Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Recyclable CFRP with Extremely High T_g: Hydrothermal Recyclability in Pure Water and Upcycling of the Recyclates in New Composite Preparation

Table S1. Summary of the recyclable CFRP based on dynamic covalent bonds.

Starting materials	Types of reversible bonds	T_g [°C]	Recycling conditions	Ref.
DGEBA, glutaric anhydride, ethylenediamine	Hydroxyl-ester	65.9	Water, 180 °C, 5 h	[1]
Epoxidized menthane diamine, adipic acid	Hydroxyl-ester	72.1 ~ 86.4	Ethanolamine, 60 °C, 30 min	[2]
Epoxidized soybean oil, camphoric acid	Hydroxyl-ester	40 ~ 48	Ethylene glycol, 190 °C, 20 h	[3]
DGEBA, hexahydro-4-methylphthalic anhydride	Hydroxyl-ester	157	0.30 M TBD-EG/NMP (10/90) solution, 170 °C, 1.5 h	[4]
Tung oil-based triglycidyl ester, menthane diamine	Hydroxyl-ester	60.5 ~ 82.6	Ethylene glycol, 90 °C, 1 h	[5]

Vanillin, 4-aminophenol, glycerol triglycidyl ether	Imine bonds	70	0.1 M ethylenediamine solution (in DMF), 50 °C, 2 h	6
Terephthaldehyde, tris (2-aminoethyl) amine, diethylenetriamine, ethylene diamine	Imine bonds	18 ~ 135	Diethylenetriamine, RT, 24 h	7
Vanillin, 4,4’-methylenebiscyclohexanamine	Imine bonds	172	0.1 M HCl in methanol /H_2O (8/2, v/v), RT, 15 h	8
DGEBA, 4-aminophenyl disulfide	Disulfide bonds	130	2-mercaptoethanol in DMF, RT, 24 h	9
DGEBA, bis(4-hydroxyphenyl) disulfide, 4-aminophenyl disulfide	Disulfide bonds	147	Dithiothreitol/DMF (0.1 mg/ml) solution, 90 °C, 1 h	10
Novolac resin, phenylboronic acid	Dynamic B-O bonds	135	Ethanol, acetone/water or ethanol/water mixtures, RT, 14 h	11
Cresol novolac resin, 4-vinlyoxybutyl glycidyl ether	Acetal linkages	110	0.1 M HCl in a THF/water (9/1, v/v), RT, 24 h	12
Vanillin, erythritol, DDS	Acetal linkages	184	0.1 M HCl in DMSO/H_2O (9/1, v/v), 50 °C, 6 h	13

Table S2. Summary of T_g and mechanical properties of different cured samples

Sample	T_g [°C]	Tensile strength [MPa]	Tensile modulus [GPa]	Elongation at break [%]	Impact strength [kJ m^{-2}]
TN-0.05TEOA	224.1	65.9 ± 5.3	1.70 ± 0.08	4.0 ± 0.4	9.2 ± 2.3
TN-0.1TEOA	203.5	75.0 ± 4.1	1.76 ± 0.08	6.0 ± 0.2	9.1 ± 1.1
TN-0.15TEOA	196.0	-		-	-
TN-2E4MI	276.9	79.4 ± 4.0	1.87 ± 0.10	2.6 ± 0.1	10.3 ± 2.0
DN-2E4MI	178.2	59.0 ± 4.6	1.32 ± 0.07	3.0 ± 0.3	7.2 ± 0.8

Table S3. Tensile properties of prepared CFRP with three layers of carbon fibric mat

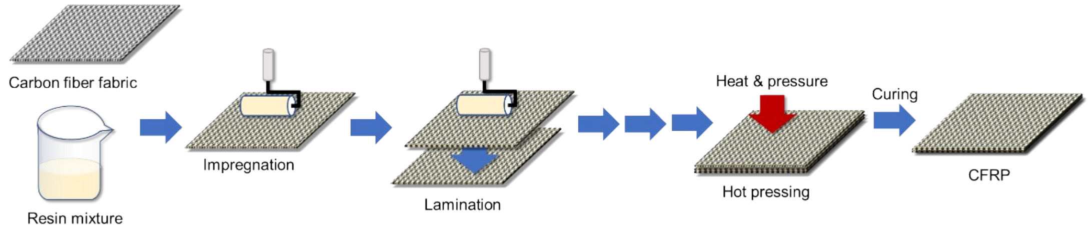
CFRP	Polymer matrix	Type of carbon fiber	Tensile strength [MPa]
TN-0.1TEOA-CF	TN-0.1TEOA	Virgin CF	502 ± 25
TN-2E4MI-CF	TN-2E4MI	Virgin CF	558 ± 67
DN-2E4MI-CF	DN-2E4MI	Virgin CF	421 ±28
DN-10rEP-CF	DN-10rEP	Virgin CF	384 ± 30
DN-20rEP-CF	DN-20rEP	Virgin CF	374 ± 13
DN-30rEP-CF	DN-30rEP	Virgin CF	383 ± 35
TN-0.1TEOA-CF	TN-0.1TEOA	Recycled CF	437 ± 37
DN-2E4MI-CF	DN-2E4MI	Recycled CF	394 ± 67
DN-20rEP-CF	DN-20rEP	Recycled CF	300 ± 27

Table S4. Formulations of new epoxy curing systems with rEP

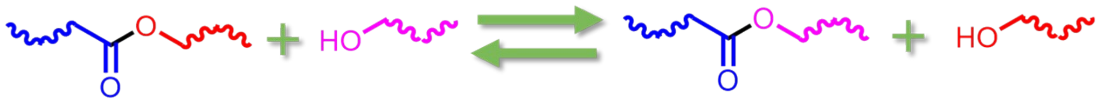
Samples	DER 331		rEP		NMA		2E4MI
	Epoxy [mmol]	Mass [g]	Epoxy [mmol]	Mass [g]	Anhydride [mmol]	Mass [g]	Mass [g]
DN-2E4MI	5.3	1	0	0	5.3	0.94	0.06
DN-10rEP	4.8	0.9	0. 2	0.1	5.0	0.89	0.06
DN-20rEP	4.2	0.8	0.4	0.2	4.6	0.81	0.05
DN-30rEP	3.7	0.7	0.6	0.3	4.3	0.77	0.05

Table S5. Summary of T_g and mechanical properties of cured epoxies resin with rEP

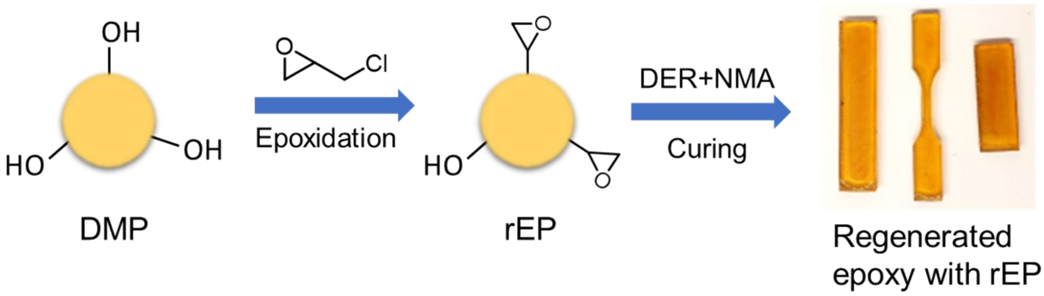
Sample	T_g [°C]	Tensile strength [MPa]	Elongation at break [%]	Impact strength [kJ m^{-2}]
DN-2E4MI	178.2	59.0 ± 4.6	3.0 ± 0.3	7.2 ± 0.8
DN-10rEP	160.0	47.6 ± 9.7	3.5 ± 0.7	14.6 ± 3.0
DN-20rEP	150.1	32.8 ± 5.3	2.2 ± 0.8	11.0 ± 2.2
DN-30rEP	137.3	30.3 ± 6.5	2.1 ± 0.4	5.9 ± 1.3



Scheme S1. Schematic illustration for the preparation of CFRP.



Scheme S2. Schematic illustration of dynamic transesterification reaction (DTR).



Scheme S3. Schematic illustration of chemical medication of DMP and preparation of new epoxy with rEP.

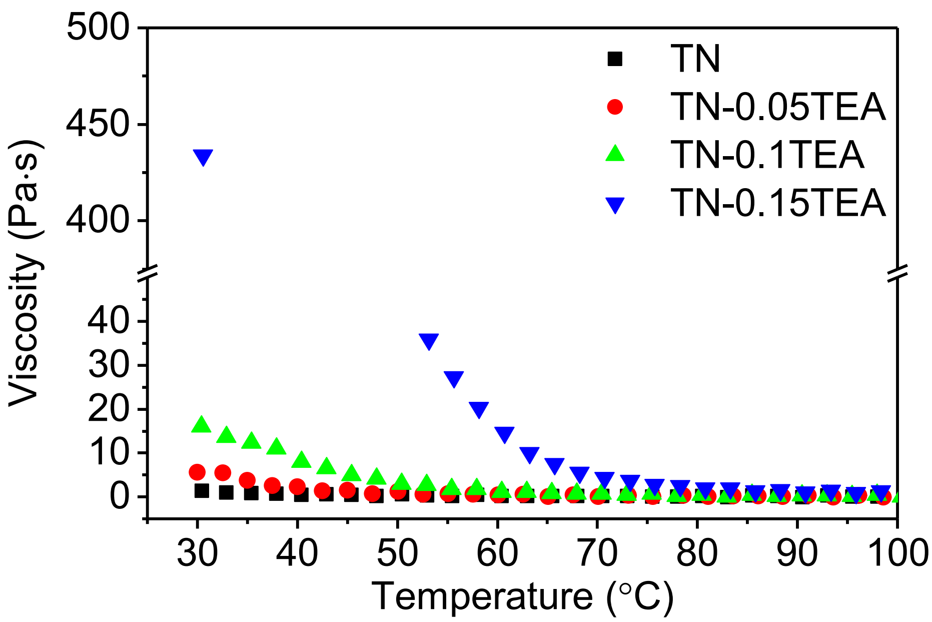


Figure S1. Viscosity of epoxy mixtures as the function of temperature.

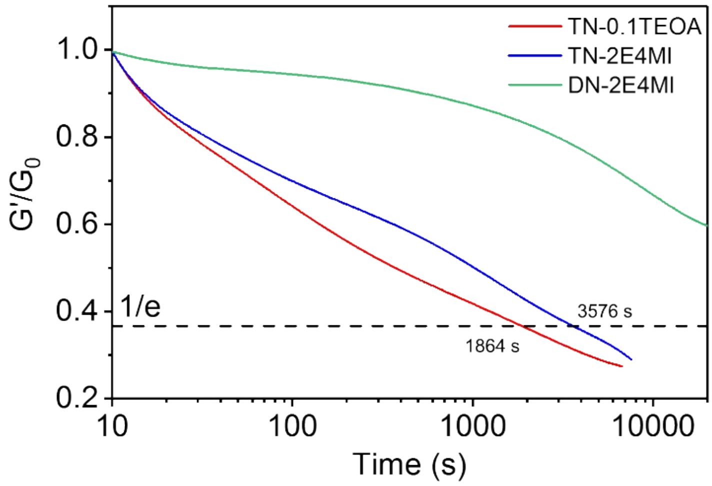


Figure S2. Stress relaxation behavior of TN-0.1TEOA, TN-2E4MI and DN-2E4MI at 200 °C.

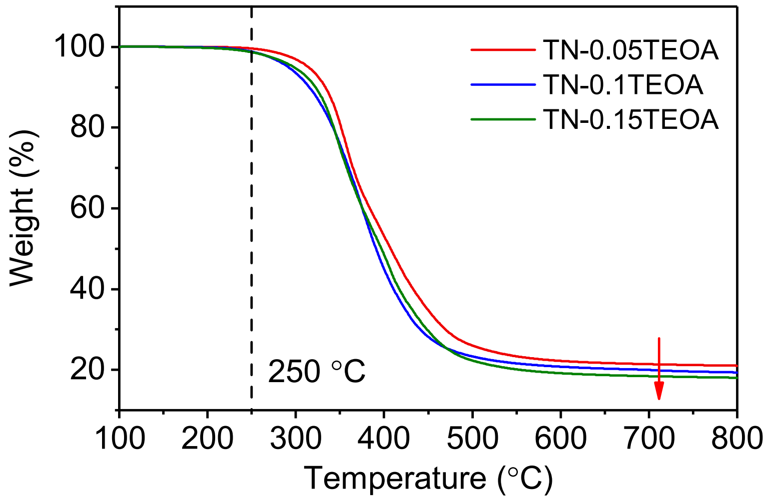


Figure S3. TGA curves of the cured TN-TEOA samples. TGA was performed under nitrogen atmosphere with a heating rate of 10 K min^{-1}.

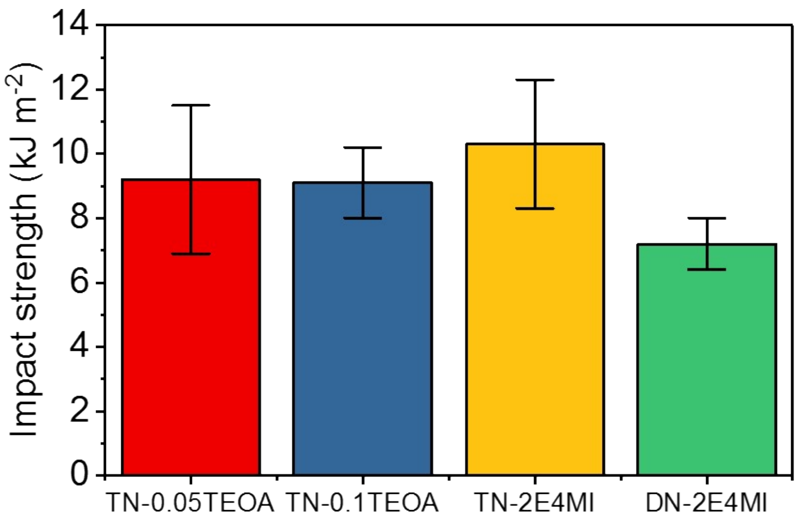


Figure S4. Impact strengths of TN−TEOAs, TN-2E4MI and DN-2E4MI.

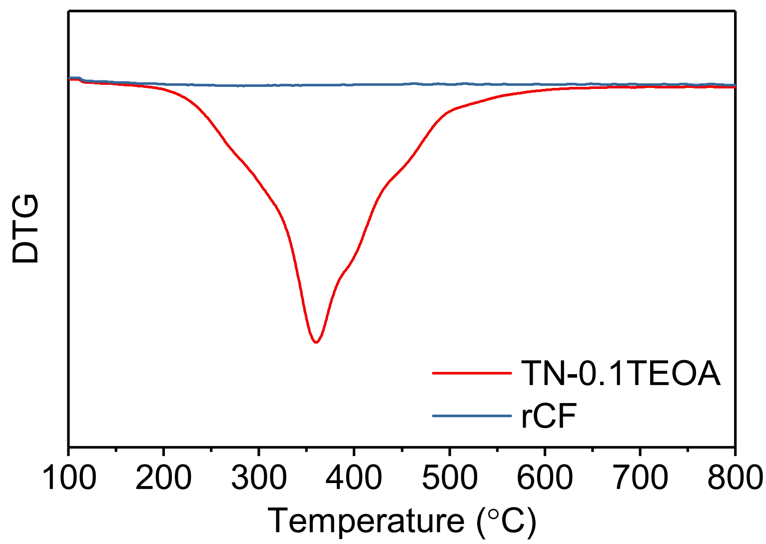


Figure S5. Thermogravimetric derivative (DTG) curves of the TN-0.1TEOA composite and rCF.

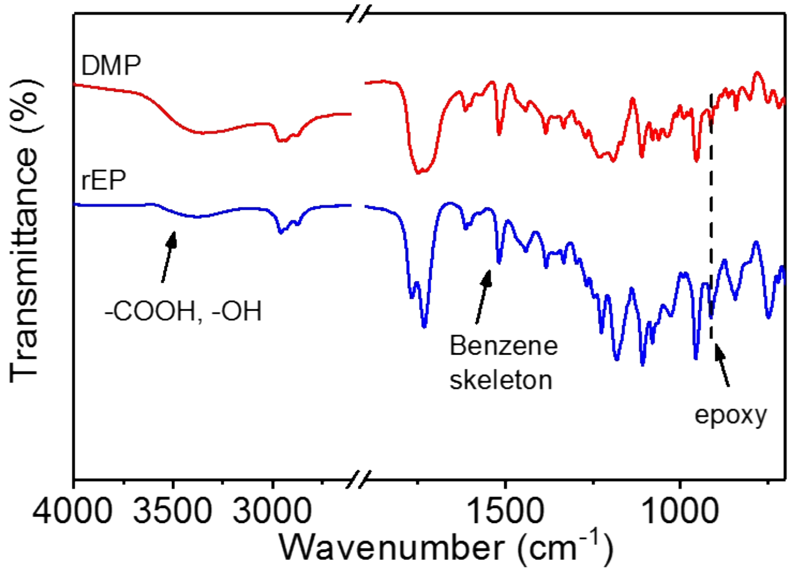


Figure S6. FTIR spectra of DMP and rEP.

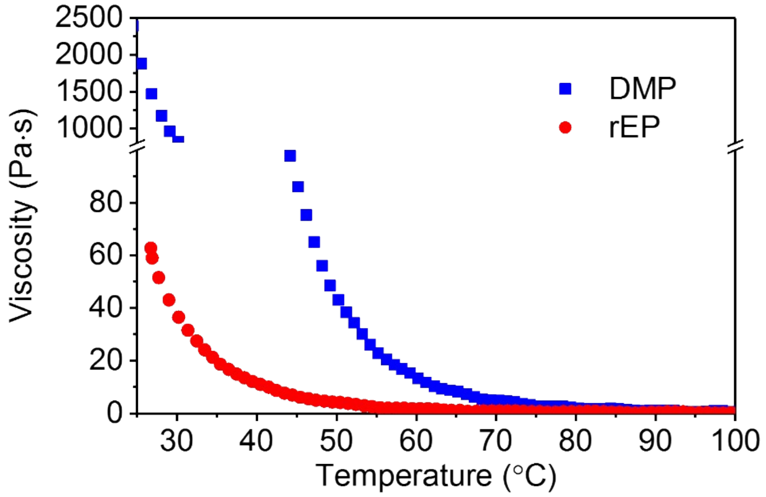


Figure S7. Apparent viscosity of DMP and rEP that was determined by rheometer.

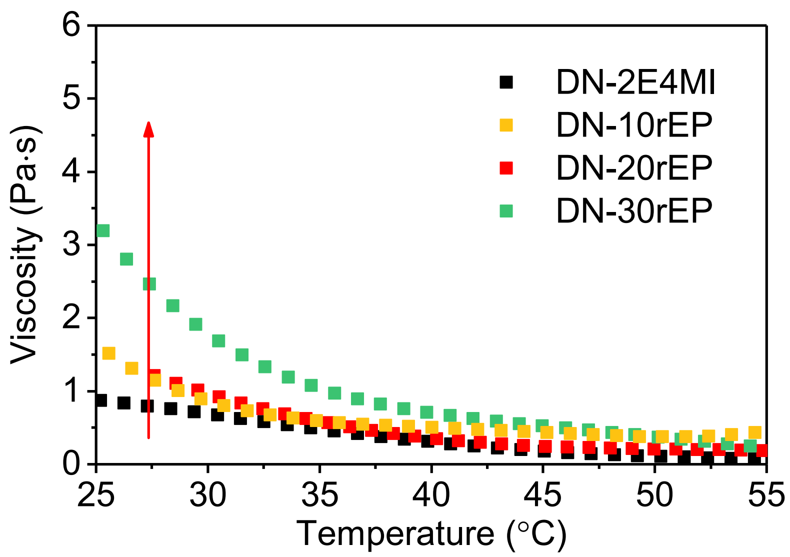


Figure S8. Apparent viscosity of epoxy resin mixture with rEP.

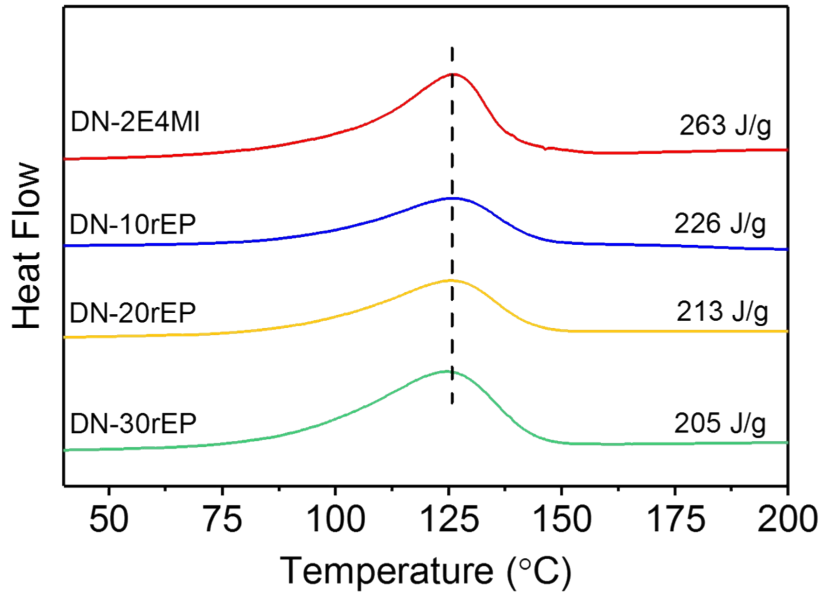


Figure S9. Exothermal curves of epoxy resin mixture with rEP as replacement for DER epoxy resin.

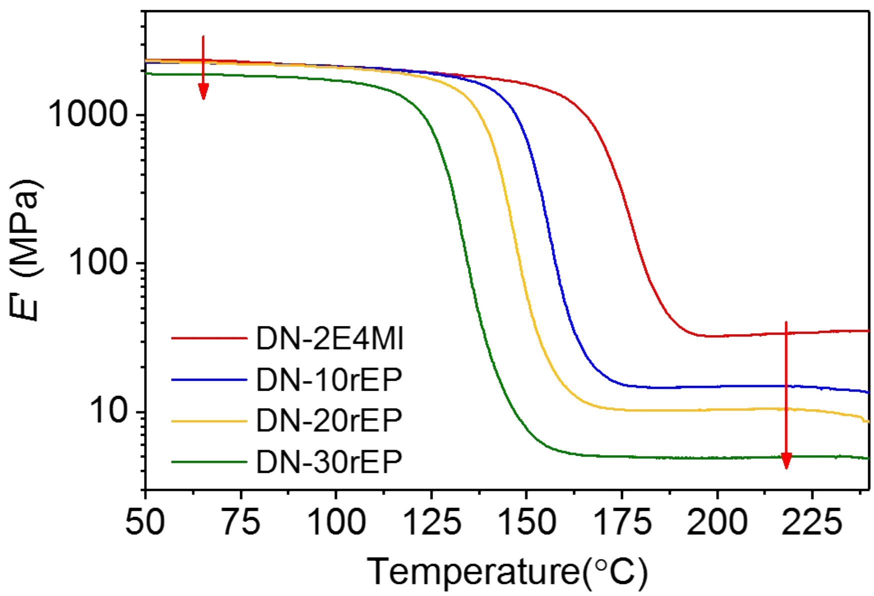


Figure S10. Storage modulus (E') of cured epoxies that use rEP to replace part of DER resin

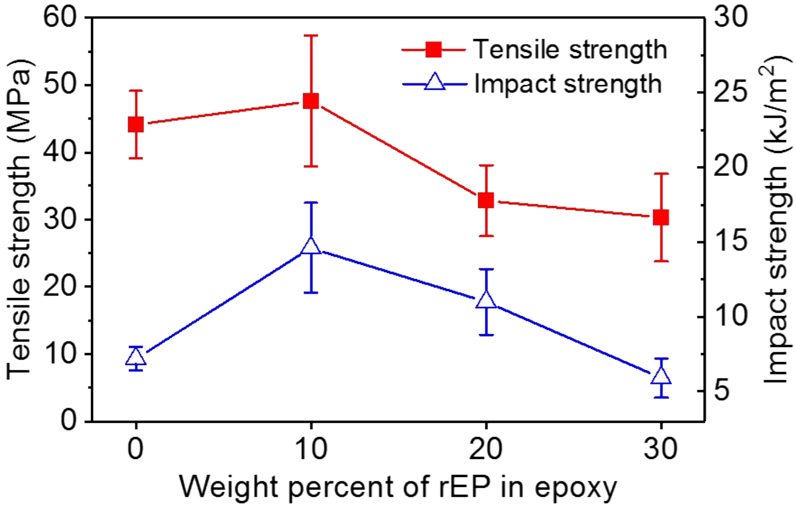


Figure S11. Tensile and impact strength of cured epoxies with different contents of rEP.

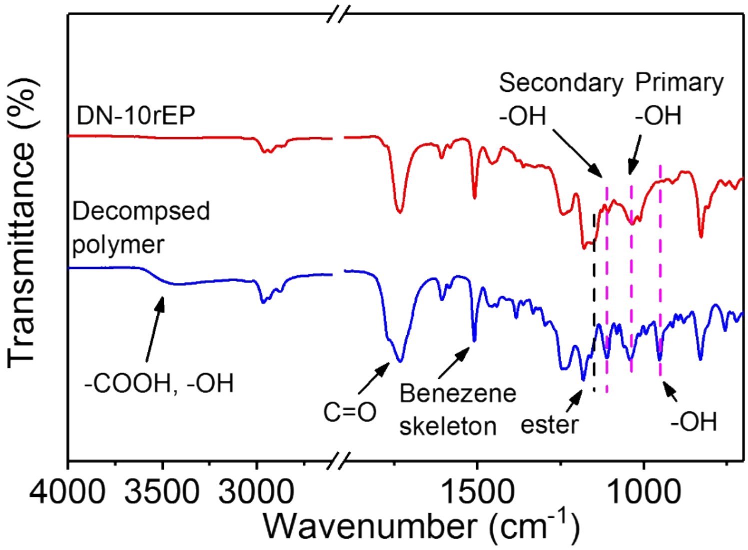


Figure S12. FTIR spectra of DN-20rEP before and after the degradation in pure water at 200 °C for 5 hours.

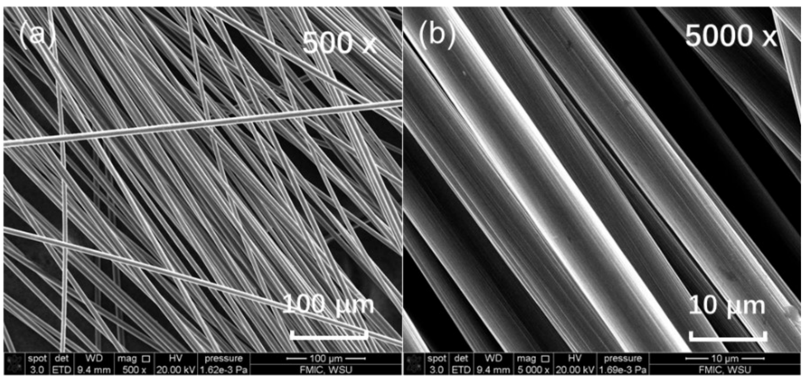


Figure S13. SEM images of recycled carbon fiber collected from DN-10rEP-rCF after the degradation in pure water at 200 °C for 5 hours.

Reference

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