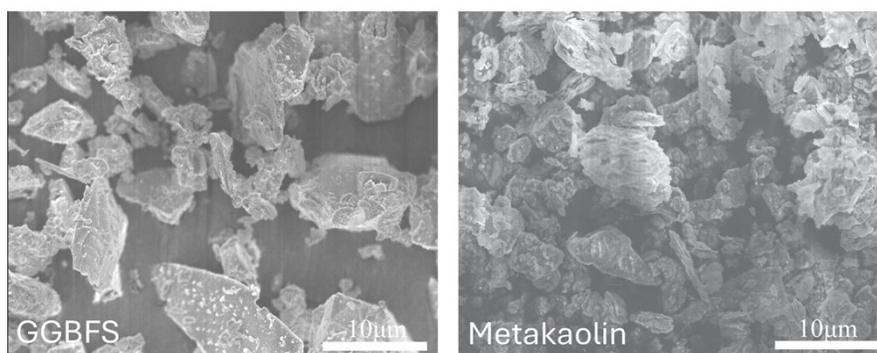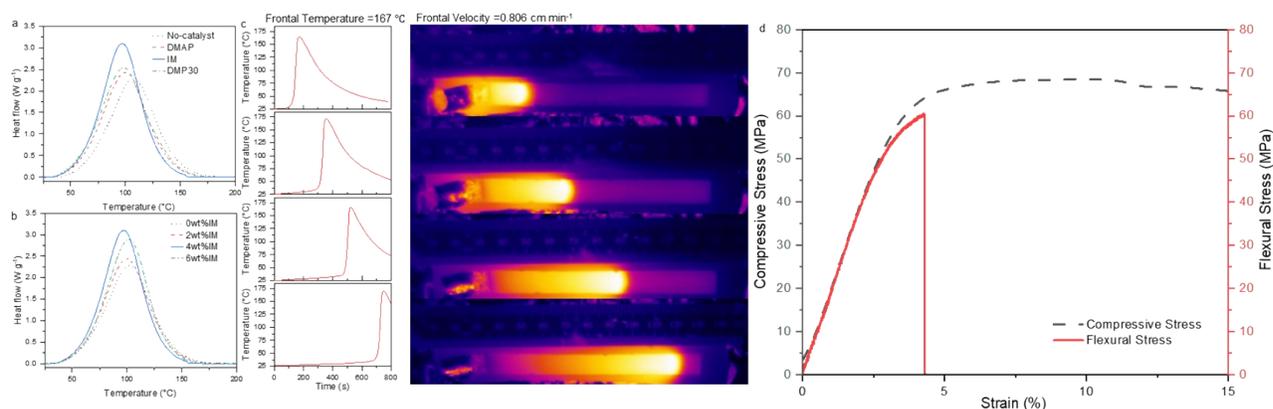Supplementary information

Frontal Curing of Aluminosilicate-Epoxy Composites for Extreme Underwater Environments
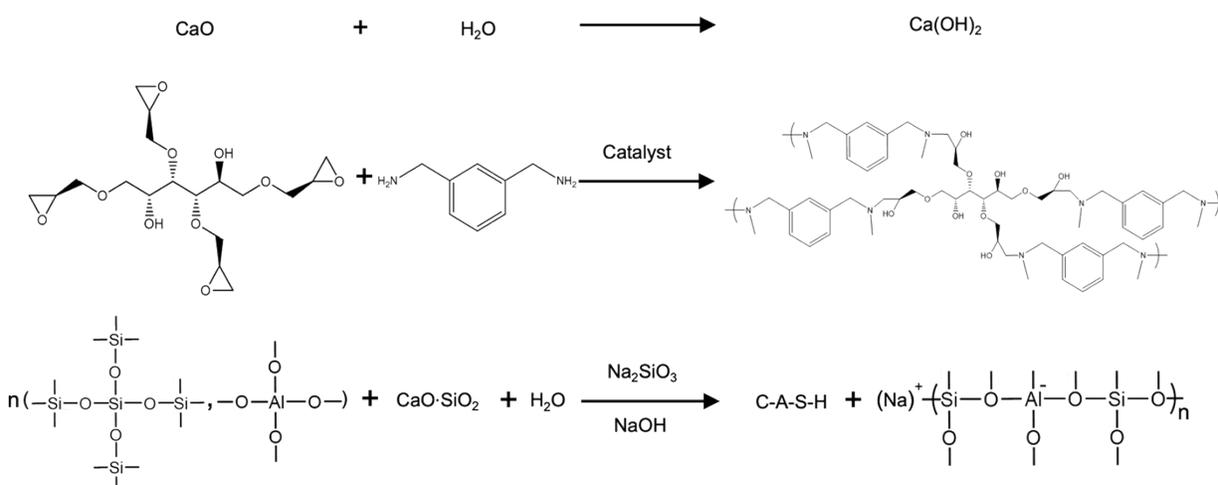
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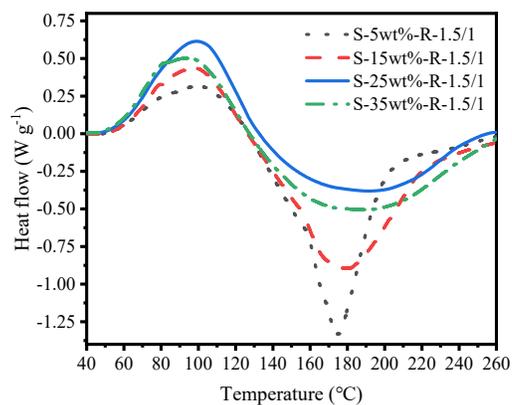Supplementary Figure S1. a, Reaction profile of catalyzed epoxy reaction with DMAP, DMP30, and IM catalysts. b, Catalyst effect of various concentrations of IM on epoxy reaction. c, Temporal evolution of the front temperature of the catalyzed epoxy reaction at different positions and the corresponding Infrared (IR) images. d, Compressive and flexural strength of the optimized, frontal-cured Epoxy system.
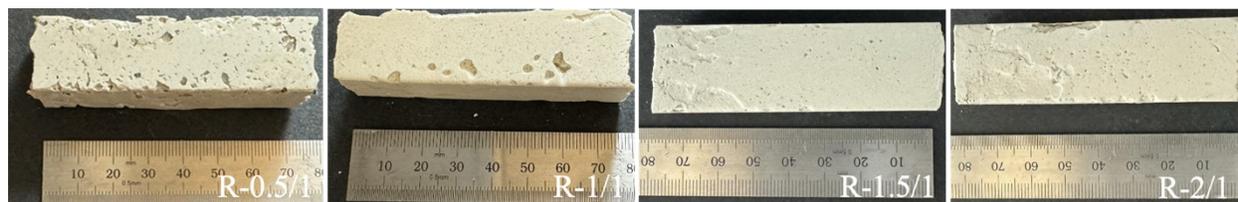

Supplementary Figure S2. Scanning electron microscopy (SEM) of MK, GGBFS particles.

Supplementary Figure S3. Reaction mechanism of calcium oxide exothermic reaction, epoxy frontal polymerization, and GGBFS-participated geopolymerization.

Supplementary Figure S4. GGBFS addition optimizing from dynamic DSC reaction profile.

Supplementary Figure S5. Photos of frontal-cured GPC/Epoxy specimens with various G-gel-to-epoxy mass ratios.
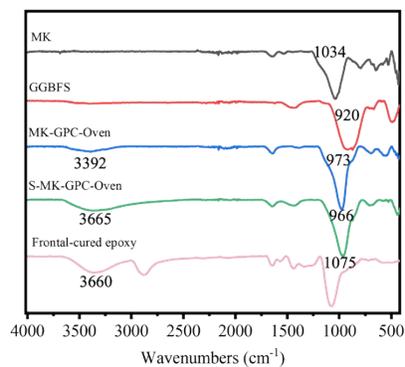
Supplementary Figure S6. FTIR spectra of raw materials, GPC reference specimens, and frontal-cured epoxy.
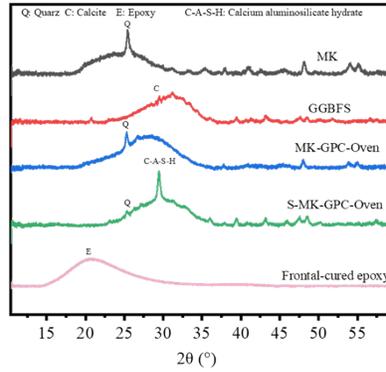
Supplementary Figure S7. XRD spectra of raw materials, GPC reference specimens, and frontal-cured epoxy.
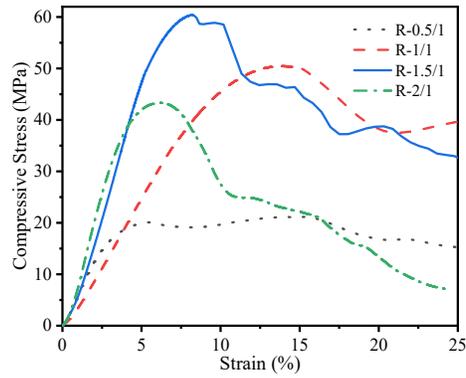
Supplementary Figure S8. Representative compressive stress-strain curves of frontal-cured GPC/Epoxy specimens.
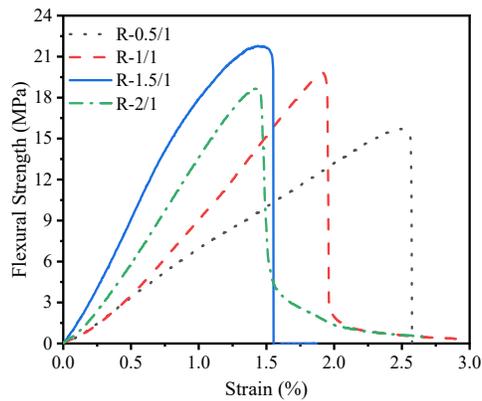
Supplementary Figure S9. Representative flexural stress-strain curves of frontal-cured GPC/Epoxy specimens.

Supplementary Figure S10. a, Digital Image Correlation Experiment set up; b, Photo of the crack morphology of GPC-Oven and GPC/Epoxy-Frontal.
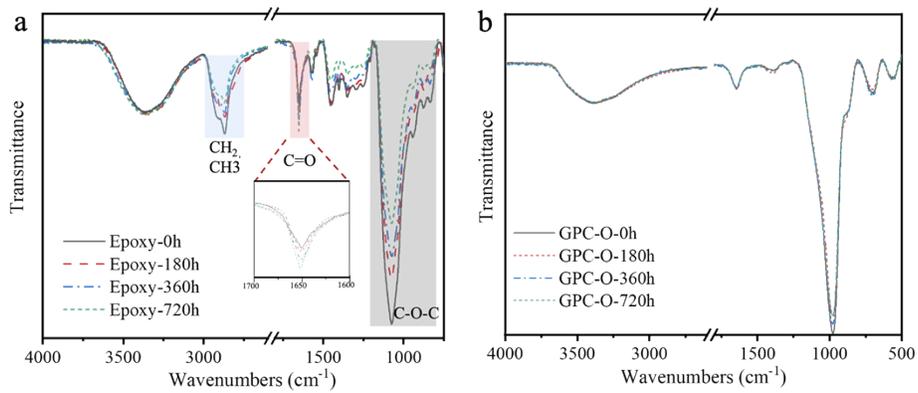
Supplementary Figure S11. FTIR spectra of a, frontal-cured Epoxy-resin, and b, GPC-O, at different accelerated UV-aging durations.

Supplementary Figure S12. Photographs of underwater frontal-cured specimen.
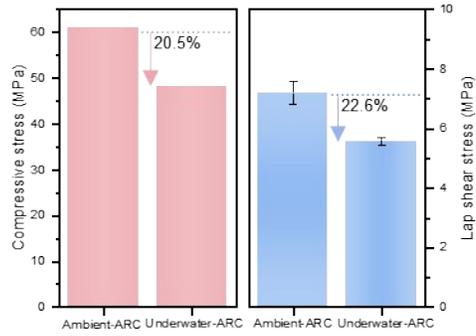
Supplementary Figure S13. Comparison of compressive strength and lap shear strength of ambient and underwater frontal-cured GPC/Epoxy composites.
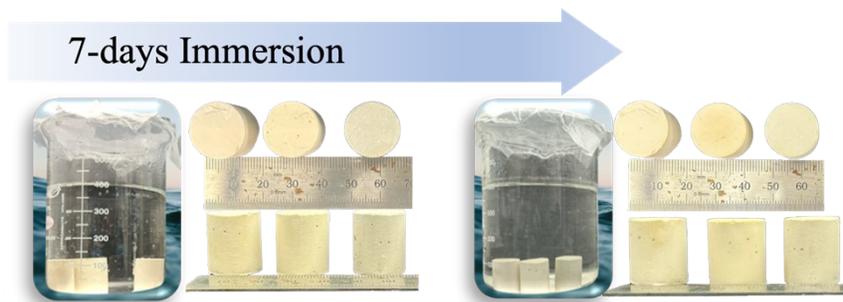
Supplementary Figure S14. Photographs of frontal-cured specimen before and after corrosion test in artificial seawater.

Supplementary Table S1. Raw material composition

	SiO$_2$ (wt%)	Al$_2$O$_3$ (wt%)	CaO (wt%)	Other oxides (wt%)	Mean particle size (μm)	Specific Gravity
MK	52.4	43.0	0.04	4.56	4.56 μm	2.5
GGBFS	34.8	14.2	39.7	11.3	3.17μm	2.89

Supplementary Table S2. Mix proportions of specimens

Sample	GGBFS (wt%)	G-gel/Bio (mass ratio)	Na$_2$SiO$_3$ Solution (g)	Na$_2$SiO$_3$ (g)	NaOH (g)	MK (g)	GGBFS (g)	Epoxy (g)	Amine (g)	Catalyst (g)
S-5wt%-R-1.5/1	5.00	1.5:1	100	8	9	85.5	4.5	116	22	4.64
S-15wt%-R-1.5/1	15.00	1.5:1	100	8	9	76.5	13.5	116	22	4.64
S-25wt%-R-1.5/1	25.00	1.5:1	100	8	9	67.5	22.5	116	22	4.64
S-35wt%-R-1.5/1	35.00	1.5:1	100	8	9	58.5	31.5	116	22	4.64
R-0.5/1	25.00	0.5:1	100	8	9	67.5	22.5	347.9	66.1	16.56
R-1/1	25.00	1:1	100	8	9	67.5	22.5	174	33	8.28
R-1.5/1	25.00	1.5:1	100	8	9	67.5	22.5	116	22	4.64
R-2/1	25.00	2:1	100	8	9	67.5	22.5	86.6	16.4	4.12
GPC-R	0	N/A	100	8	9	67.5	22.5	0	0	0
GPC-O	0	N/A	100	8	9	67.5	22.5	0	0	0
G-gel	0	N/A	100	8	9	90	0	0	0	0
S-G-gel	25	N/A	100	8	9	67.5	22.5	0	0	0
G-gel/Epoxy	0	1.5:1	100	8	9	90	0	116	22	4.64
S-G-gel/Epoxy	25	1.5:1	100	8	9	67.5	22.5	116	22	4.64
MK-GPC-Oven	0	N/A	100	8	9	90	0	0	0	0
S-MK-GPC-Oven	25	N/A	100	8	9	67.5	22.5	0	0	0
Frontal-cured epoxy	0	N/A	0	0	0	0	0	116	22	4.64

Supplementary Table S3. Parameters used for numerical simulation.

Material	Notation	Constant	Value	Reference
G-gel	k_G	Thermal conductivity	0.6 Wm^{-1}·K^{-1}	Measured
	$c_{p,G}$	Heat capacity	1400 J kg^{-1}·K^{-1}	Measured
	ρ_G	Density	1.80 g cm^{-3}	Calculated
Epoxy system	A	Pre-exponential factor	8.886·10^7 s^{-1}	Calculated
	E_a	Activation energy	57.5 kJ mol^{-1}	Calculated
	H_r	Enthalpy of reaction	395 J g^{-1}	Measured
	n	Order of reaction	1.7	Calculated
	m	Order of reaction	0.3	Calculated
	ρ_E	Density	1.15 g cm^{-3}	Calculated
	k_E	Thermal conductivity	0.2 W m^{-1}K^{-1}	Measured
	$c_{p,E}$	Heat capacity	1100 J kg^{-1}·K^{-1}	Calculated
	Mw	Molecular weight	719 g mol^{-1}	Calculated

Supplementary Table S4. Parameters used for mapping the stability window of the frontal process.

Specimens	T_0 (°C)	λ_f	P_R (J m^{-3} s^{-1})	P_T (J m^{-3} s^{-1}))	P_C (J m^{-3} s^{-1})
R-0.5/1	5	9.989069	20090406	1429596	581643.5
	10	12.87577	26151035	1449383	581643.5
	15	16.48081	33799073	1469170	581643.5
	20	20.95381	43386979	1488957	581643.5
	25	26.46929	55331095	1508745	581643.5
R-1/1	5	5.56234	10978180	1473423	500239.4
	10	7.291785	14545174	1494495	500239.4
	15	9.485514	19120962	1515567	500239.4
	20	12.24834	24948391	1536639	500239.4
	25	15.70415	32318378	1557712	500239.4
R-1.5/1	5	2.67899	5107504	1499621	406882.3
	10	3.58856	6921619	1521919	406882.3
	15	4.765577	9298111	1544216	406882.3
	20	6.276511	12386043	1566514	406882.3
	25	8.201268	16367218	1588811	406882.3
R-2/1	5	1.789599	3370437	1524630	358717.9
	10	2.426501	4626103	1547773	358717.9
	15	3.259997	6290601	1570916	358717.9
	20	4.341509	8477998	1594059	358717.9

25	5.733449	11328834	1617202	358717.9

Supplementary Table S5. Parameters used for mapping the ignitability window of calcium oxide cartridges.

Calcium oxide (g)	T_0 (°C)	T_i (°C)	T' (K)	t_i (s)	L_i(m)	λ_i	P_R (J m^{-3} s^{-1})	P_T (J m^{-3} s^{-1})	P_C (J m^{-3} s^{-1})
0.8	5	88.75	320.025	140	0.011735	0.658651	942398.1	1039966	390833.3
	10	88.75	322.525	140	0.011735	0.791675	1114255	1039966	367500
	15	88.75	325.025	140	0.011735	0.949376	1314062	1039966	344166.7
	20	88.75	327.525	140	0.011735	1.13595	1545801	1039966	320833.3
	25	88.75	330.025	140	0.011735	1.35625	1813938	1039966	297500
1.1	5	90	320.65	180	0.013307	0.813477	982943	811656.6	396666.7
	10	90	323.15	180	0.013307	0.980126	1161439	811656.6	373333.3
	15	90	325.65	180	0.013307	1.178349	1368837	811656.6	350000
	20	90	328.15	180	0.013307	1.413691	1609237	811656.6	326666.7
	25	90	330.65	180	0.013307	1.692601	1887233	811656.6	303333.3
1.4	5	91.15	321.225	215	0.014543	0.942719	1021635	681678.3	402033.3
	10	91.15	323.725	215	0.014543	1.137745	1206440	681678.3	378700
	15	91.15	326.225	215	0.014543	1.370286	1421048	681678.3	355366.7
	20	91.15	328.725	215	0.014543	1.647085	1669669	681678.3	332033.3
	25	91.15	331.225	215	0.014543	1.976032	1957019	681678.3	308700
1.7	5	91.6	321.4	240	0.015365	1.096833	1033682	538757.6	403666.7
	10	91.6	323.9	240	0.015365	1.321857	1220446	542948.3	380333.3
	15	91.6	326.4	240	0.015365	1.589681	1437293	547139	357000
	20	91.6	328.9	240	0.015365	1.907878	1688465	551329.7	333666.7
	25	91.6	331.4	240	0.015365	2.285278	1978717	555520.4	310333.3