Supplementary Information

Vapor-Phase Synthesis of a Reagent-free Self-Healing Polymer Film with Rapid Recovery of Toughness at Ambient in Room Temperature

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	Flow rate [sccm]			Pressure [mTorr]	Substrate temperature [℃]
	GMA	HEA	TBPO		
pGH1	0.26	0.42	0.49	150	30
pGH2	0.43	0.42	0.49	150	30
pGH3	0.79	0.42	0.49	150	30

Table S1. A summary of the iCVD process condition for the synthesis of poly(glycidylmethacrylate-*co*-2-hydroxyethyl acrylate), (pGH) copolymer films.

Reference	Dynamic bonding	Healed toughness ($MJ \cdot m^{-3}$)	Time for healing	Condition for healing
ACS Appl. Mater. Interfaces, 2019, 11, 46165-46175	Hydrogen bond	7.7	1 min	Room temperature (RT)
ACS Appl. Mater. Interfaces, 2020, 12, 6383-6395	Hydrogen bond, Ditelluride	105.2	10 min	Visible light, RT
	Hydrogen bond, Ditelluride	3.67	1 min	Visible light, RT
Adv. Mater., 2018, 30, 1706846	Hydrogen bond	1.84	12 h	Dodecane, RT
Nature Electronics, 2019, 2(2), 75-82.	Ionic interaction	0.151	3 h	Water, RT
J. Am. Chem. Soc., 2015, 137, 4846−4850	Hydrogen bond, Catalyst induced covalent bond	9.75	3 h	25 ℃
Adv. Mater., 2017, 29, 1702616	Hydrogen bond	0.694	1 h	RT
J. Am. Chem. Soc., 2019, 141(7), 3249-3257.	Anisyl group, ethylene base polymer	5.7	5 min	25 ℃
Nature Chemistry, 2016, 8(6), 618-624.	Metal coordination bond	0.718	4 h	RT
ACS Appl. Mater. Interfaces, 2020, 12, 9833-9841	Ionic interaction	1.71	10 min	10 MPa pressure, 80 ℃
J. Mater. Chem. C, 2020, 8, 2043-2053	Hydrogen bond	1.9	1 h	25 ℃
New J. Chem., 2019, 43, 7701-7707	Boronate ester, pi-pi interaction	2.4	2 min	Hydrogel, RT
	Boronate ester, pi-pi interaction	0.53	0.5 min	Hydrogel, RT
Biosensors and Bioelectronics, 2020, 150, 111946	Hydrogen bond	7.68	0.5 min	25 ℃
ACS Appl. Mater. Interfaces, 2017, 9, 20106−20114	Metal coordination bond	0.273	30 min	RT
Nature Mater., 2013, 12(10), 932-937.	Hydrogen bond	1.45	24 h	Hydrogel, 25 ℃
Adv. Mater., 2017, 29, 1604951	Host-guest complex	0.776	30 min	Hydrogel, RT
Adv. Mater., 2017, 29, 1605325	Host-guest complex	3.55	60 min	Hydrogel, RT
Small, 2019, 15, 1804651	Metal coordination bond	0.568	5 min	RT
Nature, 2008, 451(7181), 977-980.	Hydrogen bond	0.222	5 min	Dodecane, 40 ℃
J. Am. Chem. Soc., 2018, 140, 5280−5289	Hydrogen bond	9.42	6 h	RT
Adv. Mater., 2018, 30, 1705145	Disulfides	0.699	3 min	25 ℃
	Disulfides	26.9	2 h	25 ℃
Macromolecules, 2021, 54, 888-895	Hydrogen bond	1.68	24 h	22 ℃
Adv. Funct. Mater., 2021, 2007457	Hydrogen bond	0.058	20 min	Hydrogel, 37 ℃
J. Mater. Sci., 2021, 56, 2725-2737	Hydrogen bond	2.34	4 h	Hydrogel, RT
Adv. Funct. Mater., 2021, 2101825	Disulfide, hydrogen bond, Coordination bond	1.9	10 min	RT
ACS Appl. Mater. Interfaces 2020, 12, 35445-35452	Hydrogen bond	12.05	40 s	RT
This work	**Hydrogen bond**	**15.6**	**< 1 min**	**RT**

Table S2. Performance comparison of this work with previous reported self-healing materials.

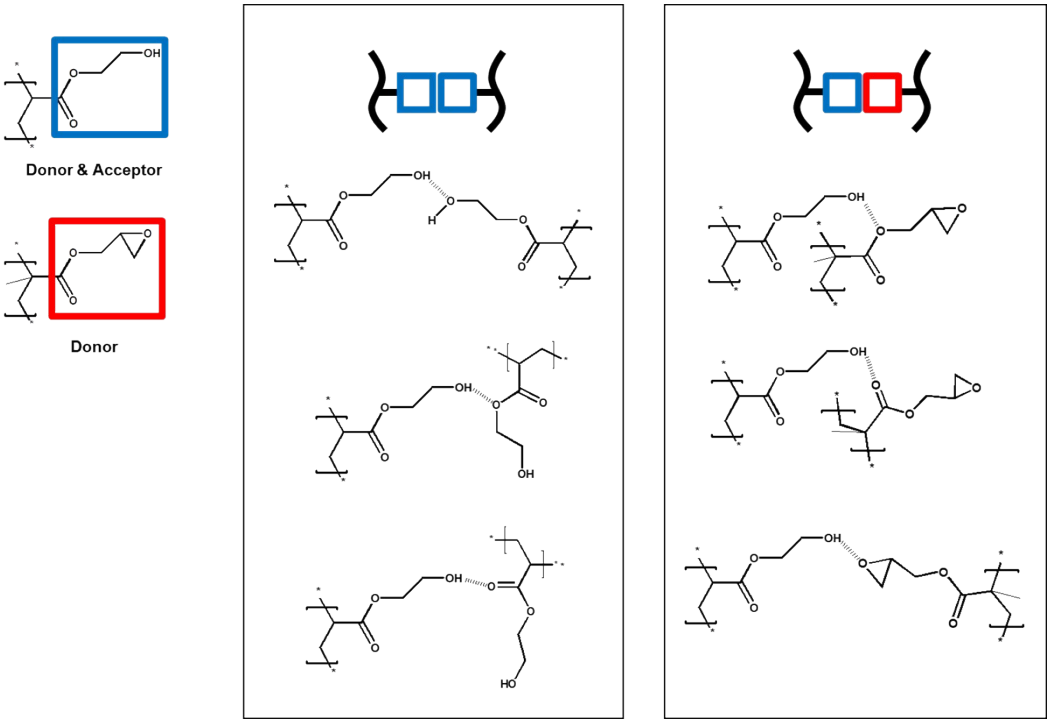

Figure S1. Possible combinations of hydrogen bonding in pGH network

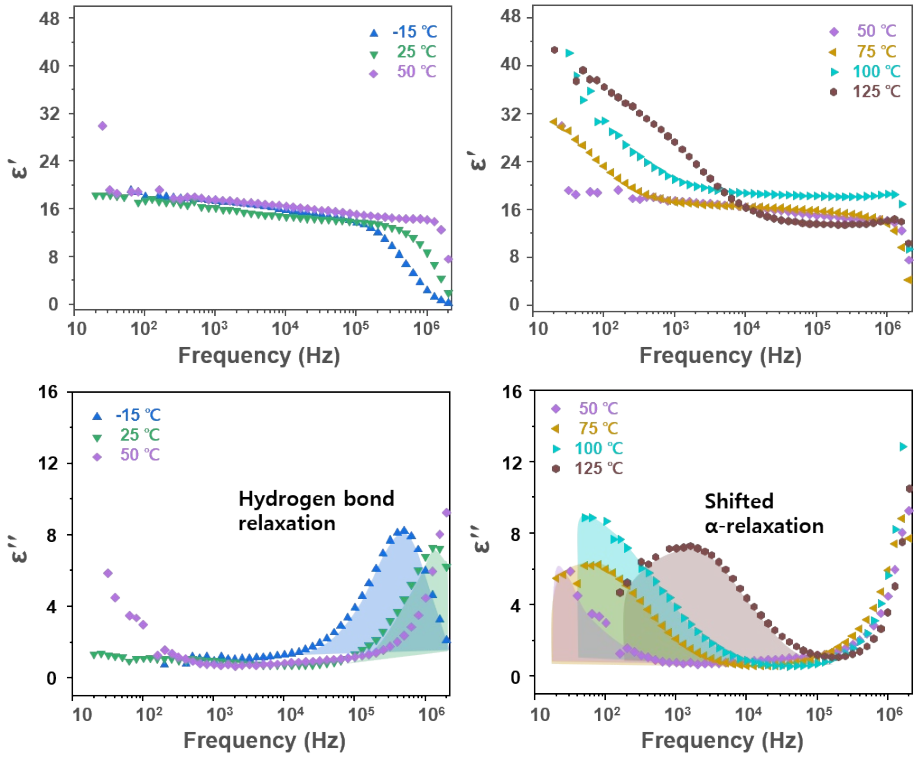

Figure S2. Dielectric relaxation spectroscopy (DRS) plot of real (ε', top) and imaginary (ε", bottom) permittivity vs frequency of pHEA at -15, 25, 50, 75, 100, 125 ℃

It was assumed that two kinds of intermolecular interactions, hydrogen bonding and α-relaxation exist in pHEA. At -15 and 25 ℃, a peak was observed at around 10^6 Hz (μsec-scale) and right-shift with increasing temperature.

Further temperature increase induced other peak is shifted from lower frequency. The peak does not disappear even at 125 ℃ which is considered to be high enough to dissociate hydrogen bonding. Thus, we expected that the later peak is related with α-relaxation of polymer chain and the first one is related to hydrogen bonding relaxation.

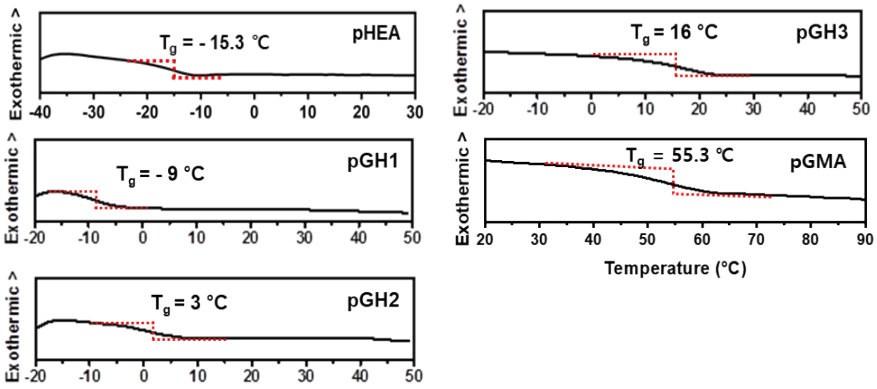

Figure S1. Glass transition temperature of pHEA, pGH1, pGH2, pGH3, and pGMA measured by differential scanning calorimetry (DSC)

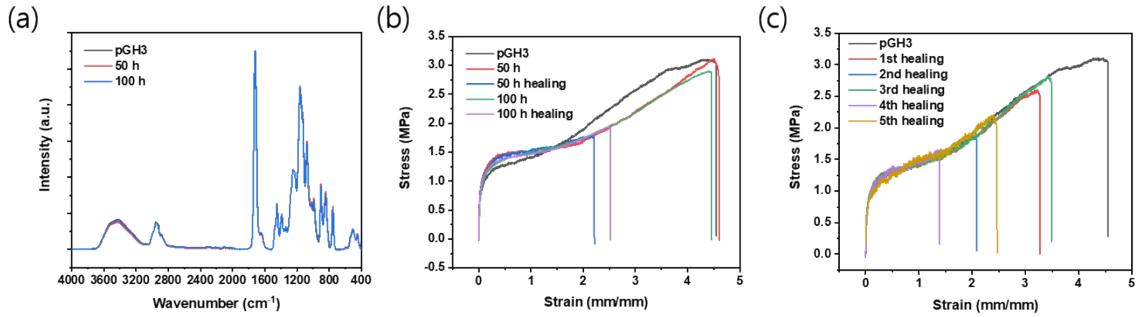

Figure S4. (a) FT-IR spectra of pGH3 with its storage time 0 h, 50 h and 100 h. (b) Strain-stress curve of pGH3, pGH3s after each storage time (50 and 100 hours), healed those, and (c) repeated damaged pGH3.

We checked the change in the FT-IR spectra of pGH3 along with the storage time. (**Figure S4a**) The first curve was measured just after the deposition process, and the same measurements were repeated after 50-hr, and 100-hr thereafter. Even after 100 hours, the FT-IR spectra were practically identical to each other, strongly suggesting no appreciable chemical degradation in this time interval. Moreover, the self-healing property also remained unchanged even after 100 hrs from the deposition, confirmed by checking the S-S curve (**Figure S4b**), confirming the excellent long-term stability of the copolymer films. The self-healing property was also repeatedly recoverable, as in **Figure S4c**, 5 times of recovery was attempted to pGH3 film.

Movie S1. Stretching of pristine pGH2 and rapid self-healing of pGH2 elastomer (2 × speed).

Captured images from this movie are shown in Figure 3b.

Movie S2. Conductivity healing of gold electrode coated on pGH1. Captured images from this movie are shown in Figure 4b.