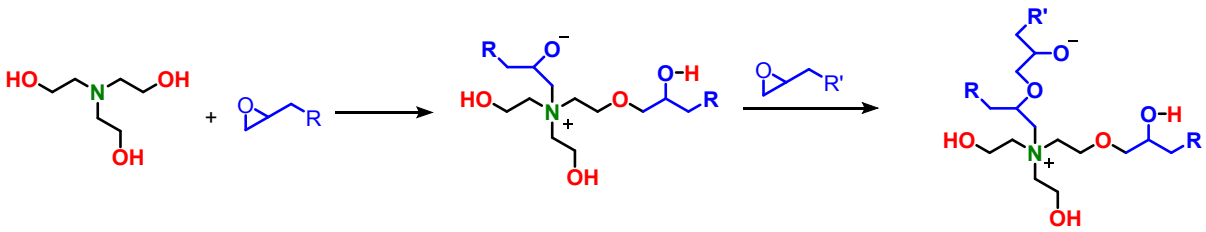
Supporting Information

Triethanolamine Mediated Covalent Adaptable Epoxy Network: Excellent Mechanical Properties, Fast Repairing and Easy Recycling

Cheng Hao, Tuan Liu, Shuai Zhang, Wangcheng Liu, Yingfa Shan, Jinwen Zhang**



Scheme S1. The possible TEOA induced polyetherification of epoxy.

Table S1. Formulations of DER-NMA-TEOA curing systems

Samples	DER [g]	NMA [g]	TEOA	
			[mg]	[wt%][a)]
DER-NMA-0.05TEOA	1	0.908	38	2.0
DER-NMA-0.1TEOA	1	0.908	76	3.8
DER-NMA-0.15TEOA	1	0.908	114	5.6
DER-NMA-0.2TEOA	1	0.908	152	7.4

[a)] Weight percent of TEOA in the curing system.

Table S2. The activation energies of different DER-NMA-TEOA curing systems from non-isothermal DSC scanning

Samples	E_a/kJ mol^{-1} [a)]
DER-NMA-0.05TEOA	98.4
DER-NMA-0.1TEOA	93.5
DER-NMA-0.15TEOA	90.5
DER-NMA-0.2TEOA	80.7

[a)] Calculated from Arrhenius equation.

Table S3. Formulations of different DER-TEOA compositions

Samples	Epoxy/TEOA [mol/mol]	DER [g]	TEOA	
			[mg]	[wt%][a)]
DER-0.05TEOA	1/0.05	1	38	3.7
DER-0.1TEOA	1/0.1	1	73	6.8
DER-0.15TEOA	1/0.15	1	114	10.2
DER-0.2TEOA	1/0.2	1	152	13.2

[a)] Weight percent of TEOA in the curing system.

Table S4. TGA results of the cured DER-NMA-TEOAs and DER-NMA-2E4MI

Samples	T_i [a)] [°C]	T_{d5} [b)] [°C]
DER-NMA-0.05TEOA	219	280
DER-NMA-0.1TEOA	216	280
DER-NMA-0.15TEOA	217	283
DER-NMA-0.2TEOA	230	280
DER-NMA-2E4MI	239	297

[a)] The initial weight loss temperature; [b)] the temperature at 5% weight loss.

Table S5. Summary of the reported epoxy vitrimers based on transesterification mechanism

Starting materials	Stress relaxation time/h[a)]	Repairing temperature/°C	T_g/°C
Epoxidized soybean oil, citric acid[1]	3.2 at 160 °C	>150	0 - 30
Dimer and trimer acids, BPA epoxy[2]	0.8 at 190 °C	>130	0 - 20
Succinic anhydride, BPA epoxy[3]	1.3 at 180 °C	>130	60 - 80
Diphenyl epoxy, sebacic acid[4]	0.7 at 190 °C	>160	55
Bisphenolic compound, carboxylic acid[5]	0.1 at 120 °C	>100	11 - 23
ENR, Dithiol-bearing boronic ester[6]	Not reported	>150	0 - 20
BPA epoxy, adipic acid[7]	Not reported	>240	39
BPA epoxy, dicarboxylic and tricarboxylic fatty acids[8]	Not reported	>150	15
BPA epoxy, C18 fatty acids derivatives[9]	0.1 at 190 °C	200	30 - 37
BPA epoxy, fatty acids Pripol 1040[10]	0.18 at 180 °C	180	30

[a)] Time when the relaxation modulus (G) decreased to 1/e of the initial modulus (G_0).

Table S6. Effect of recyclate (GR or DR) content on the properties of epoxy vitrimer.

Samples	T_g [°C]	E' [MPa]	
		E_g [a)]	E_r [b)]
DER-NMA-0.1TEOA	134.9	2251	17
DER-NMA-0.1TEOA-10GR	132.3	2089	14
DER-NMA-0.1TEOA-20GR	132.0	1808	13
DER-NMA-0.1TEOA-30GR	129.7	1661	11
DER-NMA-0.1TEOA-10DR	129.7	2100	10
DER-NMA-0.1TEOA-20DR	125.6	2021	8
DER-NMA-0.1TEOA-30DR	124.3	2019	3

[a)] Storage modulus at 50 °C; [b)] Storage modulus at 170 °C.

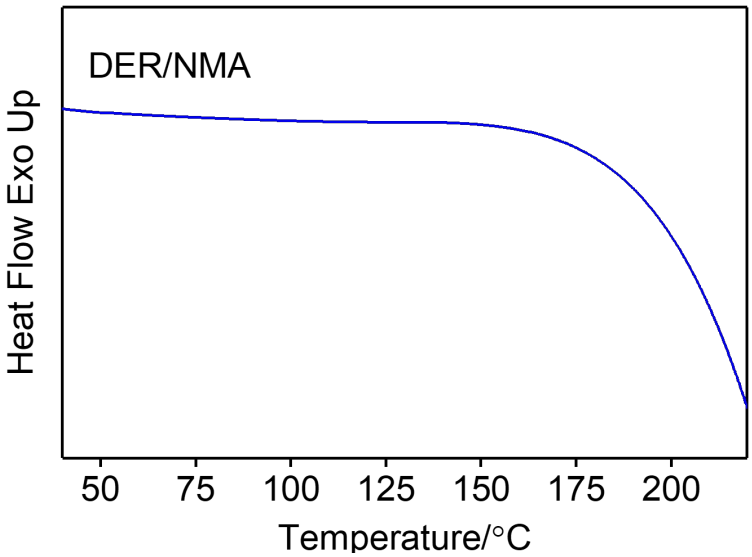


Figure S1. DSC non-isothermal thermogram of the mixture of DER and NMA without catalyst. The heating rate of 5 K min^{-1}. The drop of curve is due to the evaporation of NMA at high temperature.

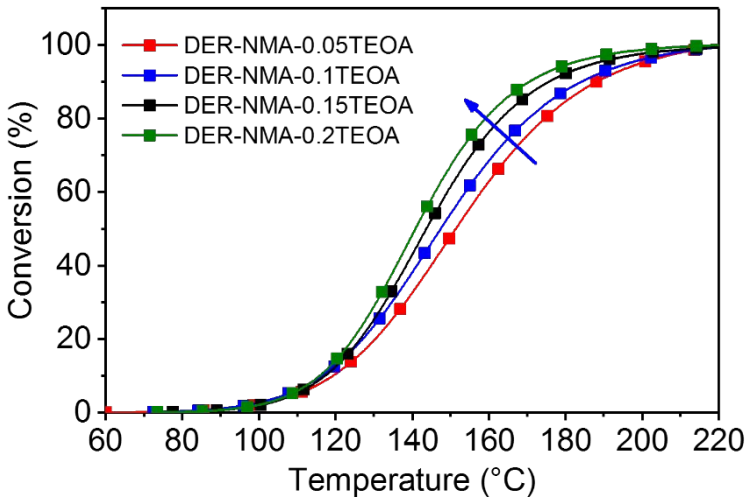


Figure S2. Effect of TEOA content on curing conversion of DER-NMA-TEOA during non-isothermal curing at a heating rate of 5 K min^{-1}.

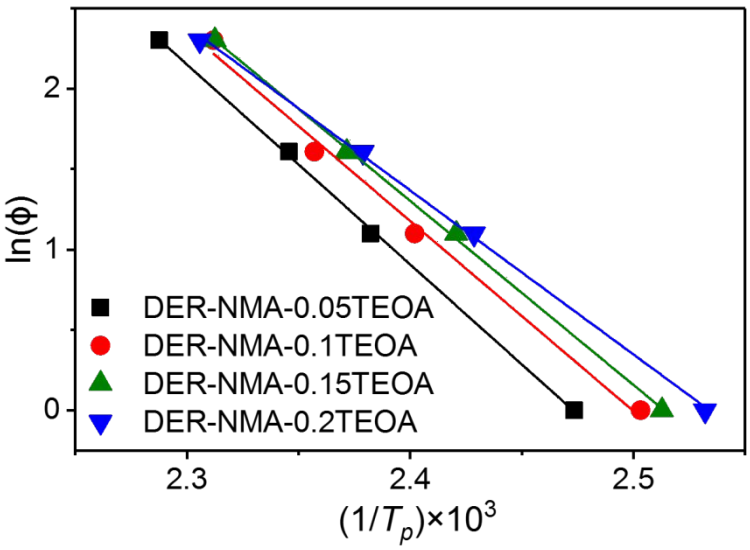


Figure S3. The plots of $1/(T_p)$ vs $\ln(\phi)$ of the DER-NMA-TEOAs, where ϕ is the heating rate, and T_p is the peak temperature at that heating rate. Data was collected at different heating rates (1, 3, 5, 10 K min^{-1}). Activation energy (E_a) can be calculated from the slope of each curve.

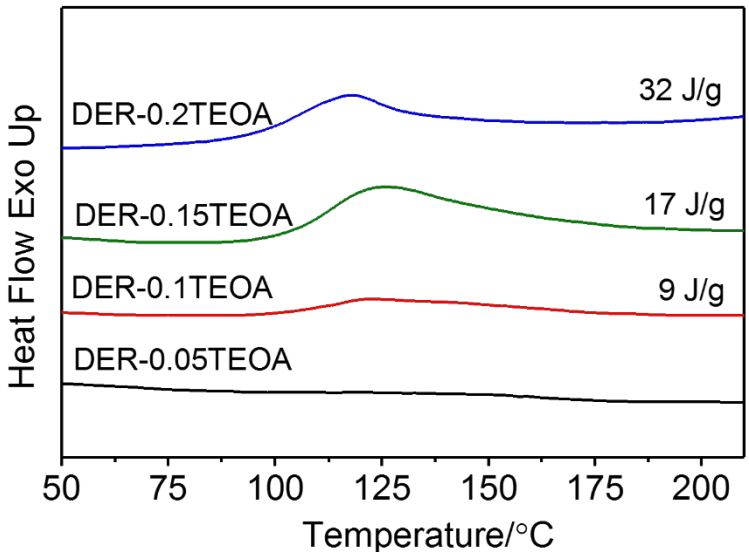


Figure S4. DSC non-isothermal thermograms of DER-TEOA curing systems with different contents of TEOA. Heating rate was 5 K min^{-1}.

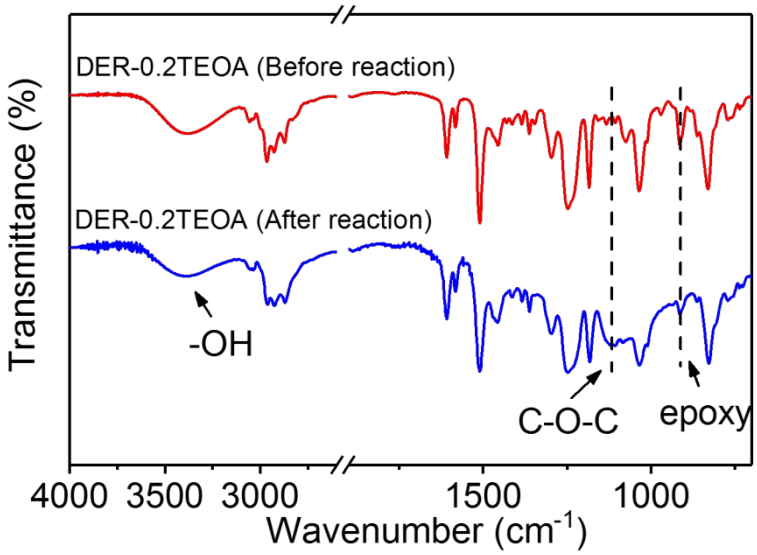


Figure S5. FTIR spectra of DER-0.2TEOA before and after reaction at 150 °C for 3 h.

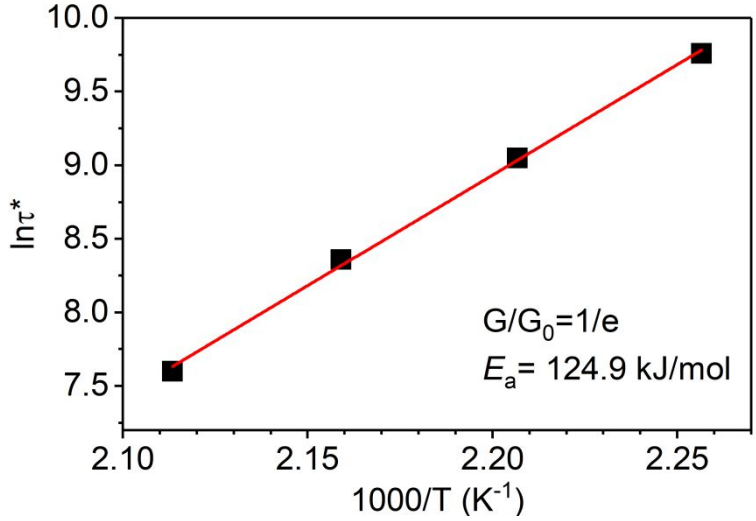


Figure S6. Fitting of relaxation time (τ*) to Arrhenius equation and the calculated activation energy of DER-NMA-0.1TEOA.

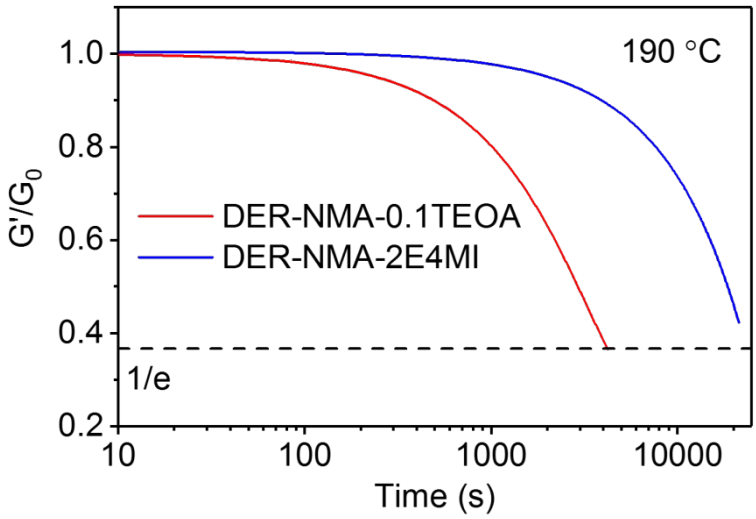


Figure S7. Stress relaxation curves of DER-NMA-0.1TEOA and DER-NMA-2E4MI at 190 °C.

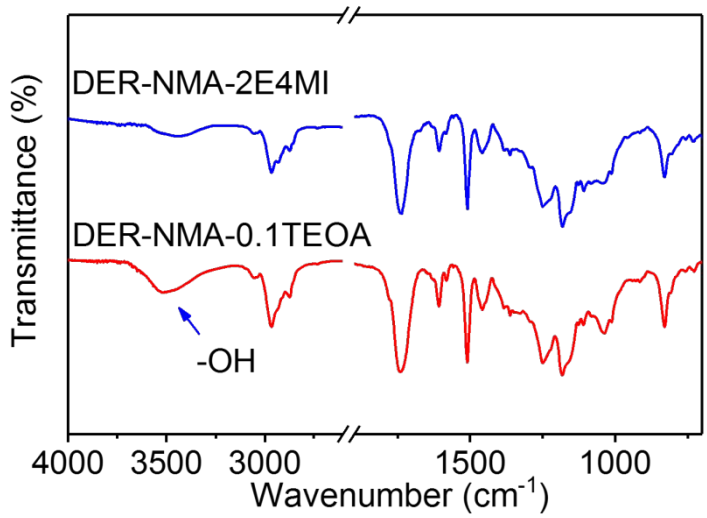


Figure S8. FTIR spectra of the cured DER-NMA-0.1TEOA and DER-NMA-2E4MI.

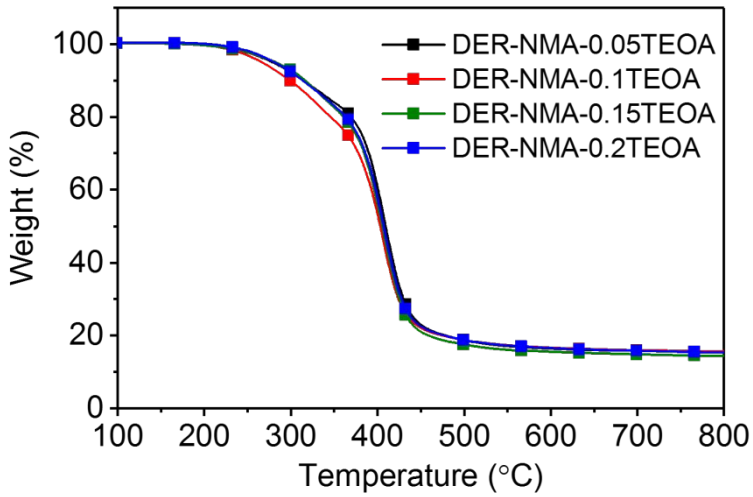


Figure S9. TGA curves of the cured DER-NMA-TEOA samples. TGA was performed under nitrogen atmosphere with a heating rate of 10 K min^{-1}.

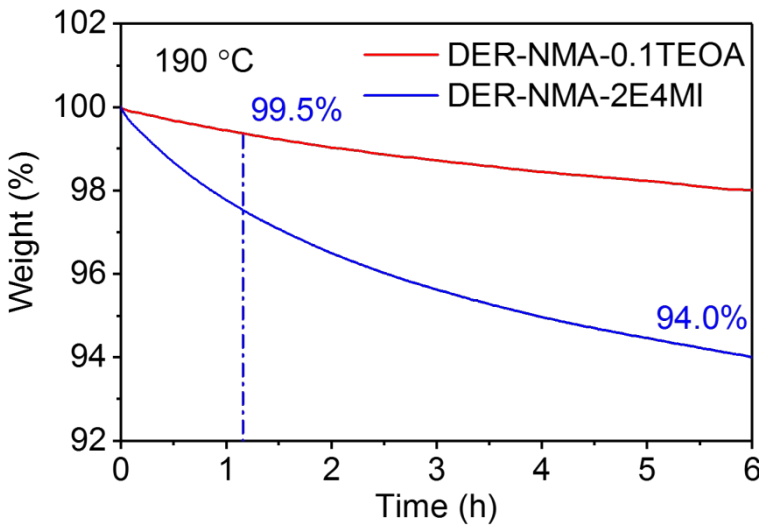


Figure S10. Weight loss of the cured DER-NMA-0.1TEOA and DER-NMA-2E4MI at 190 °C. Residue weight percent for each material at its relaxation time is labelled. Relaxation time for DER-NMA-0.1TEOA is ~1.17 h, and DER-NMA-2E4MI can't relax within ~6 h.

Figure S11. The sample setup for repairing test of the cured DER-NMA-TEOAs. Samples were placed between the two metal plates and held by clips, and the healing was conducted in a convection oven at 190 °C.

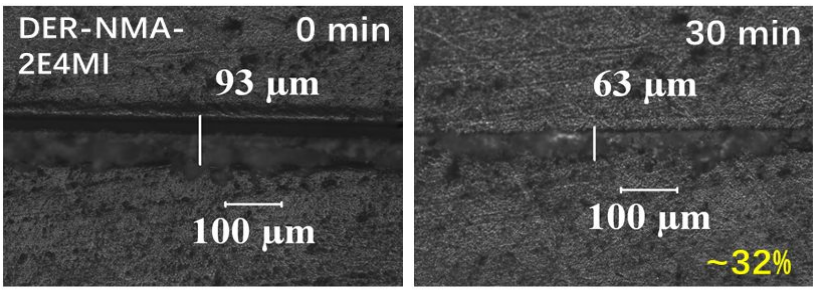
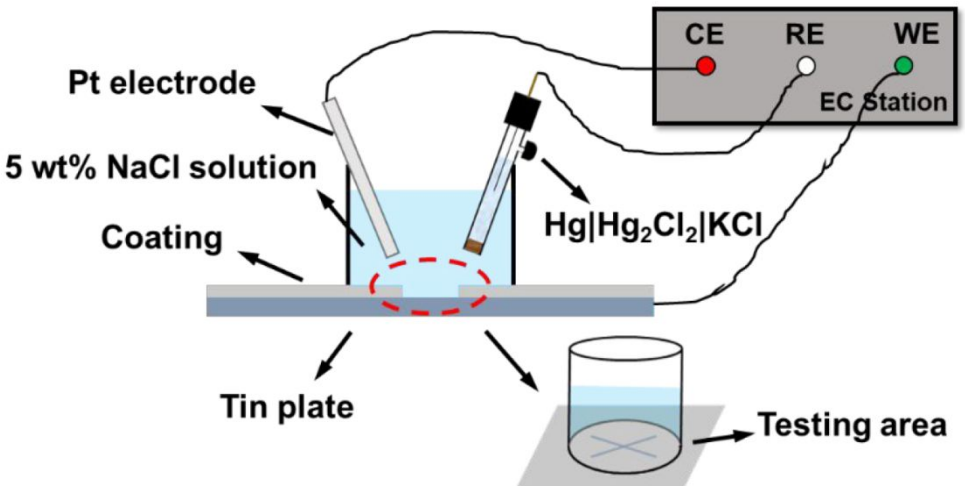


Figure S12. Images showing the self-healing of DER-NMA-2E4MI at 190 °C.



Figures S13. Schematic of electrochemical test device for corrosion resistance.

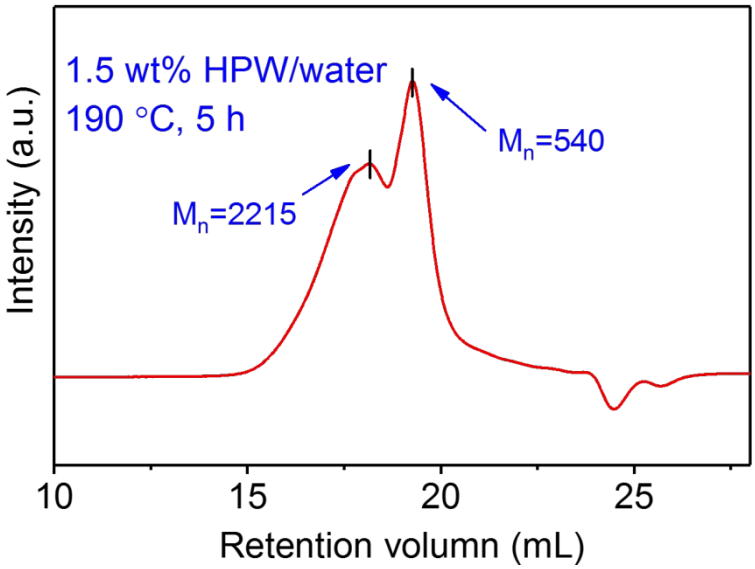


Figure S14. GPC curve of depolymerized DER-NMA-0.1TEOA sample (degradation conditions was performed in a 1.5 wt% HPW/water solution at 190 °C for 5 h).

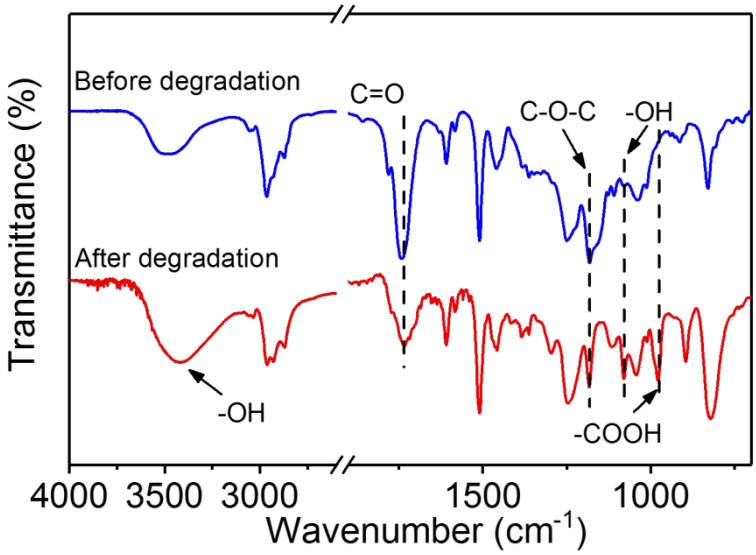


Figure S15. FTIR spectra of the DER-NMA-0.1TEOA sample before and after degradation. The degradation process was conducted in a 1.5 wt% HPW/water solution at 190 °C for 5 h.

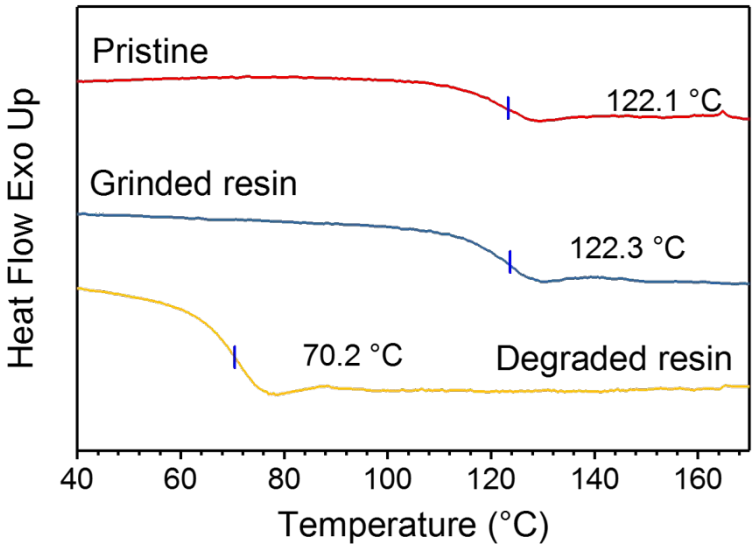


Figure S16. DSC curves of pristine, grinded resin and degraded resin. T_g's are labeled in figure.

Reference

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