A Real Recycling Loop of Sulfur-Cured Rubbers through Transalkylation Exchanges of C-S Bonds

Zhenghai Tang,[a] Yinjun Liu,[a] Qingyi Huang,[a] Jinshan Zhao,[a] Baochun Guo[*a], and

Liqun Zhang[*b]

a Department of Polymer Materials and Engineering, South China University of Technology, Guangzhou 510640, P. R. China. E-mail: psbcguo@scut.edu.cn

b State Key Laboratory of Organic/Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China. E-mail: zhanglq@mail.buct.edu.cn

Materials. Commercial styrene-butadiene rubber (SBR, styrene content of 27 wt%, vinyl content of 40 wt%, $Mn=3.95\times10^5$ g/mol) was manufactured by Beijing Yanshan Petrochemical Co. Ltd., SINOPEC, China. Ground tire rubber with a size of about 80 mesh was supplied by Guangzhou Tengwei Co. Ltd., China. The ground tire rubber comprised of 55.5% natural rubber, 28.7% carbon black, 8.0% other fillers and 7.8% volatile component. Trimethylsulfonium iodide (TMSI, 98%), 1,3-propanedithiol (98%), *n*-butyl sulfide (99%) were purchased from Sigma-Aldrich. Other chemicals were analytically pure and used as received.

Model C-S Transalkylation Reaction. Trimethylsulfonium iodide and *n*-butyl sulfide were used as model compounds to study the C-S transalkylation reaction. Trimethylsulfonium iodide (0.20 g, 1.0 mmol) and 5 equiv of butyl sulfide (0.73 g, 5.0 mmol) were dissolved in 5 mL of methanol. The mixture was kept at 50 °C with stirring. The samples were taken at certain time intervals and washed by *n*-pentane, followed by

drying at 40 °C overnight.

Transalkylation Reaction in Cross-linked Rubber Networks. The cross-linked rubber networks with only C-S cross-linking linkage were prepared by thermally initiated thiol-ene "click" reaction between 1,3-propanedithiol and SBR. Typically, a desirable amount of propanedithiol and TMSI were directly blended with SBR on an open two-roll mill. The resulted compound was then compression molded at 160 °C for 60 min. During hot press, thiol groups of propanedithiol were coupled onto the pendent vinyl groups of SBR through thiol-ene "click" reaction, yielding C-S cross-linking linkage and leading to the covalent cross-linking of SBR. In the text, propanedithiol content is fixed at 1 phr, and the content of TMSI is controlled to be 0, 1.0, 3.0 and 5.0 phr. Sample code of SBR-TSx represents propanedithiol-crosslinked SBR with x phr TMSI.

Reprocessing Scrap Rubber Powders. To examine the validity of C-S transalkylation reaction in recycling rubbers in industrial practice, scrap rubber powders were mixed with trimethylsulfonium iodide followed by compression molding. The content of trimethylsulfonium iodide is controlled to be 0, 1, 3, 5 phr, and the molding temperature is 160 °C. Sample code of recycled GTR-x represents remolded ground tire rubber with x phr TMSI.

Characterizations. Electrospray ionization-mass spectrometry (ESI-MS) analysis was performed on a Bruker maXis impact equipped with an ESI source operating in positive mode with a capillary voltage of 3.5 kV. Methanol was used as the solvent. Desolvation gas flow and temperature were set at 4.0 L/min and 180 °C, respectively. The

acquisition range was 50-500 m/z. ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 500 MHz on Inova spectrometer in CD_3OD.

Tensile test was conducted using Gotech-AI7000S instrument. The strain rate of tensile tests was 500 mm/min. Five specimens were measured for each sample.

Swelling ratio and cross-linking density were 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 swelling ratio is defined as $(m_1-m_2)/m_2$. The volume fraction of rubber in the swollen gel, V_r, was calculated by the following equation:

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

(1)

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.

The elastically active network chain density can be calculated by the well-known Flory-Rehner equation:

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

(2)

where χ is the Flory-Huggins polymer solvent interaction parameter (0.413 for SBR and toluene), and V_s is the molar volume of the solvent (106.5 cm^3/mol for toluene).

Stress relaxation experiments, creep tests, and dynamic mechanical analysis were conducted by using a TA Q800 DMA apparatus. For creep experiments, a nominal stress of 0.2 MPa was applied on the sample after a 30 min temperature equilibration. For stress relaxation test, after equilibrating at a required temperature for 30 min, the sample was stretched to a constant strain of 2% and the stress decay was monitored over time. Dynamic mechanical analysis was performed under a tensile mode with a dynamic strain of 0.5%. The samples were scanned from -80 to 120 °C, and the frequency and heating rate were fixed at 5 Hz and 3 °C/min, respectively.

Table S1. Mechanical properties and cross-linking density of recycled GTR with different TMSI contents.

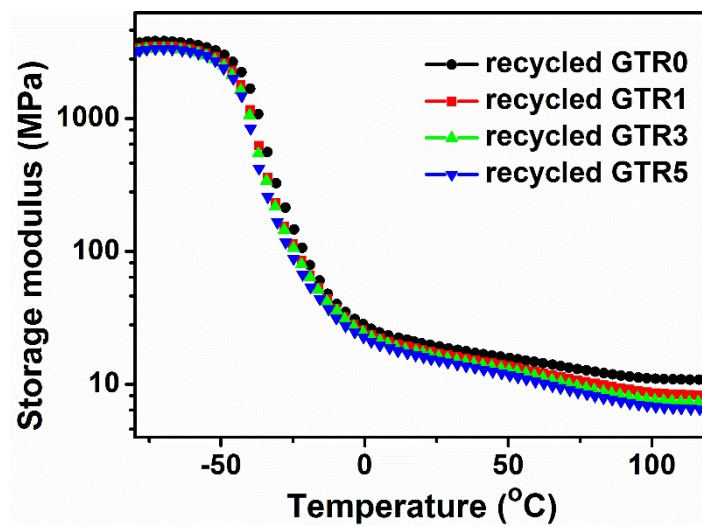| samples	tensile strength (MPa)	stress at 50% strain (MPa)	breaking strain (%)	cross-linking density (mol.cm^{-3}, 10^{-4})
Recycled GTR-0	6.4±0.6	3.8±0.1	81±8	4.1
Recycled GTR-1	8.7±0.5	3.1±0.2	119±4	3.4
Recycled GTR-3	10.8±0.7	2.9±0.1	168±12	2.9
Recycled GTR-5	9.3±0.2	2.4±0.1	166±6	2.3

Fig S1. Storage modulus versus temperature for recycled GTR with different TMSI

contents.