Supporting Information

Engineering Segregated Structures in Cross-linked Elastomeric Network Enabled by Dynamic Cross-link Reshuffling

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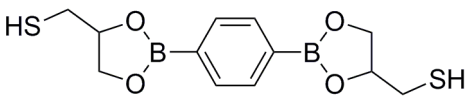
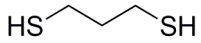
Materials. Commercial SBR (styrene content of 13.7 wt%, vinyl content of 53.3 wt%) was supplied by TSRC Co. Ltd. 1-Thioglycerol (98%), 1,3-propanedithiol (99%) and benzene-1,4-diboronic acid (98%) were supplied by Sigma-Aldrich. Multi-walled carbon nanotubes (CNTs) with a diameter of 10-15 nm (purity ≥ 97.5%, BET surface area ≥ 200 m^2 g^{-1}) were kindly supplied by CNano Technology Limited, Beijing, China.

Preparation of Segregated CNTs/SBR (s-CNTs/SBR) Composites. The cross-linker, dithiol-containing boronic ester (BDB), was synthesized from the complexation between benzene-1,4-diboronic acid and 1-thioglycerol, according to our previous study.[1] Boronic ester crosslinked SBR vitrimer was prepared by mixing 3 phr (parts per one hundred parts of rubber) BDB with SBR on an open two-roll mill for 15 min, followed by compression molding at 160 °C for optimum curing time determined using a vulcameter. Afterwards, the SBR-based vitrimers was ground to pass through an 80-mesh sieve, and the vitrimer granules were mechanically mixed with a desired amount of CNTs in a high-speed mixer for 3 min at a speed of 25000 rpm in the solid state to yield CNT-coated vitrimer complex granules. The resultant complex granules were then compression molded under 20 MPa at 160 °C for 30 min to yield segregated composites (s-CNTs/SBR). In the text, the volume fraction of CNTs in the composites was calculated by using the densities of 2.1 g/cm^3 for CNTs and 0.93 g/cm^3 for SBR.

To demonstrate the importance of boronic ester bonds in the formation of coherent composites, a control elastomer without dynamic bond was prepared by crosslinking SBR with 1,3-propanedithiol (3 phr) instead of BDB. After being subjected to the same treatment as that for the preparation of s-CNT/SBR (grinding, coating with 0.43 vol% CNTs, then compression molding), a discrete sample with many obvious holes and cracks was obtained.



Molecular structure of BDB



Molecular structure of 1,3-propanedithiol

Preparation of Randomly Dispersed CNTs/SBR (r-CNTs/SBR) Composites. For comparison, randomly dispersed CNTs/SBR composites were prepared by mixing SBR, 3 phr BDB and a desired amount of CNTs on an open two-roll mill, followed by compression molding at 160 °C for optimum curing time.

Characterizations. Surface morphology of complex granules was observed using a field-emission scanning electron microscopy (SEM, Hitachi S-4800, Japan). For optical microscopy observations, the samples were cut into 20 μm-thick films using a microtome and observed using an Olympus BX51 microscope equipped with a digital camera. Transmission electron microscopy (TEM) for the ultramicrotomed samples was conducted on Tecnai G2 F30 S-Twin electron microscope operated at an accelerating voltage of 30 kV. Tensile tests were carried out on a U-CAN UT-2060 instrument at room temperature with an extension rate of 500 mm/min. For cyclic tensile test, both loading and unloading were performed with an extension rate of 300 mm/min with a pre-set strain of 50%. Stress relaxation tests were conducted by monitoring the stress decay at 1% strain after equilibrating at required temperatures for 15 min using a TA Q800 machine. Electrical conductivity of the composites was measured by using a high resistance meter for electrical resistance > 10^9 Ω or Kisthley 2365A for electrical resistance <10^9 Ω. Mechanical property and electrical conductivities for both original and healing samples were presented as the mean and standard deviation based on at least five trials.

Figure S1. Photo of the sample prepared according to the same treatment as s-CNT/SBR by using 1,3-propanedithiol crosslinked SBR as the matrix, CNT volume fraction in the sample is 0.43 vol%.

Stress relaxation rate is increased with temperature, which is because the thermoactivated boronic ester transesterifications are accelerated and the chain mobility is promoted at elevated temperatures. According to fitting of characteristic relaxation time to temperature, the relaxation times exhibit an Arrhenius dependence on temperature with an activation energy of 28.8 kJ/mol.

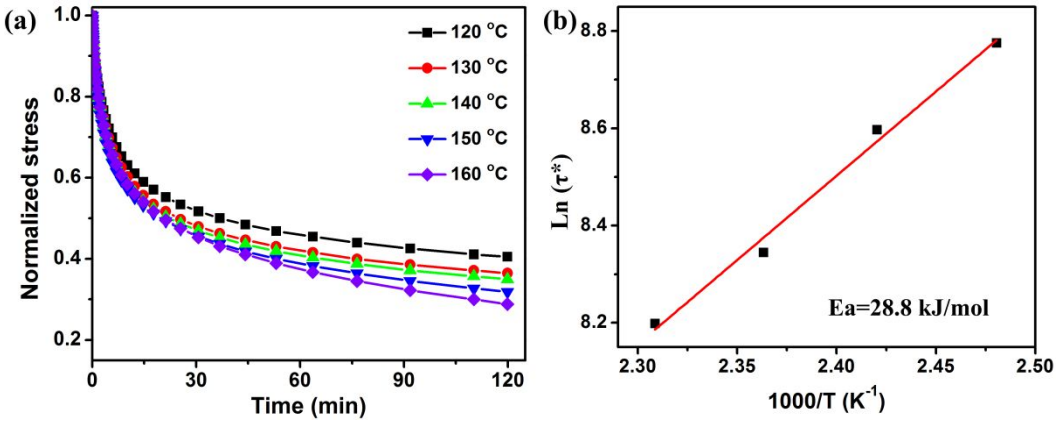


Figure S2. (a) Stress relaxation curves for boronic ester crosslinked SBR vitrimer at different temperatures under a constant strain of 1%. (b) Fitting of characteristic relaxation time to temperature according to Arrhenius law.

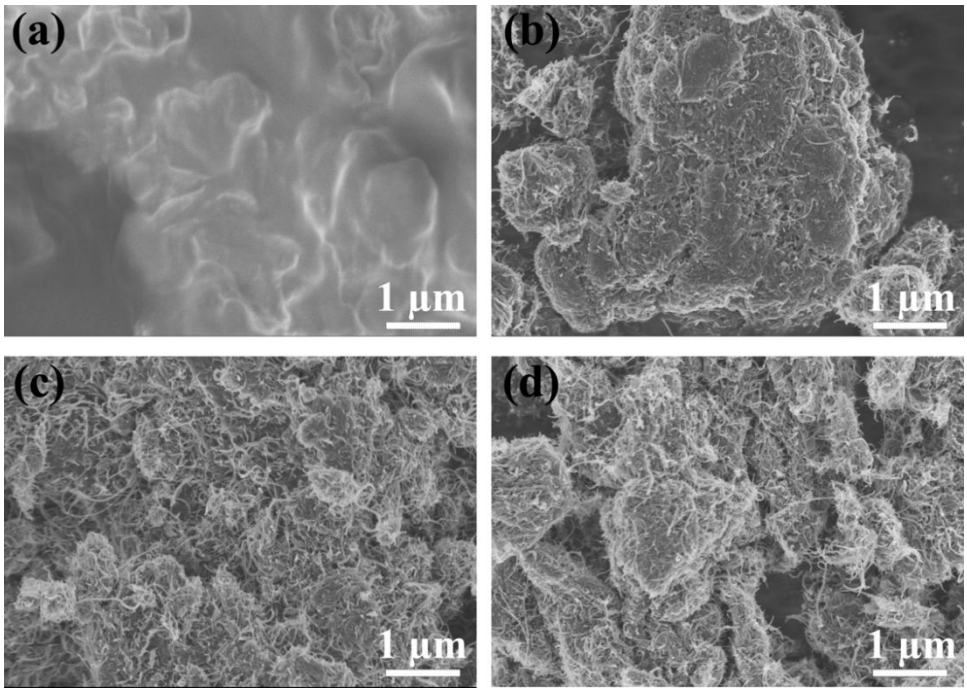


Figure S3. SEM images of (a) vitrimer granules, and complex granules containing (b) 0.043 vol%, (c) 0.43 vol% and (d) 1.06 vol% CNTs.

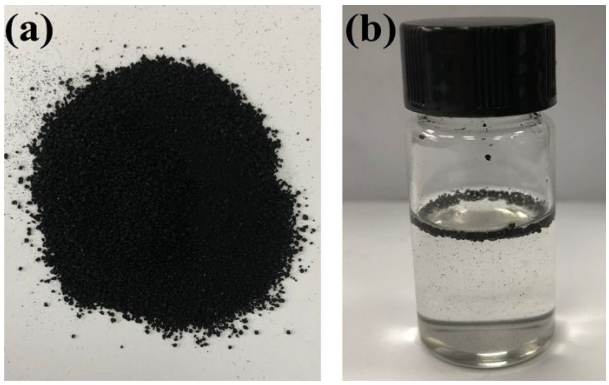


Figure S4. Photographs of (a) complex granules coated with 0.13 vol% CNTs and (b) 0.05 g complex granules (coated with 0.13 vol% CNTs) in 10 mL dimethylformamide that was subjected to sonication for 1 h.

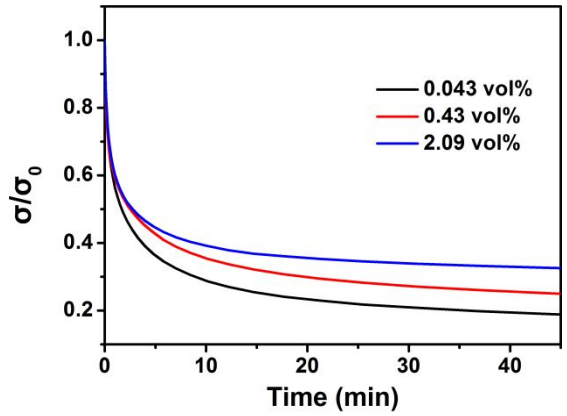


Figure S5. Stress relaxation curves for representative s-CNTs/SBR composites under a constant strain of 2% at 150 °C.

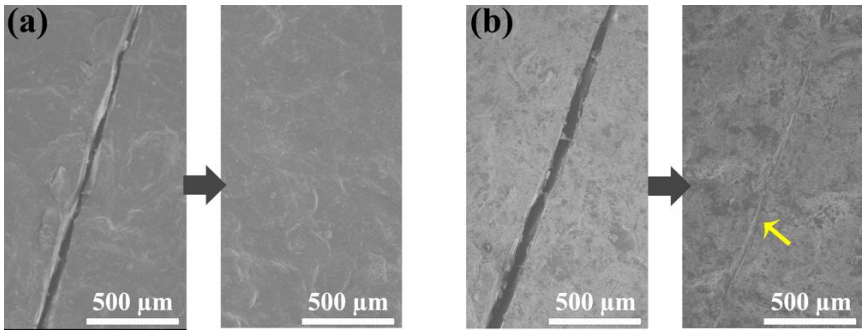


Figure S6. SEM images of cut-broken and healed s-CNTs/SBR films with (a) 0.043 vol% and (b) 2.09 vol% CNTs.

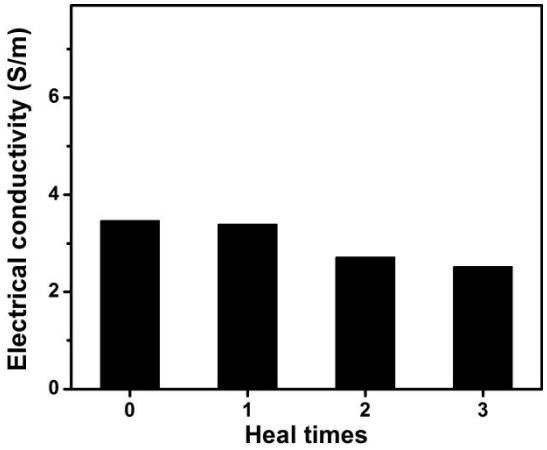


Figure S7. Electrical conductivities of the original and healed s-CNTs/SBR composite with 0.43 vol% CNTs.

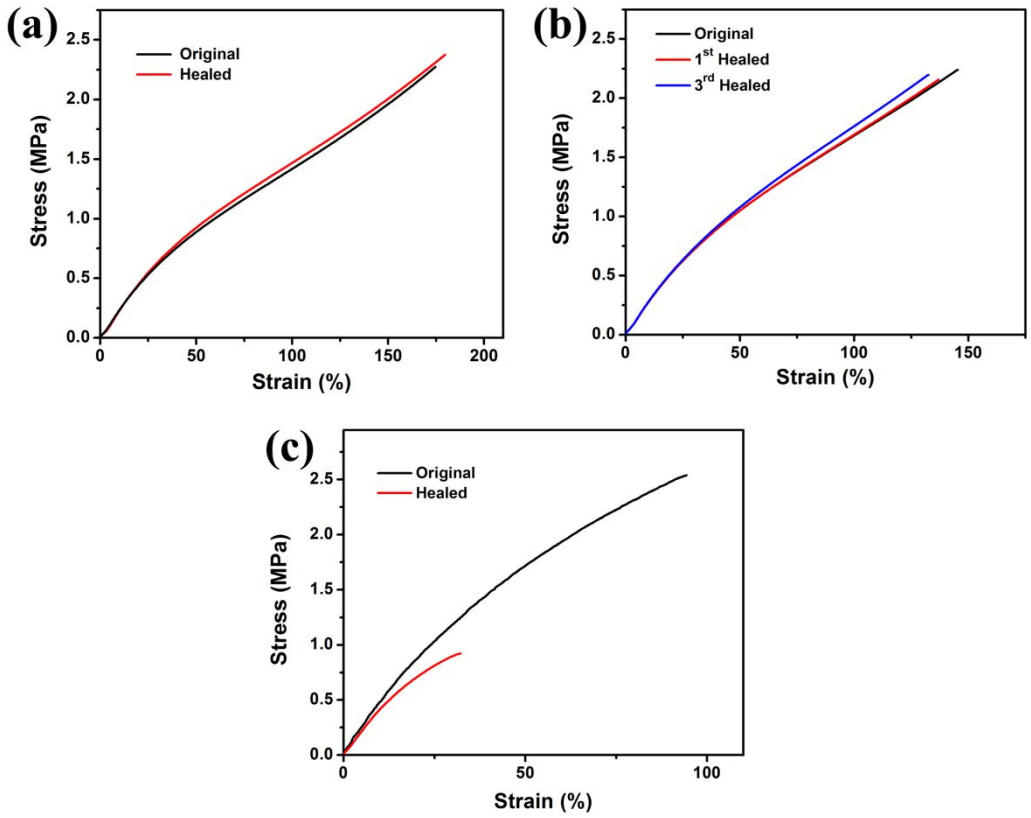


Figure S8. Typical stress-strain curves of original and healed s-CNTs/SBR with (a) 0.043 vol%, (b) 0.43 vol% and (c) 2.09 vol% CNTs.

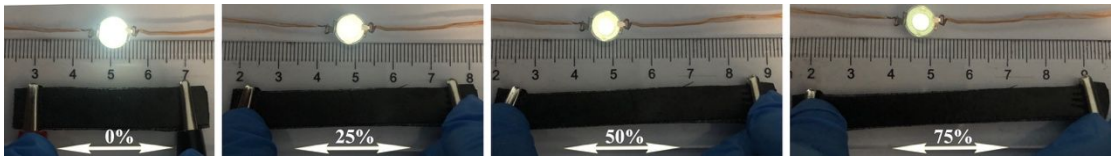


Figure S9. Change of LED brightness during stretching of the healed s-CNTs/SBR composite with 0.43 vol% CNTs on a circuit. The illuminance of LED is 328, 228, 137, 92 lux at the strain of 0, 25, 50, 75%, respectively.

Table S1. Comparison on the electrical properties between previously reported studies and our results.

Matrix	Filler	Percolation threshold (vol.%)	Filler content at electrical conductivity of about 10^{-3}S/m (vol.%)	Refs
ENR	MWCNTs	~0.97	~2.90	[2]
NR	MWCNTs/AgNP	~1.23	--	[3]
NR	MWCNTs	~4.10	--	[4]
NR	MWCNTs	1.00	--	[5]
NR	MWCNTs	~2.50	--	[6]
NR/NBR	MWCNTs	~0.85	~2.50	[7]
NBR	MWCNTs	~4.10	--	[8]
EPDM	MWCNTs	~1.68	~4.10	[9]
IR	MWCNTs/CCB hybrid	~0.30	~2.90	[10]
SBR	SWNTs	~0.12	~0.59	[11]
SBR	MWCNTs	0.85 ~ 1.27	~2.09	[12]
SBR	MWCNTs	0.035	0.085	Our work

Acronyms: ENR (epoxidized natural rubber), NR (natural rubber), NBR (nitrile rubber), EPDM (ethylene-propylene-diene terpolymer), IR (isoprene rubber), SBR (styrene-butadiene rubber), AgNP (silver nanoparticles), CCB (conductive carbon black)

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