Electronic Supplementary Material

Catalyst-free and recycle-reinforcing elastomer vitrimer with exchangeable links

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Figures and Tables

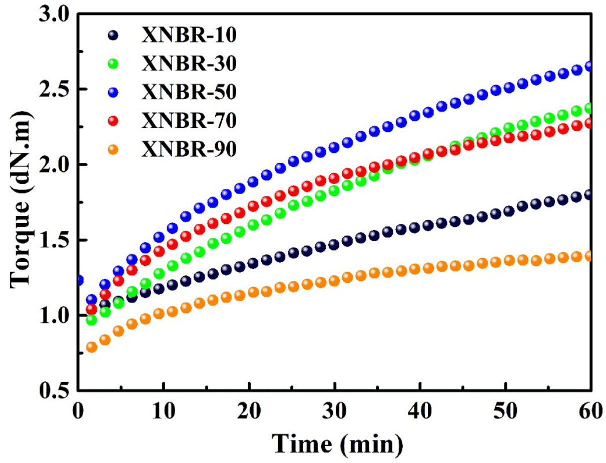

Figure S1. Curing profiles of XNBR-χ elastomers.

Table S1. Vulcanization properties of XNBR-χ elastomers

Samples	Tc_{50} (min:s)	Tc_{90} (min:s)	M_L (dN.m)	M_H (dN.m)	ΔM (dN.m)
XNBR-10	23:18	52:16	0.9	1.7	0.8
XNBR-30	22:02	50:06	0.8	2.4	1.6
XNBR-50	17:28	48:54	0.9	2.5	1.6
XNBR-70	15:39	47:13	0.7	2.1	1.4
XNBR-90	12:43	44:10	0.6	1.2	0.6

$^{*}\Delta M = M_H - M_L$

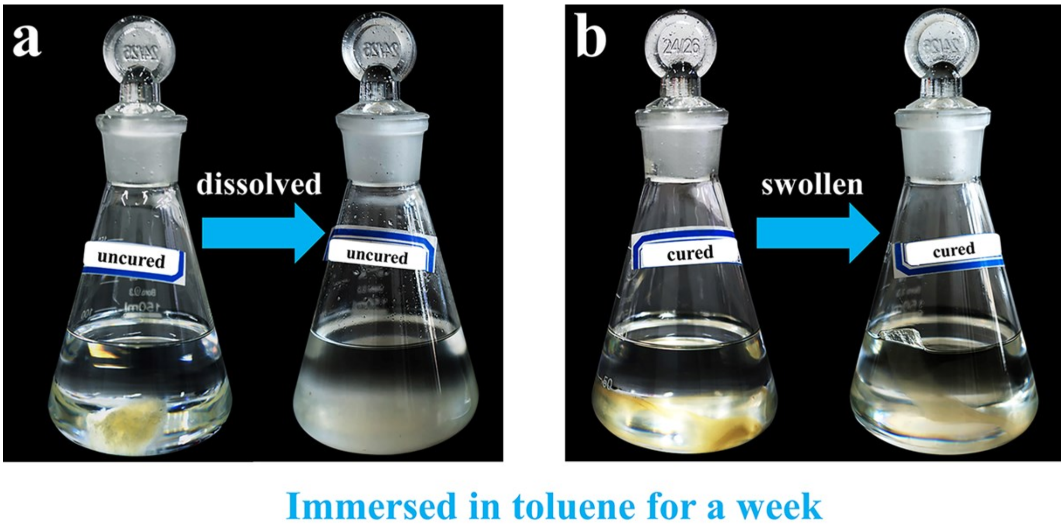

Figure S2. Photographs of XNBR-50 in dissolution/swell experiment. (a) Uncured XNBR-50. (b) Cured XNBR-50.

Table S2. Crosslinking densities and mechanical properties and of XNBR-χ elastomers

Samples	Crosslinking densities (10^{-4} mol/cm^3)	Young's modulus (MPa)	100% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
XNBR-10	1.3 ± 0.1	1.5 ± 0.2	0.6 ± 0.1	/	1.3 ± 0.1	253 ± 5
XNBR-30	1.6 ± 0.1	1.6 ± 0.1	0.7 ± 0.1	1.5 ± 0.2	2.0 ± 0.4	314 ± 50
XNBR-50	3.7 ± 0.1	2.1 ± 0.2	0.9 ± 0.1	2.4 ± 0.1	2.8 ± 0.3	342 ± 32
XNBR-70	3.1 ± 0.1	2.1 ± 0.3	0.9 ± 0.1	2.2 ± 0.2	3.6 ± 0.4	512 ± 65
XNBR-90	2.2 ± 0.1	1.8 ± 0.1	0.6 ± 0.1	1.0 ± 0.1	2.2 ± 0.1	901 ± 55

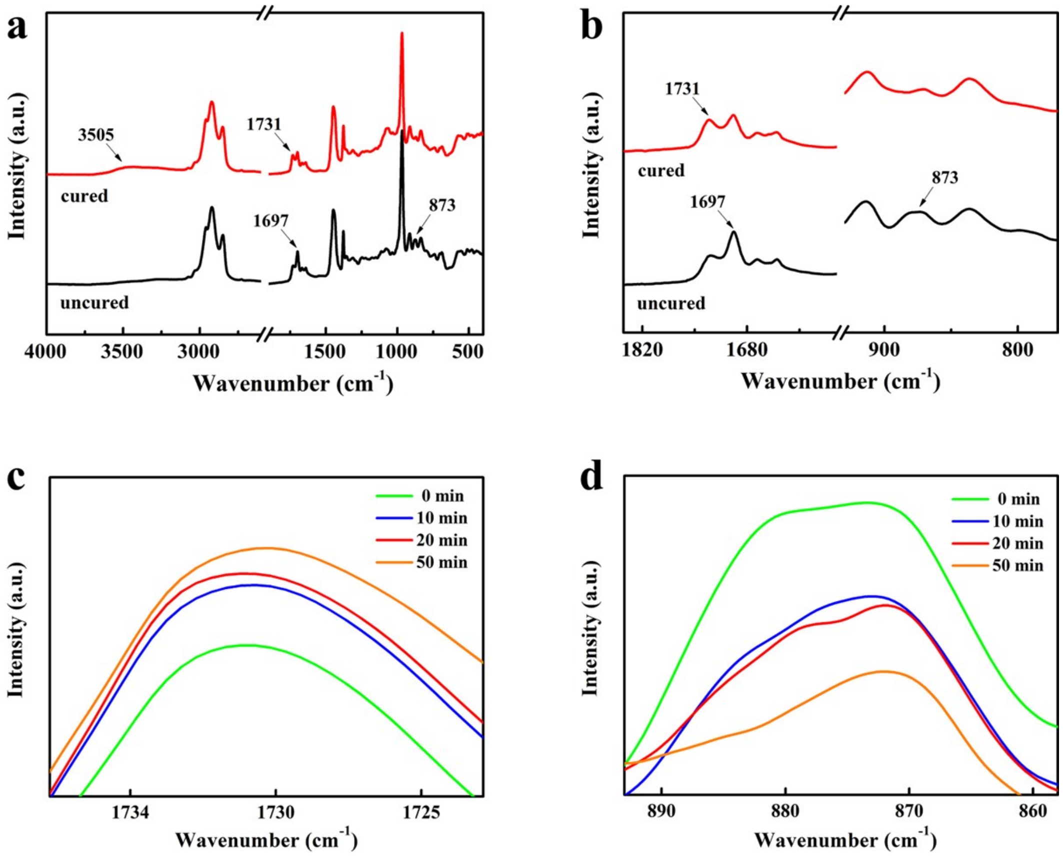

Figure S3. (a) FTIR spectra of uncured and cured XNBR-50. (b) Comparison of epoxy (960~700 cm^{-1}), carbonyl and carboxyl groups (1800~1550 cm^{-1}) of uncured and cured XNBR-50 in the FTIR spectra. (c) Evolution of ester groups, (d) epoxy groups of FTIR spectra during the curing of XNBR-50 at 160 °C.

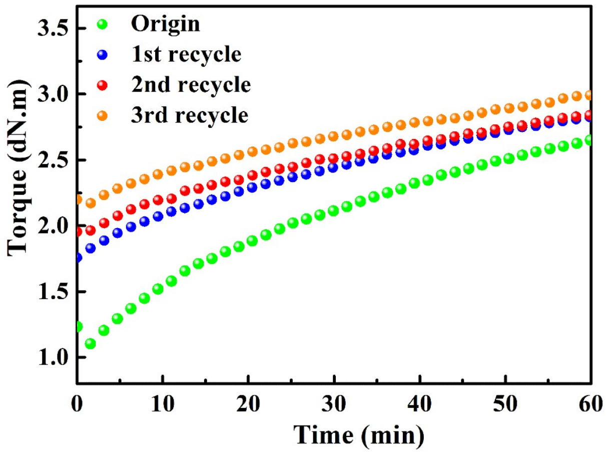

Figure S4. Curing curves of the original and recycled XNBR-50s.

Table S3. Vulcanization properties and crosslinking densities of the original and recycled XNBR-50s.

Samples	Tc_{50} (min:s)	Tc_{90} (min:s)	M_L (dN.m)	M_H (dN.m)	Crosslinking densities (10^{-4} mol/cm^3)
Origin	17:54	49:00	0.8	2.5	3.7 ± 0.1
1st recycle	19:19	49:44	1.5	2.7	3.5 ± 0.1
2nd recycle	18:39	49:59	1.7	2.7	3.3 ± 0.1
3rd recycle	18:10	50:44	1.9	2.8	3.3 ± 0.1

Table S4. Mechanical properties of the original and recycled XNBR-50s.

Samples	Tensile strength (MPa)	Young's modulus (MPa)	100% Modulus (MPa)	300% Modulus (MPa)	Breaking Elongation (%)	Shore A hardness (kN·m^{-1})
Origin	2.8 ± 0.3	2.1 ± 0.2	0.9 ± 0.1	2.4 ± 0.1	342 ± 32	38
1st recycle	5.1 ± 0.4	2.4 ± 0.1	0.7 ± 0.1	1.4 ± 0.1	835 ± 29	40
2nd recycle	5.5 ± 0.1	2.3 ± 0.1	0.6 ± 0.1	1.1 ± 0.1	823 ± 42	41
3rd recycle	6.4 ± 0.5	2.1 ± 0.2	0.5 ± 0.1	1.0 ± 0.1	740 ± 23	42

Table S5. Comparison of mechanical properties of vitrimers during recycling.

Samples	Recycling	Tensile strength (MPa)	Elongation at break (%)	Retention ratio of Tensile strength (%)	Retention ratio of Breaking Elongation (%)
XNBR-50 (our work)	Origin	2.8 ± 0.3	342 ± 32	/	/
	1st Recycle	5.1 ± 0.4	835 ± 29	≈ 182	≈ 244
	2nd Recycle	5.5 ± 0.1	823 ± 42	≈ 196	≈ 241
	3rd Recycle	6.4 ± 0.5	740 ± 23	≈ 229	≈ 216
4,4’-disulfanediyldianiline-Epoxy Resin [1]	Origin	11.0 ± 2.2	0.6 ± 0.2	/	/
	1st Recycle	9.1 ± 1.1	0.5 ± 0.1	≈ 83	≈ 83
	2nd Recycle	6.3 ± 0.8	0.3 ± 0.1	≈ 57	≈ 50
	3rd Recycle	2.8 ± 0.3	0.2 ±0.1	≈ 25	≈ 33
Poly(oxime−ester) Vitrimer-b [2]	Origin	2.2 ± 0.3	160 ± 22	/	/
	1st Recycle	2.1 ± 0.2	156 ± 19	≈ 95	≈ 98
	2nd Recycle	2.2 ± 0.3	148 ± 31	≈ 100	≈ 93
	3rd Recycle	2.0 ± 0.3	149 ± 29	≈ 91	≈ 93
Sulfur vulcanized Polybutadiene Rubber/$CuCl_2$/fillers system [3]	Origin	≈ 3.3	≈ 381	/	/
	1st Recycle	≈ 2.7	≈ 289	≈ 82	≈ 76
	2nd Recycle	≈ 1.8	≈ 248	≈ 55	≈ 65
	3rd Recycle	≈ 1.4	≈ 155	≈ 42	≈ 41

ENR/Bentonite Composites [4]	Origin	4.5 ± 1.3	400 ± 20	/	/
	1st Recycle	≈ 4.3	≈ 364	≈ 96	≈ 91
	2nd Recycle	≈ 4.1	≈ 333	≈ 91	≈ 83
	3rd Recycle	≈ 3.3	≈ 253	≈ 73	≈ 63
The acetal dynamic networks PC-5% OH [5]	Origin	28.8 ±1.9	4.4 ± 0.7	/	/
	1st Recycle	29.2 ± 2.7	5.0 ± 0.9	≈ 101	≈ 114
	2nd Recycle	27.2 ± 1.6	3.4 ± 0.3	≈ 94	≈ 77
ENR/TEMPO oxidized cellulose nanocrystals [6]	Origin	≈ 5.8	≈ 784	/	/
	1st Recycle	≈ 4.8	≈ 707	≈ 83	≈ 90
	2nd Recycle	≈ 3.9	≈ 690	≈ 67	≈ 88
Sulfur vulcanized chloroprene rubber [7]	Origin	≈ 9.1	≈ 634	/	/
	1st Recycle	≈ 8.5	≈ 557	≈ 93	≈ 88
	2nd Recycle	≈ 7.8	≈ 549	≈ 86	≈ 87
Polyhydroxyurethane Vitrimer [8]	Origin	72.1 ± 11.1	6.9 ± 3.8	/	/
	1st Recycle	53.1 ± 8.1	4.8 ± 0.8	≈ 74	≈ 70
ENR/Dithiodibutyric acid [9]	Origin	12 ± 2	5.3 ± 0.2	/	/
	1st Recycle	5 ± 1	4.2 ± 0.2	≈ 42	≈ 79
ENR/ modified carbon black [10]	Origin	15.7 ± 1.2	338 ± 13	/	/
	1st Recycle	≈ 13.1	≈ 399	≈ 83	≈ 118

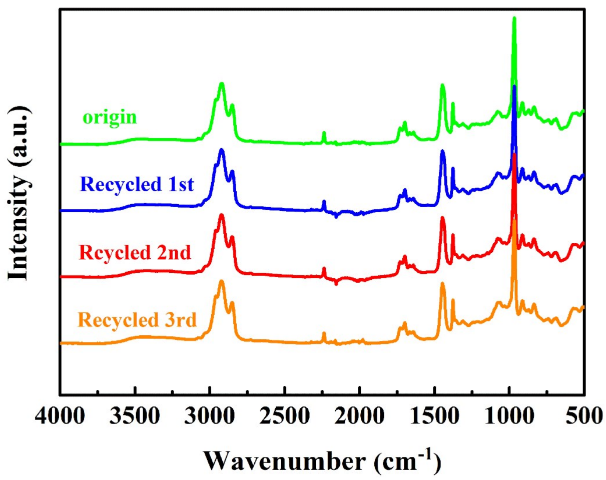

Figure S5. Comparison of FTIR spectra of the original and recycled XNBR-50s.

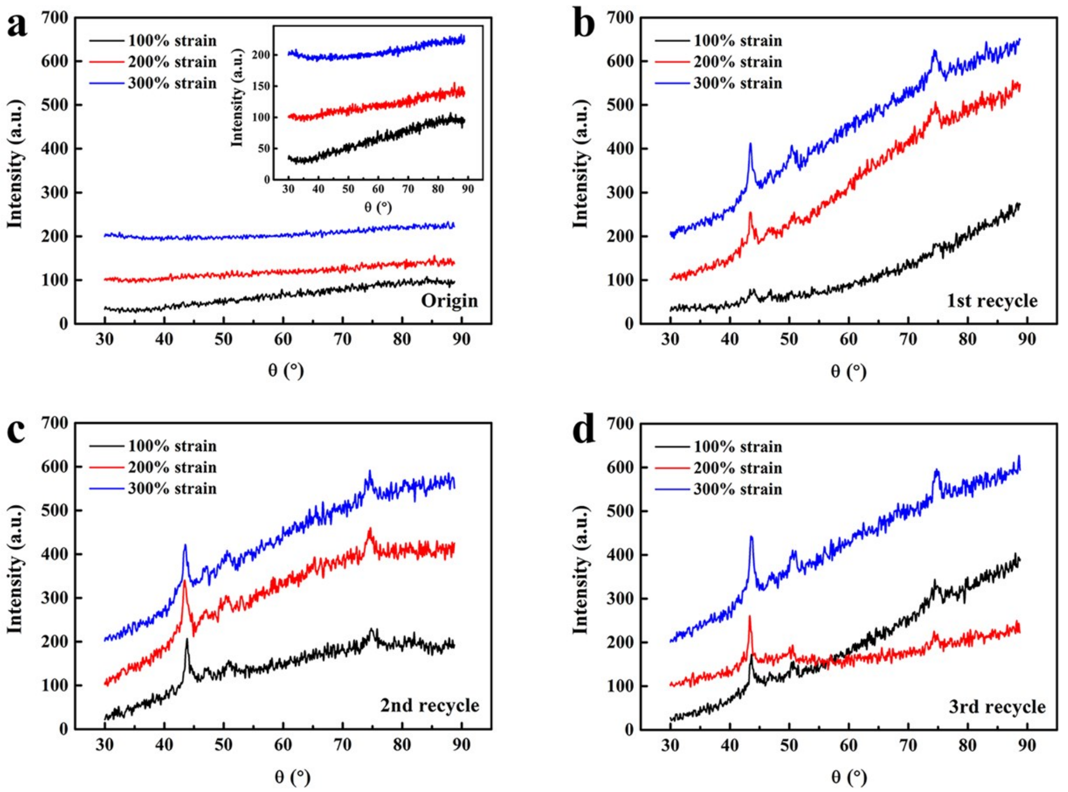

Figure S6. XRD curves of XNBR-50s at 100%, 200% and 300% strain. (a) Original sample. (b) First recycled sample. (c) Second recycled sample. (d) Third recycled sample.

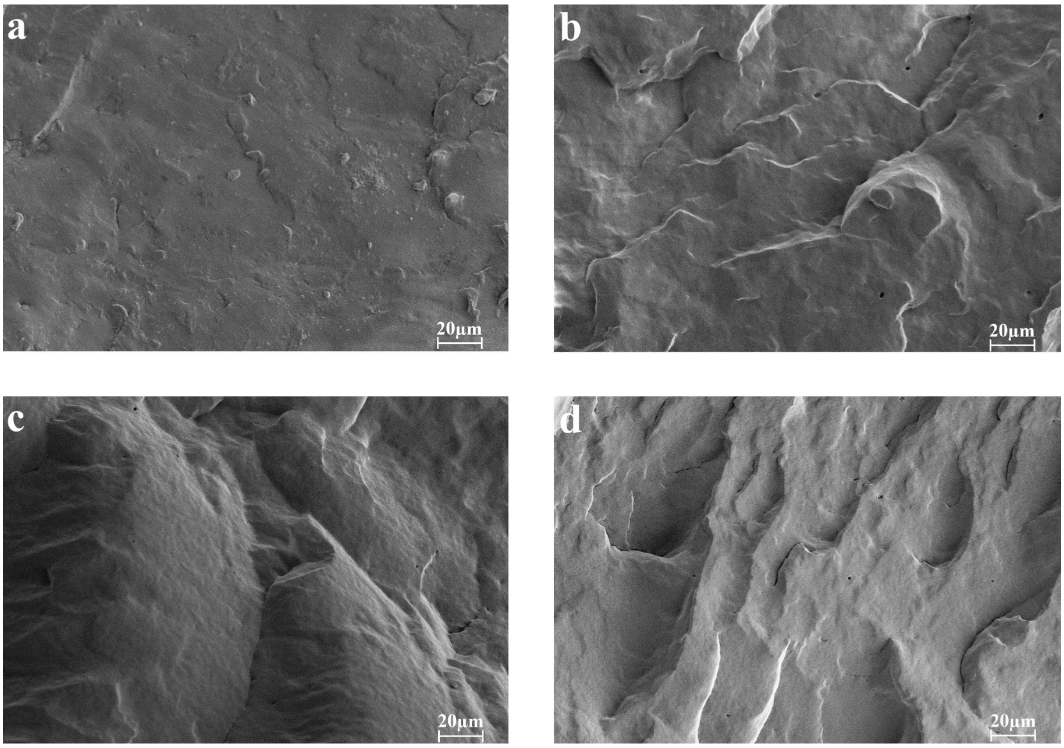

Figure S7. SEM images of XNBR-50s. (a) Original sample. (b) First recycled sample. (c) Second recycled sample. (d) Third recycled sample.

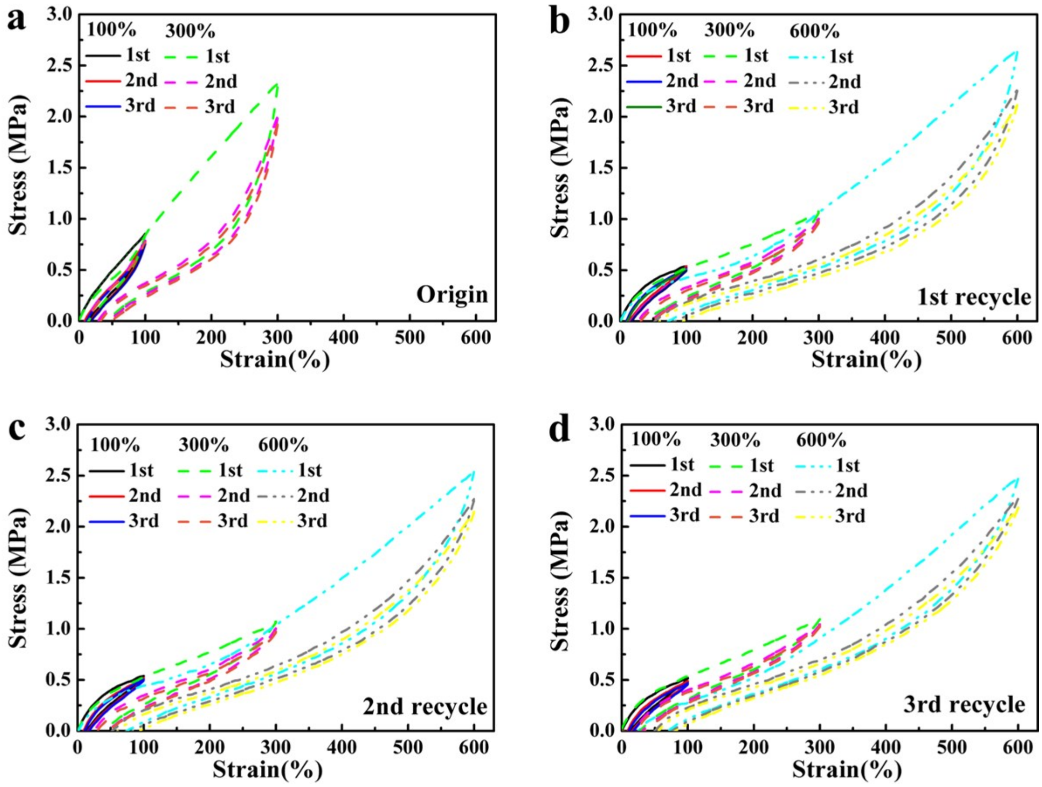

Figure S8. Cyclic loading-unloading curves of XNBR-50s at 100%, 300% and 600% strain. (a) Original sample. (b) First recycled sample. (c) Second recycled sample. (d) Third recycled sample.

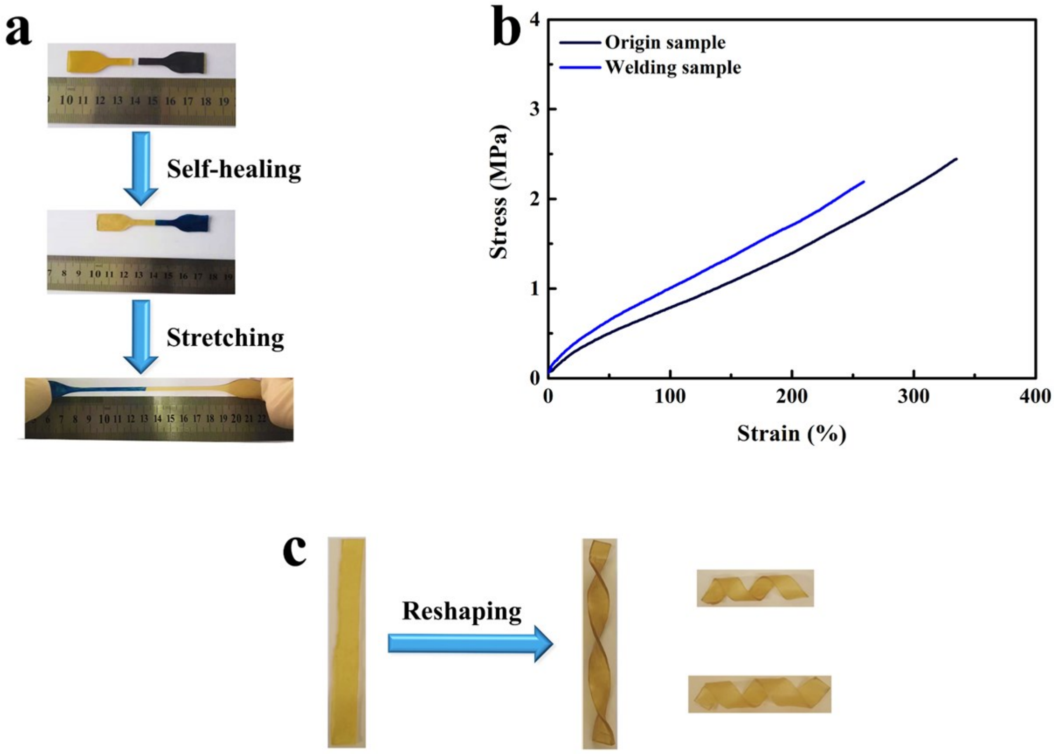

Figure S9. (a) Self-healing process of XNBR-50. (b) Stress-strain curves of original sample and the welding sample of XNBR-50. (c) Reshaping plots of XNBR-50.

References

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