Supplementary Information for

Robust and stretchable cross-linked rubber network with recyclable and self-healable capabilities based on dynamic covalent bonds

Liming Cao, Jianfeng Fan, Jiarong Huang, Yukun Chen*

Lab of Advanced Elastomer, School of Mechanical and Automobile Engineering, South Chain University of Technology, Guangzhou 510640, China. Email: cyk@scut.edu.cn

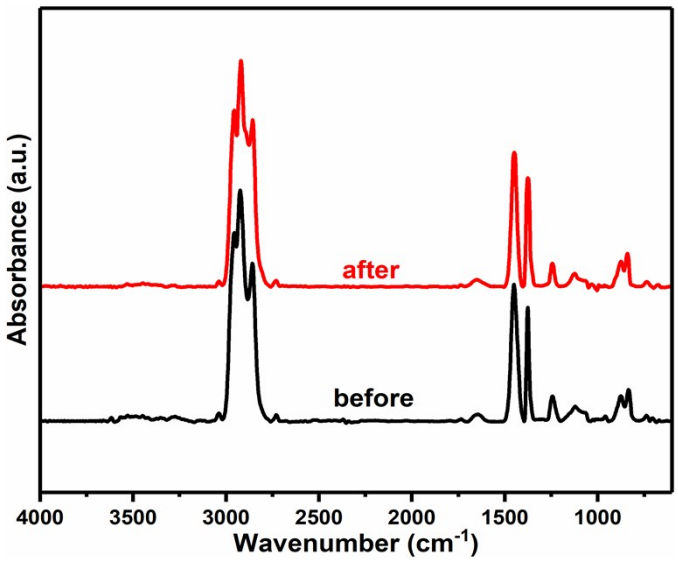

Fig. S1. FTIR spectra of neat ENR before and after compression molding at 180 ℃.

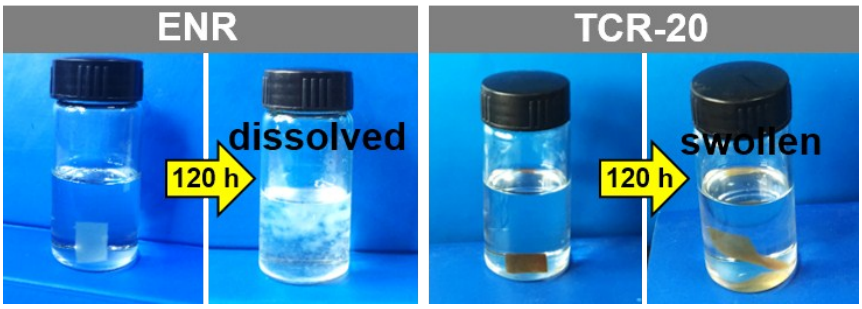

Fig. S2. Photos of equilibrium swelling experiments for neat ENR and TCR-30 sample.

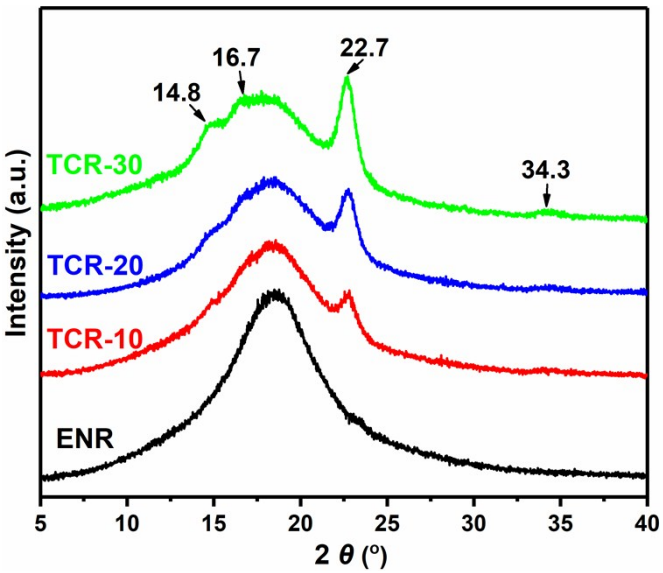

Fig. S3. XRD patterns of TCR samples with different TOCNs content.

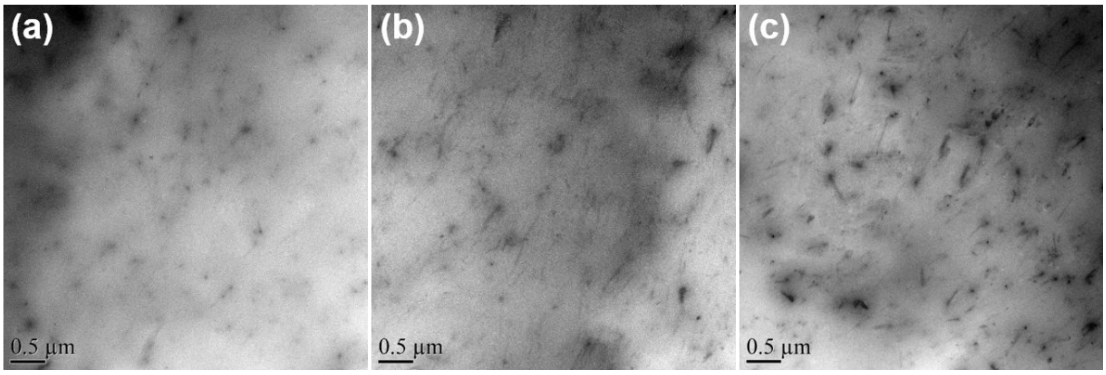

Fig. S4. TEM images of the TCR samples: (a) TCR-10; (b) TCR-20 and (c) TCR-30.

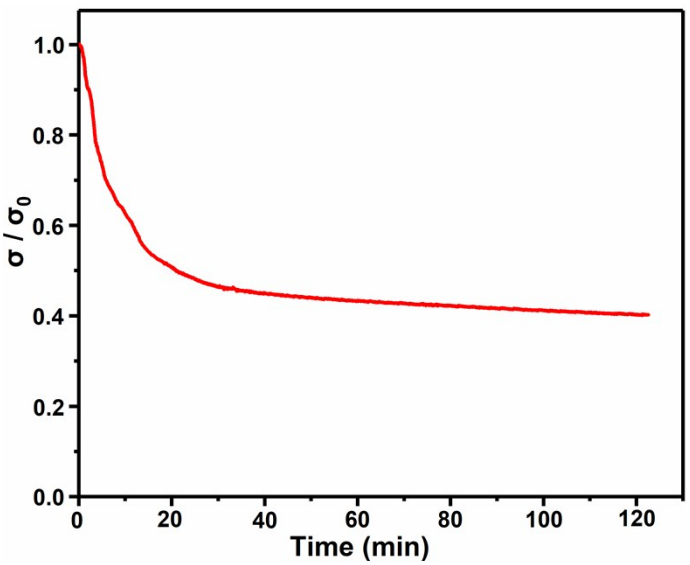

Fig. S5. Stress relaxation behavior of ENR/t-CNs-20 at 180 ℃.

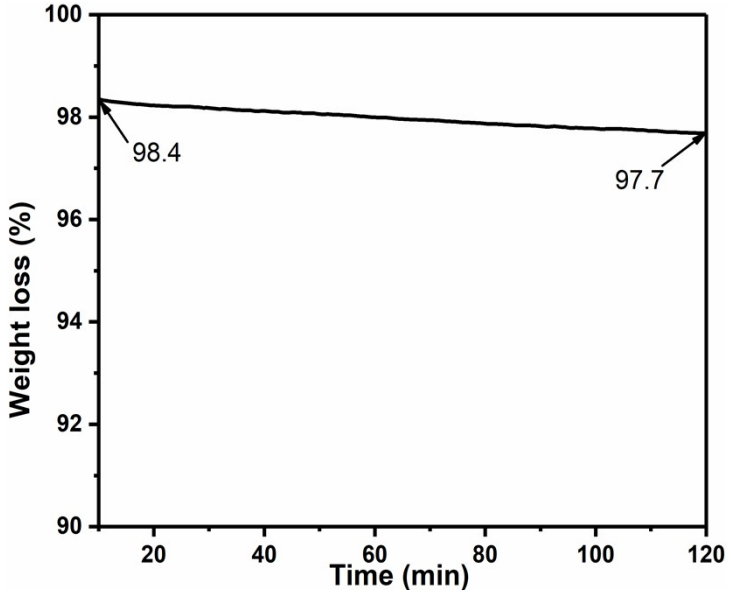

Fig. S6. Isothermal TGA curve of TCR-20 sample under air atmosphere at 180 ℃ for 2 h. The weight loss before 180 ℃ was due to the evaporation of the absorbed water.

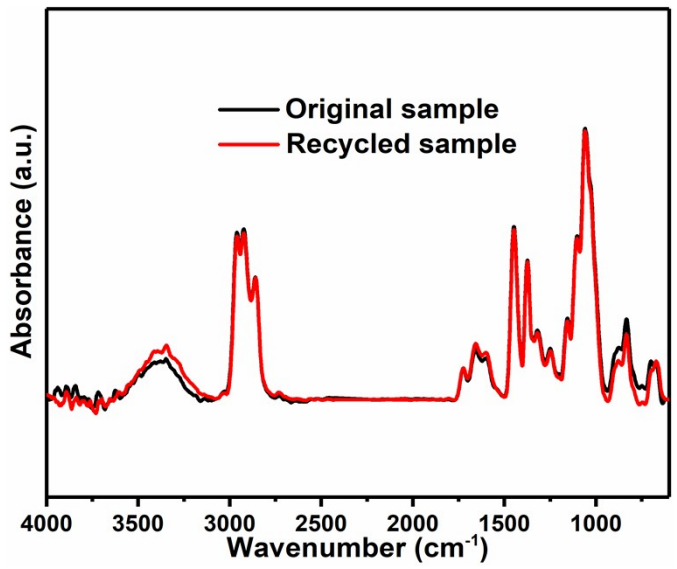

Fig. S7. FTIR spectra of TCR-20 before and after reprocessing.

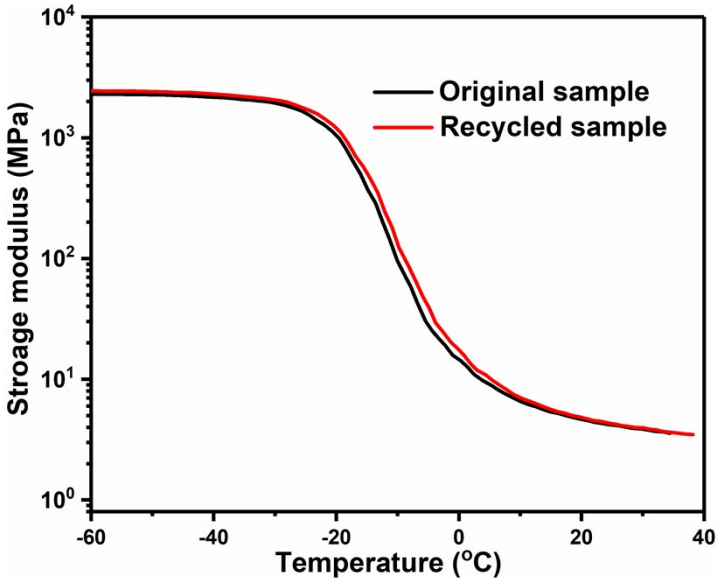

Fig. S8. Temperature dependence of *E'* of TCR-20 sample before and after reprocessing.

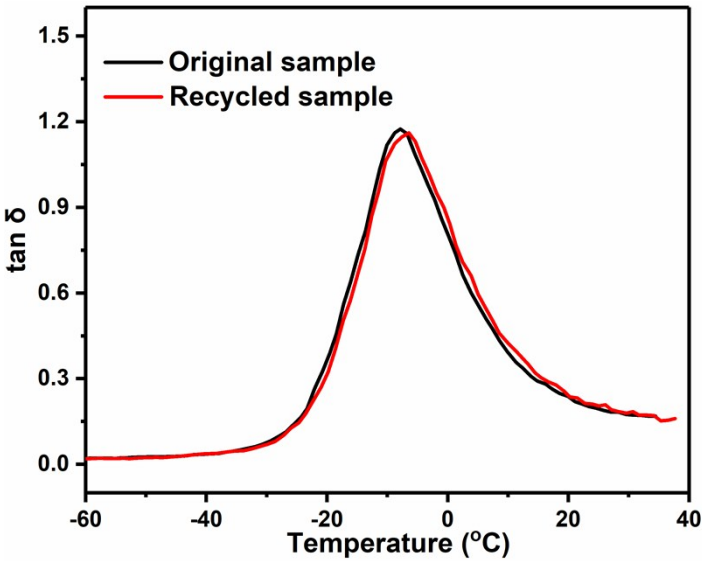

Fig. S9. Tan δ-temperature curves of TCR-20 sample before and after reprocessing.

Fig. S10. Resistance change before and after self-healing of electric device taking TCR-20 sample as substrate.

Table S1. *E'* of neat ENR and TCR samples at glassy (-50 ℃) and rubbery (20 ℃) state.

Samples	*E'* (-50 ℃, MPa)	*E'* (20 ℃, MPa)
ENR	1800	1.6
TCR-10	2084	2.8
TCR-20	2076	4.7
TCR-30	2596	7.5

Table S2. Mechanical properties of ENR/TOCNs composites.

Samples	Tensile strength (MPa)	Strain at break (%)	100% modulus (MPa)	300% modulus (MPa)	500% modulus (MPa)
ENR	0.88	370	0.45	0.60	--
TCR-10	3. 64	815	0.58	1.04	1.55
TCR-15	5.19	791	0.71	1.42	2.29
TCR-20	5.76	764	0.84	1.64	2.64
TCR-25	6.58	648	0.92	2.17	4.25
TCR-30	7.26	596	1.19	2.84	5.47

Table S3. Comparison of mechanical properties between the reported elastomeric vitrimers and TCR samples prepared in this work.

Material system	Exchange bond	Tensile strength (MPa)	Strain at break (%)	Ref.
Polybutadiene rubber and liquid polysulfide polymers	disulfide	~1.5	~155	1
ENR and dithiodibutyric acid	disulfide	12 ± 2	530 ± 20	2
Polybutadiene rubber	disulfide	~3.3	~380	3
ENR and citric acid-modified bentonite (20 phr)	transesterification	~4.5	~400	4
Carboxyl styrene butadiene rubber and epoxidized silica (30phr)	transesterification	9.9 ± 0.7	226 ± 16	5
Polybutadiene rubber, benezene-1, 3, 5-tricarbaldehyde	Imine bond	0.39 ± 0.2	52 ± 9	6
Polydimethylsiloxane and pripol 1017	transesterification	~0.45	~45	7
ENR and carboxyl cellulose nanocrystals (20 phr)	transesterification	~5.76	~764	This work

References

1 H. Xiang, JH. Yin, G. Lin, X. Liu, M. Rong and M. Qiu, *Chem. Eng. J.*, 2019, **358**, 878-890.

2 L. Imbernon, E. K. Oikonomou, S. Norvez and L. Leibler, *Polym. Chem.*, 2015, **6**, 4271-4278.

3 H. P. Xiang, H. J. Qian, Z. Y. Lu, M. Z. Rong and M. Q. Zhang, *Green Chem.*, 2015, **17**, 4315-4325.

4 C. Xu, R. Cui, L. Fu and B. Lin, *Compos. Sci. Technol.*, 2018, **167**, 421-430.

5 Y. Liu, Z. Tang, Y. Chen, C. Zhang and B. Guo, *ACS Appl. Mater. Interfaces*, 2018, 10, 2992-3001.

6 H. Zhang, D. Wang, W. Liu, P. Li, J. Liu, C. Liu，J. Zhang, N. Zhao and J. Xu, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 2011-2018.

7 H. Zhang, C. Cai, W. Liu, D. Li, J. Zhang, N, Zhao and J. Xu, *Sci. Rep.*, 2017, **7**, 11833