Crosslinking diene rubbers by inverse vulcanised co-polymer

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Materials. Butadiene styrene rubber (SBR, trade name: SBR1502, styrene content of 23.5 wt%) was purchased from Jilin Chemical Industry Co. Ltd., Jilin, China. *Cis*-1,4-polybutadiene rubber (BR, trade name: BR 9000) was purchased from Beijing Yanshan Petrochemical Co. Ltd., China. Carbon black (CB, trade name: N330) was provided by Shanghai Yutong Chemical Technology Co. Ltd. Styrene (99.5%, stabilized with HQ) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 99%) and 4-dimethylaminopyridine (DMAP, 99%) were purchased from Beijing InnoChem Science & Technology Co. Ltd., Beijing, China. Styrene was uninhibited by vacuum distillation before use. Other rubber additives were industrially available and used as received without further purification.

Copolymerization of sulfur and styrene

Elemental sulfur (7.0 g, 218 mmol) was added to a 50 mL explosion-proof tube and maintained at 130 °C until a yellow uniform liquid formed. 0.5 g TBD was dissolved in styrene (3.0 g, 29 mmol), which was then added to the molten sulfur in a dropwise fashion. The reaction mixture was stirred at 130 °C for 1 h. In the text, the sulfur co-polymer synthesized by adding 5.0 wt% (relative to the weights of reactants) TBD is named as TSP. For a comparison, the copolymerization of sulfur and styrene in the absence of TBD was also prepared according to the abovementioned procedures, which is coded as SP. The number-average molecular weights of SP and TSP are 456 and 298 g/mol, respectively by gel permeation chromatography in tetrahydrofuran.

Other organic bases such as DBU and DMAP have also been explored for their effects on inverse vulcanization following the same protocols by replacing TBD with DBU or DMAP.

To investigate the effect of TBD loading on curing process, sulfur co-polymers catalyzed by different TBD loadings were synthesized according to the abovementioned procedures. Besides 5.0 wt%, other TBD contents were controlled to be 2.0, 3.5, and 6.5 wt%.

Preparation of SBR/TSP-x, SBR/S, and SBR/DSP-5 and SBR/DMSP-5

For the preparation of SBR/TSP-x, 100 g of SBR and various amount of TSP (3, 5, 7, 9 g) were mixed using a two-roll mill. The obtained compounds were then subjected to compression moulding at 160 °C for optimum time to produce TSP-cured SBR. In the context, the sample code of SBR/TSP-x means TSP-cured SBR, where x is the weight fraction of TSP relative to SBR. Traditional sulfur-cured SBR (SBR/S) was prepared according to the abovementioned protocols based on the below formulation: SBR 100 g; zinc oxide 5.0 g; stearic acid 1.0 g; dibenzothiazoledisulfide (DM) 0.5 g; N-cyclohexyl-2-benzothiazole sulphonamide (CZ) 1.5 g and sulfur 2.0 g.

To study the effects of TBD loading on the curing process of SBR, sulfur co-polymers that were catalyzed by different TBD contents were added into SBR according to the abovementioned protocols, and the sulfur fraction in all the samples was kept a constant of 2.0 wt% relative to SBR.

To examine the effectiveness of the DBU-catalyzed sulfur co-polymer (DSP) and DMAP-catalyzed sulfur co-polymer (DMSP) in crosslinking SBR, SBR/DSP-5 and SBR/DMSP-5 were prepared according to the abovementioned protocols by adding 5 phr DSP and DMSP into SBR.

Preparation of CB/SBR/TSP-5 and CB/SBR/S composites

100 g of SBR, 40 g of carbon black (CB), and 5 g of TSP were mixed using a two-roll mill and the obtained compounds were subjected to compression molded at 160 °C for optimum time to yield TSP-cured CB-filled SBR composite (CB/SBR/TSP-5). Traditional sulfur-cured CB-filled SBR composite (CB/SBR/S) was prepared according to the

abovementioned protocols based on the below formulation: SBR 100 g; CB 40 g; zinc oxide 5.0 g; stearic acid 1.0 g; dibenzothiazoledisulfide (DM) 0.5 g; N-cyclohexyl-2-benzothiazole sulphonamide (CZ) 1.5 g and sulfur 2.0 g.

Preparation of BR/TSP-5 and BR/S

For the preparation of BR/TSP-5, 100 g of BR and 5.0 g of TSP were mixed using a two-roll mill and the obtained compounds were subjected to compression moulding at 160 °C for optimum time to yield TSP-cured BR. Traditional sulfur-cured BR (BR/S) was prepared according to the abovementioned protocols based on the below formulation: BR 100 g; zinc oxide 5.0 g; stearic acid 1.0 g; dibenzothiazoledisulfide (DM) 0.5 g; N-cyclohexyl-2-benzothiazole sulphonamide (CZ) 1.5 g; sulfur 2.0 g.

Characterizations

^{1}H nuclear magnetic resonance (NMR) spectra were recorded at 600 MHz. The samples were dissolved in $CDCl_3$ and TMS was used as an internal standard.

Fourier transform infrared (FTIR) spectroscopy was performed on a Bruker Vertex 70 FTIR spectrometer.

Cross-linking kinetics was determined at 160 °C on a U-CAN UR-2030 vulcameter.

Differential scanning calorimetry (DSC) was conducted on a TA DSC Q20 machine by heating the samples from -50 to 150 °C with 10 °C/min.

The tensile stress-strain test was performed at room temperature by using a Gotech AI-7000 S universal testing machine following ISO standard 37-2005. Five specimens were measured for each sample. For cyclic loading-unloading test, the samples were stretched to a pre-defined strain of 100% at 500 mm/min at room temperature.

Cross-linking density was determined by equilibrium swelling experiment in toluene based on Flory-Rehner equation. Equilibrium swelling experiment was conducted by immersing vulcanizations in toluene at room temperature for 72 h. After swelling, the solvent was wiped off quickly from the sample surface using filter paper, and the samples were immediately weighed and then dried in a vacuum oven at 60 °C until constant weight. Three specimens were measured for each sample. The crosslinking density (V_e) is calculated

according to equation (1)

$$V_e = - \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s(V_r^{1/3} - V_r/2)}$$ (1)

where χ is the Flory-Huggins polymer solvent interaction parameter (0.413 for SBR and toluene), V_s is the molar volume of the solvent (106.5 cm³/mol for toluene). V_r is the volume fraction of SBR in the swollen gel, which is calculated by the following equation (2):

$$V_r = \frac{(m_2 - m_0\varphi)/\rho_r}{(m_2 - m_0\varphi)/\rho_r + (m_1 - m_2)/\rho_s}$$ (2)

where m_0 is the sample mass before swelling, m_1 and m_2 are the weights of the swollen and deswollen sample, respectively, φ is the weight fraction of the insoluble components, ρ_r and ρ_s are the densities of the rubber and solvent, respectively.

Dynamic mechanical analysis was conducted by using a TA Q800 DMA apparatus. The measurement was performed under a tensile mode with a dynamic strain of 0.5%. The samples were scanned from -80 to 80 °C, and the frequency and heating rate were fixed at 1 Hz and 3 °C/min, respectively.

Electron paramagnetic resonance were obtained using an Electron parameter resonance system (EMXPlus-10/12), which equipped with temperature control and data acquisition systems. The measurement was carried out by placing the un-cured compounds in the cavity of the EPR spectrometer and heating the samples to 373, 393, 413 and 433 K for concomitant continuous recording of EPR spectra.

The molecular weights of TSP and SP were determined using gel permeation chromatography (Agient1260) on two columns in series (i.e., the PL-gel 5 μm 10^3 Aᵒ and PL-gel 3μm Mixed-E column). Also, monodisperse polystyrene was used as the standard. Each sample was dissolved in tetrahydrofuran, and a 10 μL sample in solution was injected. The column was operated at 30 ºC and eluted with tetrahydrofuran at a flow rate of 1 mL/min.
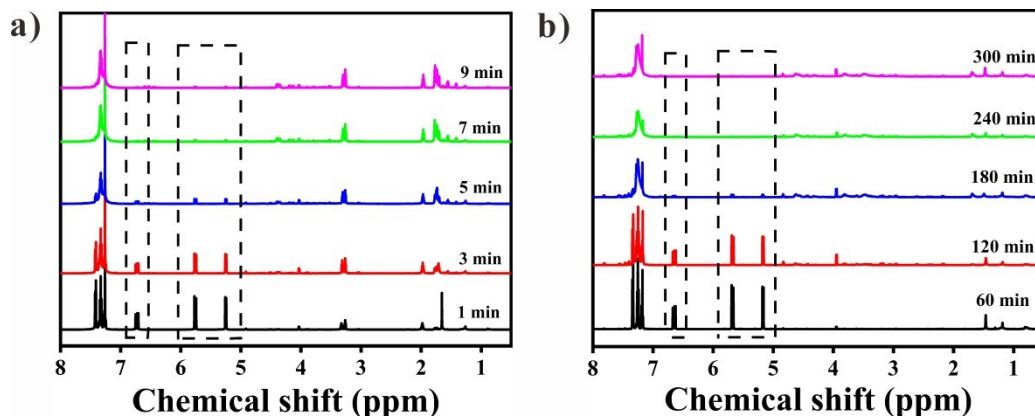
Fig. S1 ^{1}H NMR of aliquots removed from the reaction mixture (a) with TBD and (b) without TBD at different time.
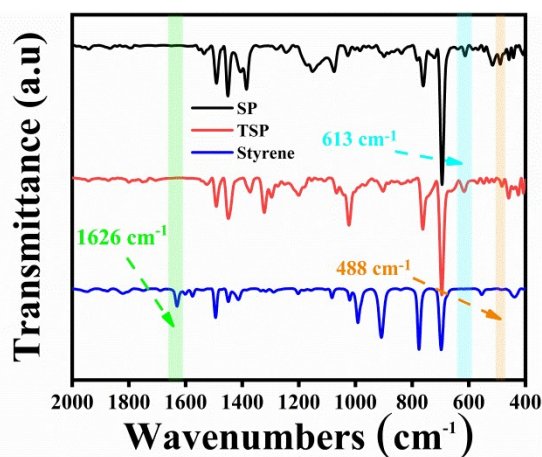

Fig. S2 FTIR spectra of SP, TSP and styrene.

Compared with styrene, the absorption related to the stretching vibration of C=C bond is absent in the spectra of SP and TSP. Furthermore, the FTIR spectra of SP and TSP exhibit absorptions at 613 and 488 cm^{-1}, which can be attributed to C-S and S-S stretching vibrations, respectively.
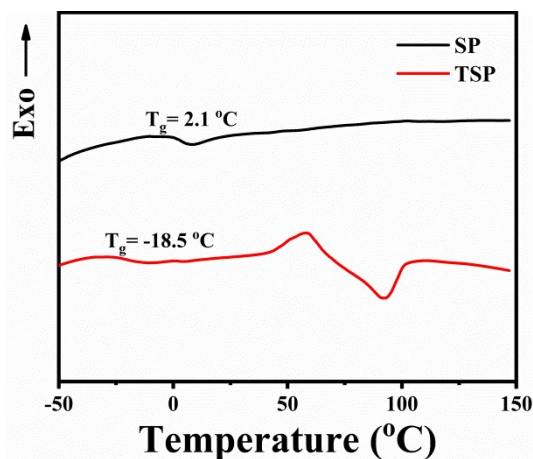
Fig. S3 DSC curves of SP and TSP.

Element sulfur underwent a solid-solid orthorhombic to monoclinic transition at around 106 °C and then melts at 118 °C. In the DSC curve of SP, the melting peak related to S_8 is absent and a glass transition at 2.1 °C is observed, which confirm the conversion of crystalline sulfur into sulfur co-polymer. Compared with SP, TSP exhibits a cold crystallization peak and a melting peak at approximately 80 °C. The presence of melting peak in TSP is likely because the formation of long polysulfide chains that promote crystallization and the cold crystallization may be due to the partial organization of polymer chains, typical of network-stabilized polymeric sulfur domains.[1, 2]

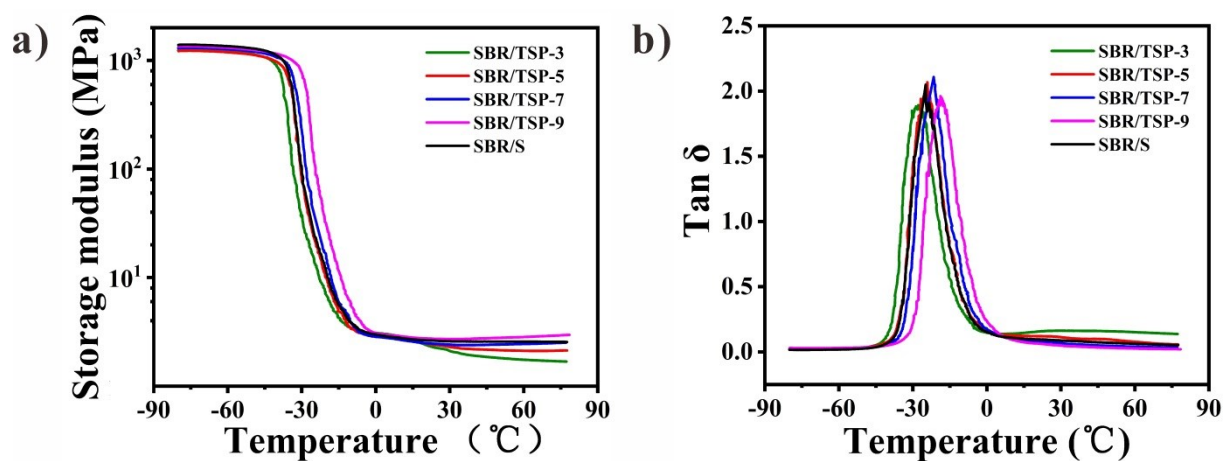**Fig. S4** Solubility experiments of TSP in THF, CH$_2$Cl$_2$ and toluene.

Fig. S5 Temperature dependences of (a) storage modulus and (b) tan δ of SBR/TSP-*x* and SBR/S.
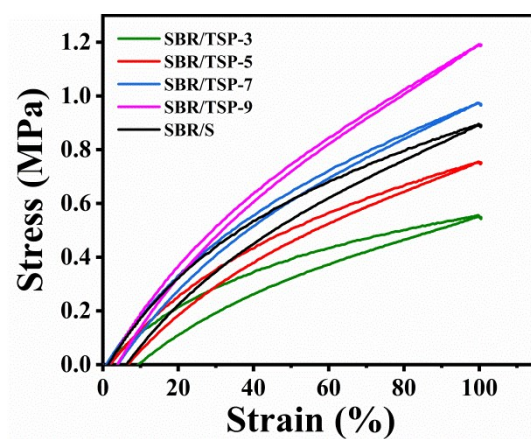

Fig. S6 Loading-unloading tensile curves by stretching the samples to a pre-defined strain of 100%.
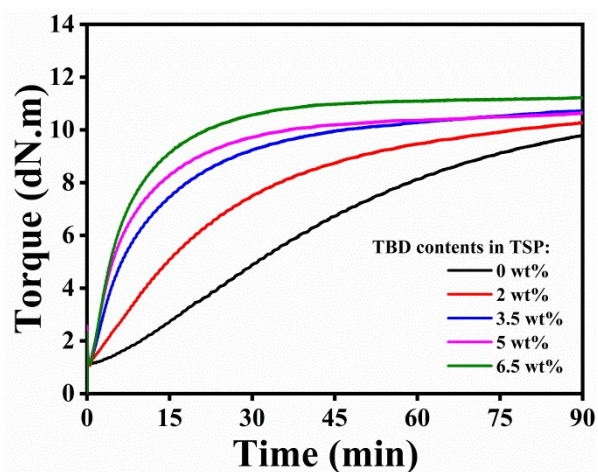

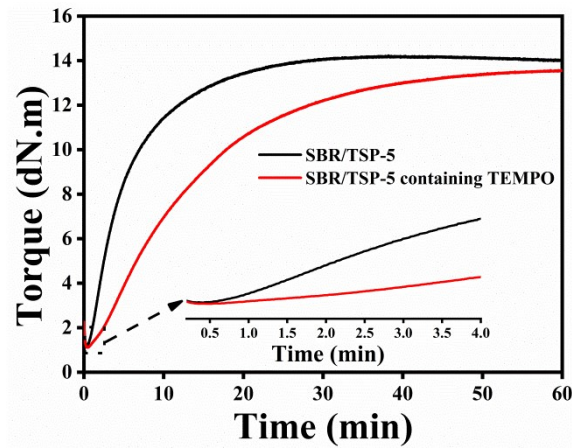**Fig. S7** Crosslinking kinetics of SBR/TSP with different TBD contents in TSP.

Fig. S8 Crosslinking kinetics of SBR/TSP-5 and SBR/TSP-5 containing 2 phr TEMPO.
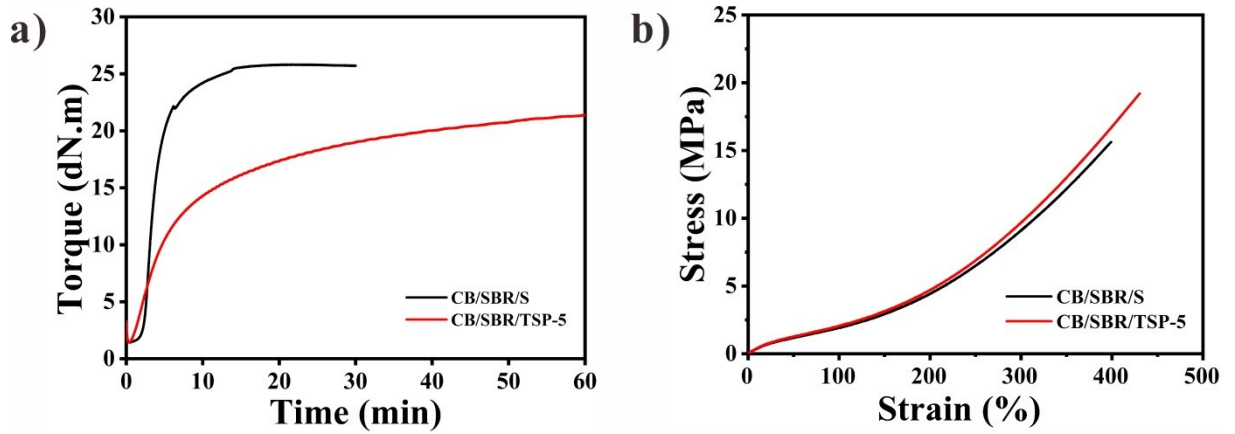

Fig. S9 (a) Crosslinking kinetics of CB/SBR/TSP-5 and CB/SBR/S samples. (b) Typical stress-strain curves of CB/SBR/TSP-5 and CB/SBR/S samples.
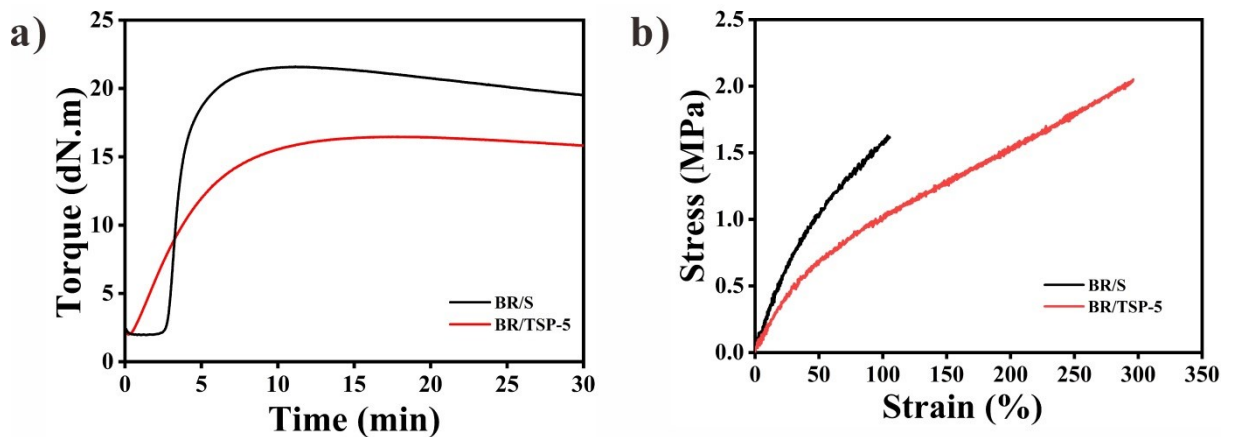

Fig. S10 (a) Crosslinking kinetics of BR/TSP-5 and BR/S samples. (b) Typical stress-strain curves of BR/TSP-5 and BR/S samples.
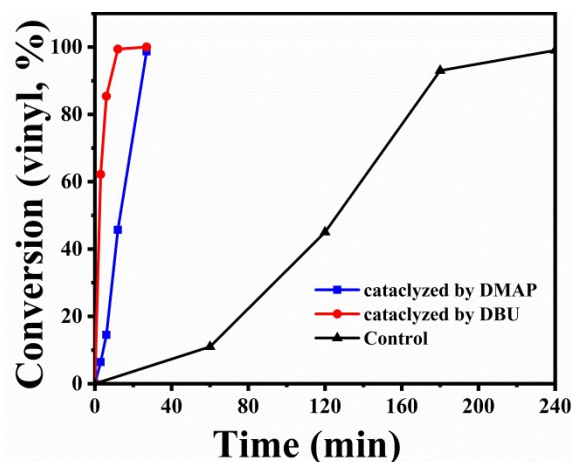
Fig. S11 Conversion of styrene versus time for inverse vulcanization between sulfur and styrene catalyzed by DBU, DMAP, and in absence of catalyst.
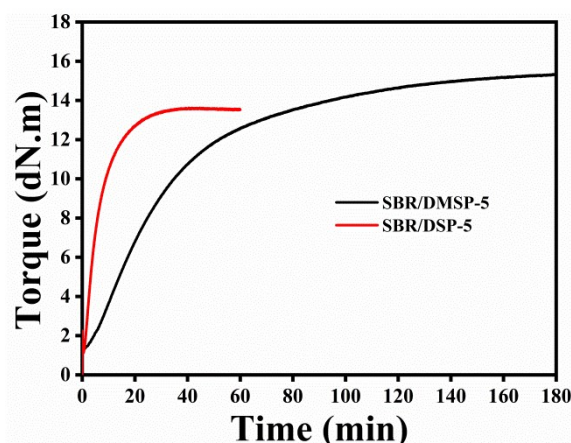

Fig. S12 Crosslinking kinetics of SBR/DSP-5 and SBR/DMSP-5.

Table S1. Comparison on the MSDS information of commonly used curing additives and TBD.

tetramethylthiuram tisulfide (TMTD)	
HEALTH HAZARDS	
Acute toxicity (Oral)	Category 4
Skin corrosion/irritation	Category 3
Serious eye damage/eye irritation	Category 2B
Skin sensitization	Category 1
Germ cell mutagenicity	Category 1B
Reproductive toxicity	Category 2
Specific target organ toxicity -Single exposure [Category 1]	Nervous system

Specific target organ toxicity -Repeated exposure [Category 1]	Thyroid gland
Specific target organ toxicity -Repeated exposure [Category 2]	Nervous system Testis
ENVIRONMENTAL HAZARDS	
Acute aquatic hazard	Category 1
Long-term aquatic hazard	Category 1

dibenzothiazoledisulfide (DM)	
HEALTH HAZARDS	
Skin sensitization	Category 1
Reproductive toxicity	Category 2
ENVIRONMENTAL HAZARDS	
Acute aquatic hazard	Category 1
Long-term aquatic hazard	Category 1

N-cyclohexyl-2-benzothiazolylsulfenamide (CZ)	
HEALTH HAZARDS	
Serious eye damage/eye irritation	Category 2A
Skin sensitization	Category 1
Reproductive toxicity	Category 1B
Specific target organ toxicity -Repeated exposure [Category 2]	Kidney
ENVIRONMENTAL HAZARDS	
Acute aquatic hazard	Category 1
Long-term aquatic hazard	Category 1

zinc oxide (ZnO)	
HEALTH HAZARDS	
Skin corrosion/irritation	Category 2
ENVIRONMENTAL HAZARDS	
Acute aquatic hazard	Category 1
Long-term aquatic hazard	Category 1

1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)	
HEALTH HAZARDS	
Skin corrosion/irritation	Category 1B
Serious eye damage/eye irritation	Category 1
ENVIRONMENTAL HAZARDS	Not classified

Table S2. Mechanical properties and crosslinking densities of vulcanizes.

Samples	Stress at 100% strain (MPa)	Tensile strength (MPa)	Breaking strain (%)	Crosslinking density (mol/cm³×10⁻⁴)
SBR/TSP-3	0.63±0.02	2.42±0.10	586±13	0.60
SBR/TSP-5	0.84±0.03	2.22±0.01	368±19	1.08
SBR/TSP-7	1.04±0.02	2.08±0.04	256±8	1.45
SBR/TSP-9	1.23±0.01	2.11±0.07	203±9	1.82
SBR/S	0.91±0.02	1.81±0.18	283±37	1.14

References

1 I. Gomez, O. Leonet, J. A. Blazquez and D. Mecerreyes, *Chemsuschem,* 2016, **9**, 3419-3425.

2 M. S. Karunarathna, M. K. Lauer, T. Thiounn, R. C. Smith and A. G. Tennyson, *J. Mater. Chem. A*, 2019, **7**, 15683-15690.