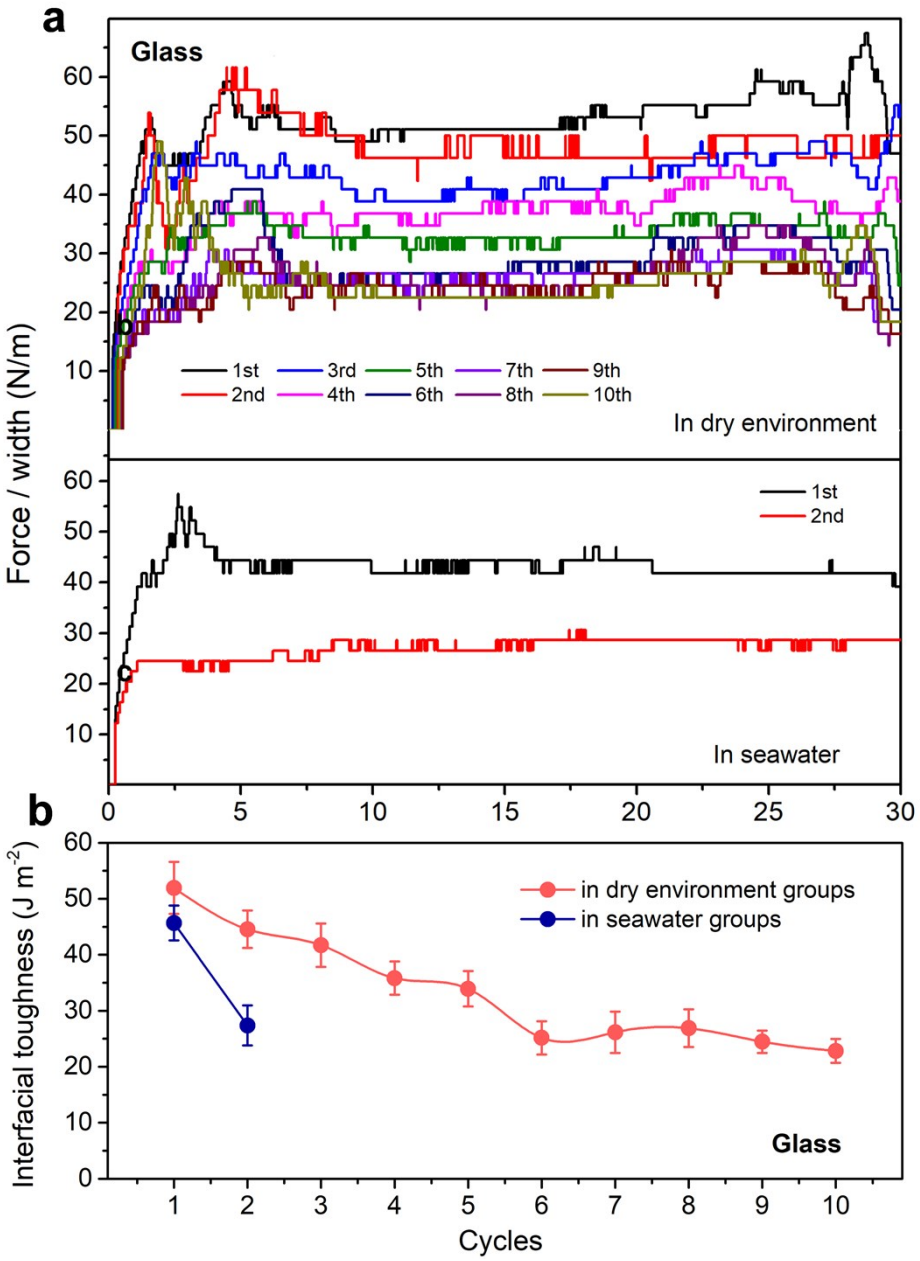

Figure S4. Reversible surface adhesion tests on the glass of PAM_{12}-$Alg_{1.5}$-$PDA_{0.6}$ hydrogel by 90-degree peeling test in dry environment and in seawater (a). Mechanical testing machine (FLR-303, Flora Automatic Technology, China) pulled the hydrogel sheet [length (L) × width (W) × thickness (T) = 45 × 24 × 3 mm] together with stiff backing (a combination of A4 paper and double-sided tape, T = 60 μm) in 90 degrees from the substrate. (b) The interfacial toughness was calculated by dividing the steady-state (or plateau) peeing force with the sample width.

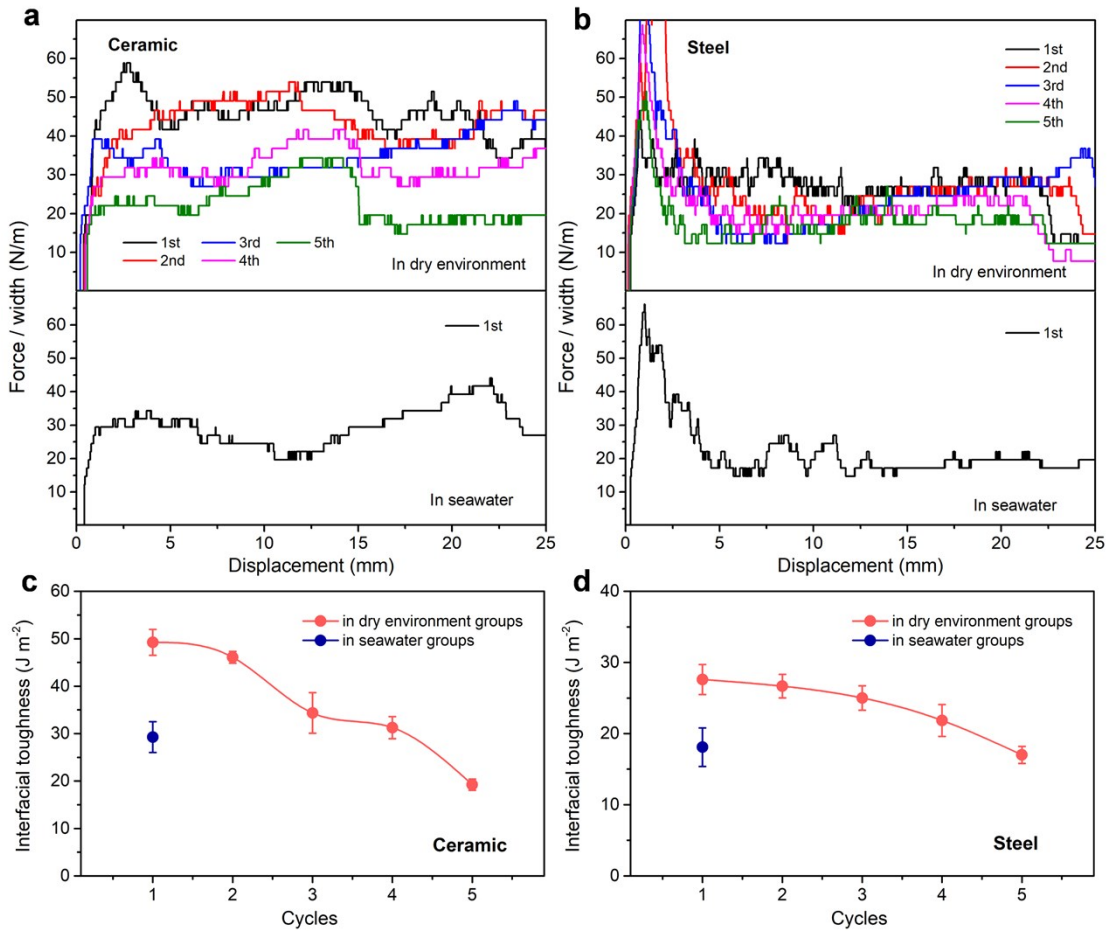

Figure S5. Reversible surface adhesion tests on ceramic (a, c) and steel (b, d) of PAM_{12}-$Alg_{1.5}$-$PDA_{0.6}$ hydrogel by 90-degree peeling test in dry environment and in seawater.

Table S3. Post Hoc Test by Tukey HSD Analysis to Determine Statistical Differences in the Mean Values of Shear Adhesion Strength of Multiple Hydrogel Groups with Varying Am Content in Dry Environment (Bottom Left) and in Artificial Seawater (Upper Right).

Dry \ Seawater	8 wt%	10 wt%	12 wt%	14 wt%	16 wt%
8 wt%			**	**	*
10 wt%			**		**
12 wt%	**	**			**
14 wt%	**	**			**
16 wt%	**				

*p < 0.05; **p < 0.01

Table S4. Post Hoc Test by Tukey HSD Analysis to Determine Statistical Differences in the Mean Values of Shear Adhesion Strength of Multiple Hydrogel Groups with Varying DA Content in Dry Environment (Bottom Left) and in Artificial Seawater (Upper Right).

Dry \ Seawater	0 %	0.2 %	0.4 %	0.6 %	0.8 %	1.0 %	1.2 %
0 %			**	**	**		
0.2 %			**	**	**		*
0.4 %	**	**		**		**	**
0.6 %	**	**			**	**	**
0.8 %	**	**		*		**	**
1.0 %			**	**	**		
1.2 %			**	**	**		

*p < 0.05; **p < 0.01

Table S5. Post Hoc Test by Tukey HSD Analysis to Determine Statistical Differences in the Mean Values of Shear Adhesion Strength of Multiple Hydrogel Groups with Varying Alg-Na Content in Dry Environment (Bottom Left) and in Artificial Seawater (Upper Right).

Dry \ Seawater	0 wt%	0.5 wt%	1 wt%	1.5 wt%	2 wt%	2.5 wt%	3 wt%
0 wt%		**	**	**	**	**	**
0.5 wt%	**		**	**	**		
1 wt%	**			**		**	**
1.5 wt%	**				*	**	**
2 wt%	**					**	**
2.5 wt%		**	**	**	**		
3 wt%		**	**	**	**		

*p < 0.05; **p < 0.01

Table S6. Adhesion Strength Comparison between the PAM-Alg-PDA Hydrogel and Other Types of Adhesives Reported in the Literature.

No.	Type of Adhesive	Adhesive Substrate	Curing Weight	Curing Temperature	Curing Time	Curing Environment	Testing Machine	Adhesion Strength (kPa)	Refs.
1	hydrogel	glass	100 g	NM	2 min	air	Instron 5583	~ 105	1
2	hydrogel	glass	NM	60℃	30 min	air	Instron 1185	2990 ± 120	2
3	hydrogel	glass	NM	NM	NM	air	Instron 5542	1084.9 ± 104.6	3
4	hydrogel	glass	NM	RT	none	air	Zwell/Roell	~ 6	4
5	hydrogel	glass	metal clip	RT	6 h	air	FLR-303	167.4 ± 11.5	this work
6	hydrogel	glass	NM	NM	24 h	water	Shimadzu AGS-X	~ 45	5
7	hydrogel	glass	metal clip	RT	24 h	seawater	FLR-303	146.8 ± 7.8	this work
8	hydrogel	aluminum	metal clip	RT	24 h	water	Hengyi HY-0580	~ 1500	6
9	hydrogel	porcine skin	metal clip	RT	2 h	PBS buffer	Instron 5544	~ 215	7
10	hydrogel	porcine skin	metal clip	RT	2 h	PBS buffer	Instron 5544	~ 53	8
11	hydrogel	porcine skin	NM	RT	2 h	PBS buffer	Instron 5544	72.2 ± 3.7	9
12	hydrogel	porcine skin	NM	RT	2 h	air	Instron 5544	30.4 ± 3.4	10
13	copolymer	glass	NQ	RT	4 h	air	Shimadzu AG-I	15.8 ± 1.7	11
14	copolymer	glass	NM	RT	NM	air	NM	~ 1500	12
15	copolymer	glass	35 kPa	NM	15 min	water	Instron 5944	27.8 ± 2.5	13
16	copolymer	glass	binder clips	RT	12 h	water	NM	~ 200	12
17	copolymer	glass	20 g	NM	6 d	seawater	Shimadzu AGX	~ 300	14
18	copolymer	aluminum	metal clip	NM	24 h	water	Instron 3342	~ 765	15
19	copolymer	aluminum	35 kPa	NM	15 min	water	Instron 5944	24.1 ± 3.1	13
20	copolymer	aluminum	55 g	RT	24 h	seawater	Instron 5544	400 ± 200	16
21	protein glue	glass	NQ	RT	5 min	air	Instron 5965	216 ± 80.4	17
22	protein glue	aluminum	55 g	37℃	24 h	air	Instron 5544	2600 ± 600	18

23	protein glue	aluminum	NQ	37℃	NM	water	Instron 5544	240 ± 90	18

*NM means not mentioned. RT means room temperature. NQ means not quantified.

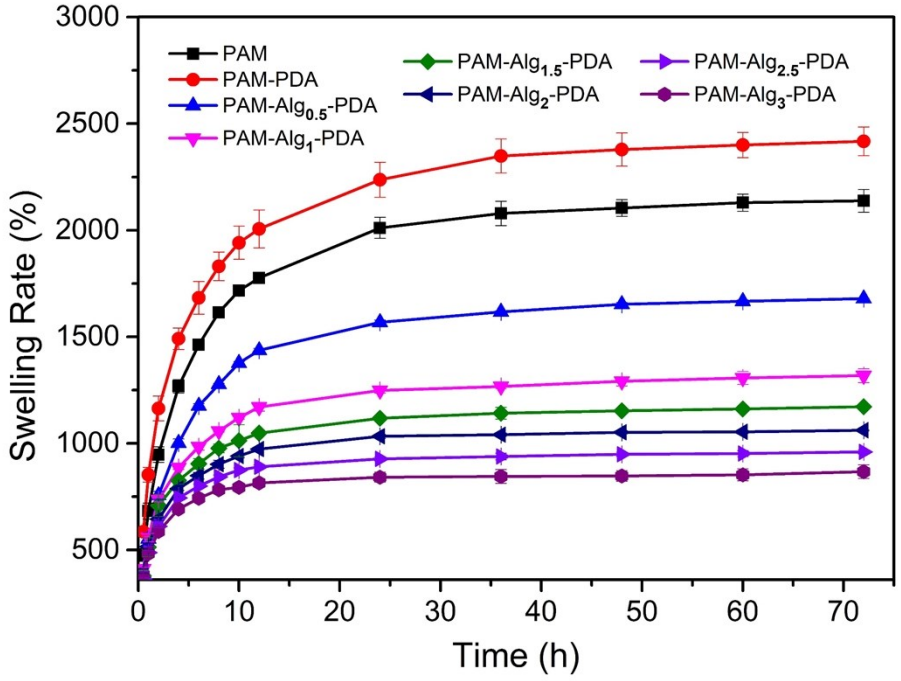

Figure S6. The swelling behavior of various freeze-dried hydrogels.

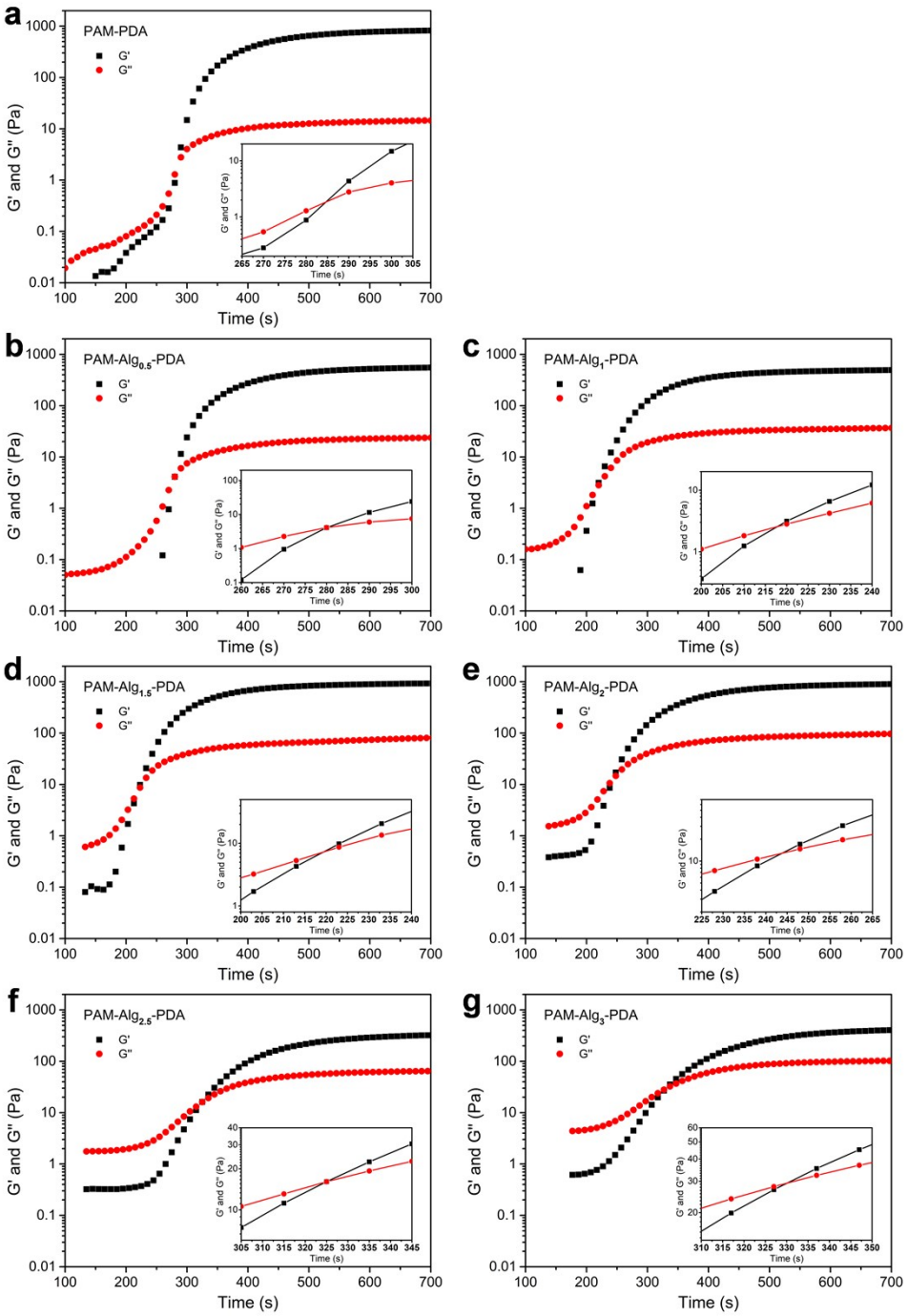

Figure S7. The time required for precursor solution of different hydrogels in the phase transition process of sol-gel. (a) PAM-PDA hydrogel; (b) PAM-$Alg_{0.5}$-PDA hydrogel; (c) PAM-Alg_1-PDA hydrogel; (d) PAM-$Alg_{1.5}$-PDA hydrogel; (e) PAM-Alg_2-PDA hydrogel; (f) PAM-$Alg_{2.5}$-PDA hydrogel; (g) PAM-Alg_3-PDA hydrogel. The gelation time of PAM hydrogel was too fast (~30 s), so that it cannot be measured by rheometer.

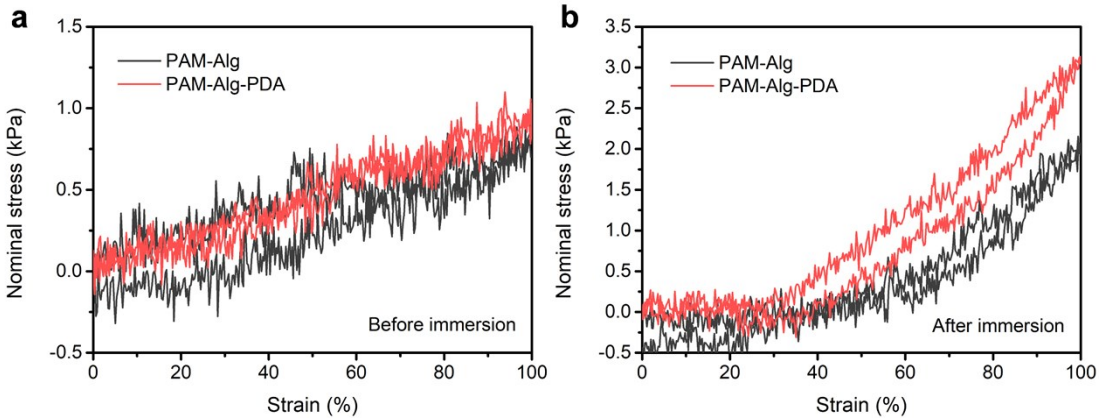

Figure S8. Loading-unloading curves of PAM-Alg and PAM-Alg-PDA hydrogels before immersion (a) and after immersion in seawater for 3 days (b), respectively (Instron 5940, Instron, America). Each sample is stretched to a strain of 100%.

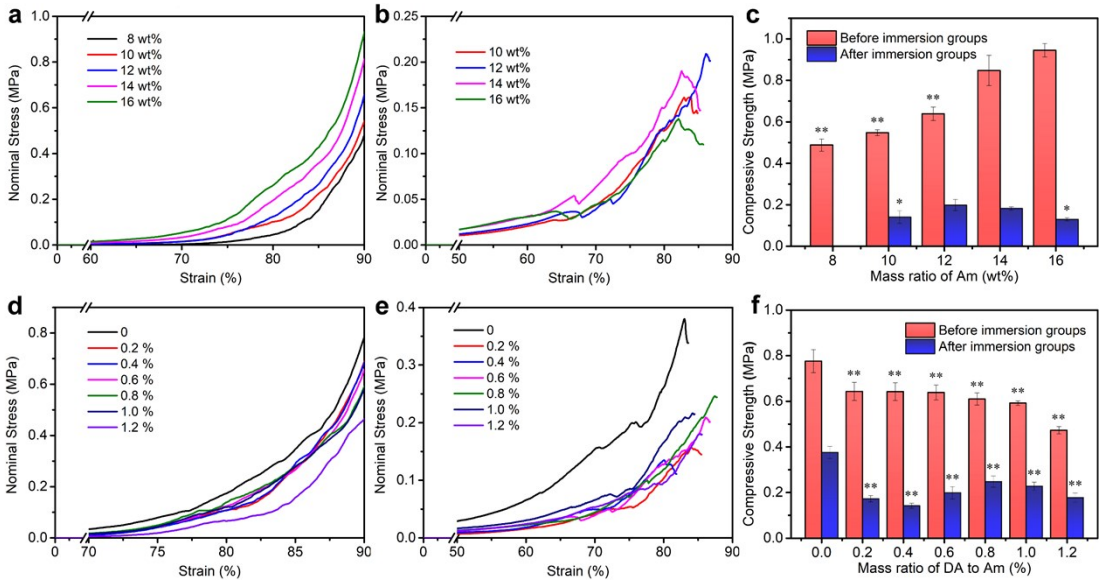

Figure S9. Compressive stress-strain curves of hydrogels with different content of Am and DA before immersion (a, d) and after immersion in artificial seawater for 3 days (b, e), respectively; (g) Compressive strength of PAM-Alg-PDA hydrogel with different content of Am (c) and DA (f), respectively ($^{*}p < 0.05$, $^{**}p < 0.01$, vs. the maximum compressive strength in the same test environment).

Table S7. Post Hoc Test by Tukey HSD Analysis to Determine Statistical Differences in the Mean Values of Compressive Strength of Multiple Hydrogel Groups with Varying Am Content before Immersion (Bottom Left) and after Immersion (Upper Right).

Before \ After	8 wt%	10 wt%	12 wt%	14 wt%	16 wt%
8 wt%		—	—	—	—
10 wt%			*		
12 wt%	**				*
14 wt%	**	**	**		
16 wt%	**	**	**		

*p < 0.05; **p < 0.01

Table S8. Post Hoc Test by Tukey HSD Analysis to Determine Statistical Differences in the Mean Values of Compressive Strength of Multiple Hydrogel Groups with Varying DA Content before Immersion (Bottom Left) and after Immersion (Upper Right).

Dry \ Seawater	0 %	0.2 %	0.4 %	0.6 %	0.8 %	1.0 %	1.2 %
0 %		**	**	**	**	**	**
0.2 %	**				**		
0.4 %	**				**	**	
0.6 %	**						
0.8 %	**						*
1.0 %	**						
1.2 %	**	**	**	**	**	**	

Table S9. Post Hoc Test by Tukey HSD Analysis to Determine Statistical Differences in the Mean Values of Compressive Strength of Multiple Hydrogel Groups with Varying Alg-Na Content before Immersion (Bottom Left) and after Immersion (Upper Right).

Dry \ Seawater	0 wt%	0.5 wt%	1 wt%	1.5 wt%	2 wt%	2.5 wt%	3 wt%
0 wt%			**	**	**		
0.5 wt%			**	**	**		
1 wt%					**	**	**
1.5 wt%		**	*		**	**	**
2 wt%	*	**	**			**	**
2.5 wt%	**	**	**	*			
3 wt%	**	**	**	**			

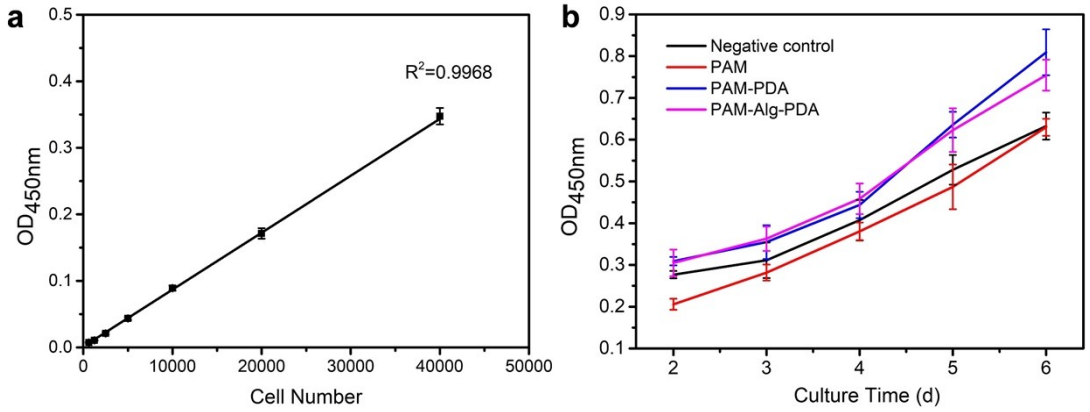

Figure S10. (a) Zooxanthellae cell number determination using CCK-8; (b) The growth curve of zooxanthellae cell cultured with various hydrogels.

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