Supplementary Information (SI) for Journal of Materials Chemistry A.

Mediating Carbon Black-Natural Rubber Interface by Thioamide-Functionalized Polysulfide for Energy-Saving Composites

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EXPERIMENTAL SECTION

Materials

Natural rubber (NR, grade 3L) was purchased from Yunnan, China. Carbon black (CB, grade N330) was purchased from Cabot Chemical Co. Ltd., China. 2-(1-cyclohexenyl) ethylamine (CA) was purchased from Bide Pharmatech Co. Ltd., Shanghai, China. Sulfur (S_8, 98%) was purchased from Macklin Biochemical Co. Ltd., Shanghai, China. Rubber additives were industrial grade and used as received.

Synthesis of Thioamide-Functionalized Polysulfide (SCA)

SCA was synthesized via inverse vulcanization of S_8 with CA. Briefly, S_8 was melted at 130 °C in a three-necked flask under an argon atmosphere. Upon complete liquefaction, a pre-determined amount of CA was added under stirring. The reaction was terminated when the C=C bond in CA was disappeared as detected by ^{1}H NMR measurement. The product was dissolved in tetrahydrofuran, followed by filtration to remove unreacted S_8. The solvent was then evaporated to produce SCA. In the context, the mass feeding ratio of S_8 and CA is 7:3, 5:5, and 3:7, which are denoted as S_7CA_3, S_5CA_5, and S_3CA_7, respectively. The yields of S_3CA_7, S_5CA_5, and S_7CA_3 are 36%, 61%, and 52% respectively.

Preparation of SCA-Modified CB Model Compound (mCB)

To clarify the interaction between CB and SCA, a model compound was prepared. 10.0 g of CB and 0.5 g of S_5CA_5 were thoroughly mixed in 100 mL of tetrahydrofuran under stirring, followed by the evaporation of solvent. The mixture was then treated at 150 °C for 1 h to initiate the reaction between S_5CA_5 and CB. Finally, the mixture underwent Soxhlet extraction with tetrahydrofuran for 72 h to remove un-grafted S_5CA_5.

Preparation of Composites

NR, antioxidant, CB, and SCA were sequentially incorporated into a Banbury mixer and blended at room temperature for 7 min. Then the temperature was elevated to 150 °C, and the mixture was further mixed for an additional 2 min. After cooling to room temperature, the mixture was mixed with activators, accelerators, and sulfur on an open two-roll mill. After 24 h of aging at room temperature, the resultant compound was molded at 143 °C for the optimal curing time measured by vulcameter to produce vulcanizate composite. In the context, the abbreviation of NR/SCA-*y* designates the composite modified with *y* phr of SCA.

A control composite NR/Blank without adding SCA was prepared under the same procedures. Detailed formulations are provided in **Table S1**.

Characterizations

^{1}H NMR spectra were recorded on a Bruker AVANCE III HD 600 instrument. The samples were dissolved in $CDCl_3$, and TMS was used as an internal standard. FTIR spectra were collected on a Bruker Vertex 70 PTIR spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed on an Escalab Xi+ equipped with an Al Kα radiation source. Thermal gravimetric analysis (TGA) was performed on a TA Q50 thermogravimetric analyzer under nitrogen atmosphere at a 10 °C/min heating rate. Morphologies of the composites were observed by a JEM-2100F transmission electron microscopy (TEM) and a Hitachi SU-70 scanning electron microscopy (SEM). Ultrasmall-angle X-ray scattering (USAXS) experiments were conducted on Beamline BL10U1, respectively, at Shanghai Synchrotron Radiation Facility, China. For freezing point measurements, the composites were soaked in cyclohexane for 72 h, and then the swollen samples were cooled from 40 to -50 °C at 5 °C/min using a TA DSC Q200 instrument. Element analysis was performed on a Vario EL cube. Dynamic rheological behaviors of the composites were measured using RPA 2000 analyzer (Alpha) with strain from 0.1 to 20% under 1 Hz at 60 °C. Heat build-up of the composites was tested on a U-CAN UD-3801 Flexometer based on ISO 4666-3:2016. Uniaxial tensile tests were performed using a Gotech AI-7000 S universal testing machine following ISO 37-2005. Rolling resistance of rubber wheels was measured on an RSS-II model rolling resistance testing machine (Beijing Wanhuiyifang Technology Co., Ltd.). The load and rotation speed were 30 kg and 1200 r/min, respectively. X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (PANalytical, Netherlands). Dynamic mechanical analysis (DMA) was performed on a NETZSCH DMA 242 apparatus, and the samples were heated from 0 to 80 °C at 3 °C /min under 10 Hz frequency and 5%

dynamic strain. Crosslink density was determined based on equilibrium swelling tests by immersing the vulcanizates in toluene, as described elsewhere.[1]

Grafting Efficiency of SCA onto CB is determined using the following formula:

$$Grafting\ efficiency = \frac{W_2 - W_1}{W_3 - W_1} * \frac{m_{CB}}{m_{SCA}} * 100\%$$

where W_1, W_2, W_3 are the mass loss between 30 and 500 °C for CB, mCB and SCA, respectively, and m_{CB} and m_{SCA} are the feed masses of CB (10.0 g) and SCA(0.5 g) in the preparation of model compound mCB , respectively.

Bound rubber was determined by extracting the uncured compounds with toluene for 72 h at 25 ^{o}C, and the solvent was renewed each 24 h. The remnants were dried overnight in vacuum and subjected to TGA measurement. The bound rubber was calculated as follows:

$$Bound\ rubber = \frac{W\ (loss)}{1 - W(loss)} \times z$$

where W (loss) is the weight loss of the remnants, *z* represents the weight fraction of CB relative to NR.

Noda's rules are summarized as follows:[2]

Φ (v_1, v_2) and Ψ (v_1, v_2) represent the correlation peaks in synchronous and asynchronous map, respectively.

(1) If Φ (v_1, v_2) and Ψ (v_1, v_2) are simultaneously positive or negative, then the movement of v_1 is before than that of v_2.

(2) If Φ (v_1, v_2) and Ψ (v_1, v_2) are one positive one negative, then the movement of v_1 is after than that of v_2.

(3) If Φ (v_1, v_2) is not equal to 0 but Ψ (v_1, v_2) is equal to 0, then the movements of v_1 and v_2 are simultaneous.

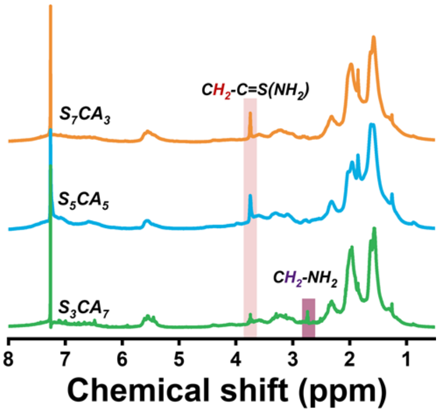


Figure S1 ^{1}H NMR spectra of S_7CA_3, S_5CA_5, and S_3CA_7.

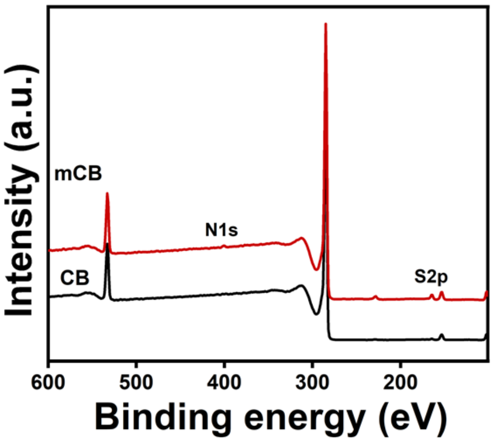


Figure S2 XPS spectra full spectra of CB and mCB.

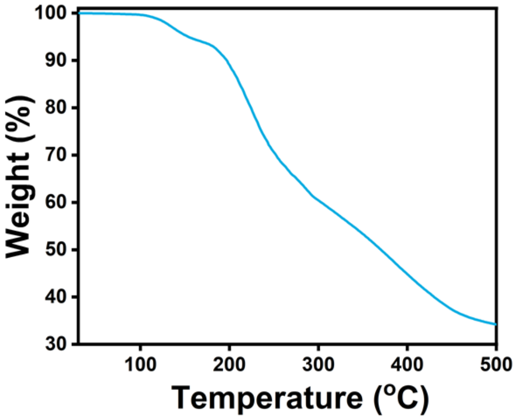


Figure S3 TGA curve of S_5CA_5.

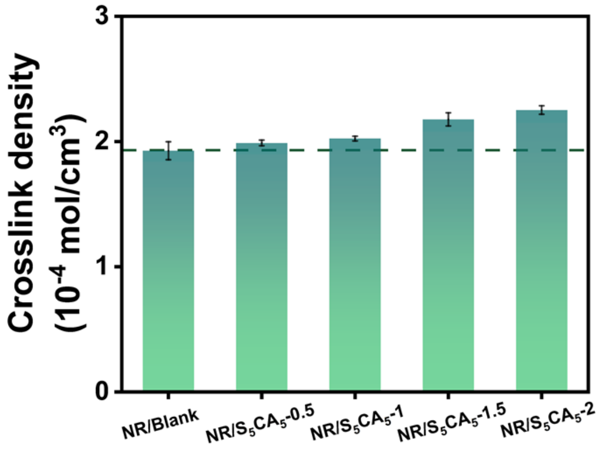


Figure S4 Crosslink density of NR/Blank and NR/S_5CA_5-*y* composites.

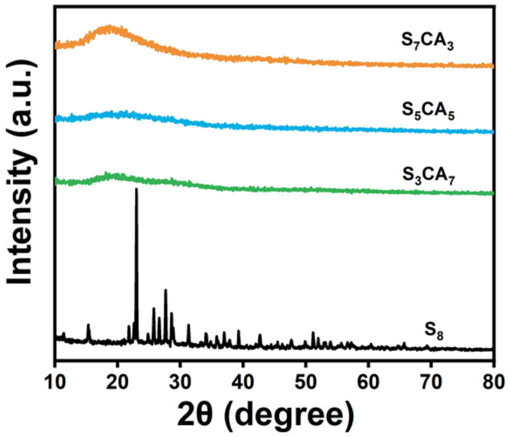


Figure S5 X-ray diffraction patterns of S_3CA_7, S_5CA_5, S_7CA_3, and S_8.

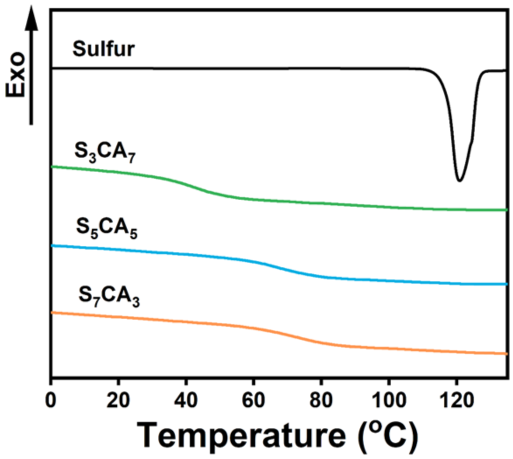


Figure S6 DSC curves of S_3CA_7, S_5CA_5, S_7CA_3, and S_8.

Table S1 Formulations of the composites (the unit is gram).

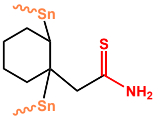
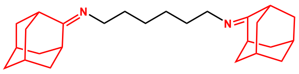
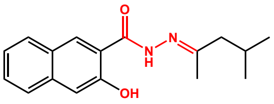
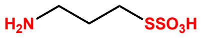
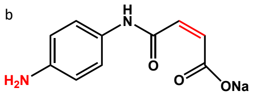
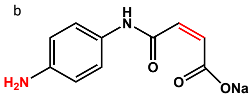
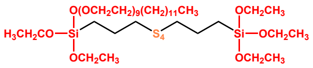
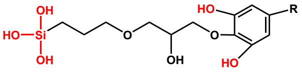
Ingredient	NR	CB	SCA
NR/Blank	100	40	0
NR/S_5CA_5	100	40	0.5/1/1.5/2
NR/S_3CA_7	100	40	1.5
NR/S_7CA_3	100	40	1.5

Basic formula is as follows: Antioxidant N-isopropyl-N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamin 1 g; Activator zinc oxide 5 g; Activator stearic acid 1 g; Accelerator N-cyclohexylbenzothiazole-2-sulphenamide 1.5 g; Accelerator 2, 2'-dibenzothiazoledisulfde 0.5 g; S_8 1.5 g.

Table S2 Mechanical properties of all the composites.

Samples	Tensile strength (MPa)	Breaking strain (%)	Modulus (MPa)
NR/Blank	31.3±1.2	504±13	14.9±0.3
NR/S_5CA_5-0.5	32.6±2.8	522±33	15.0±0.4
NR/S_5CA_5-1	34.0±1.5	533±14	15.2±0.3
NR/S_5CA_5-1.5	32.7±0.7	502±9	15.9±0.3
NR/S_5CA_5-2	32.9±2.1	493±25	16.8±0.3
NR/S_3CA_7-1.5	32.7±0.9	532±12	15.0±0.3
NR/S_7CA_3-1.5	32.2±0.6	471±20	18.1±0.3

Table S3 Comparison on the reduction in hysteresis loss and heat build-up of NR/CB composites modified with IMs.

CB content and type	IM content	Hysteresis loss decrease in percentage	Heat build-up decrease in percentage	IM molecular structure
40 phr CB (N330)	2 phr	33 %	32 %	
50 phr CB (N330) [3]	1 phr	25 %	24%	
50 phr CB (N330) [4]	2 phr	37 %	29 %	
45 phr CB (N330) [5]	1 phr	25 %	/	a 
45 phr CB (N330) [5]	1 phr	25 %	/	b 
40 phr recovered CB [6]	2 phr	23 %	/	b 
50 phr CB (N234) [7]	3 phr	~12 %	7 %	
50 phr CB [8]	4 phr	~27 %	~6 %	
35 phr CB (N134) [9]	0.8 phr	26 %	20 %	

Note: commercially viable, a: SUMILINK@100; b: SUMILINK@200

Table S4 Element analysis results of S_3CA_7, S_5CA_5, and S_7CA_3.

	S (%)	C (%)	N (%)	H (%)
S_3CA_7	15.5	71.2	6.6	6.6
S_5CA_5	42.7	48.1	4.8	4.4
S_7CA_3	62.8	30.7	2.8	2.6

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