Materials Today Communications 4 (2015) 35–41

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

A combined experimental and molecular dynamics simulation study on the structures and properties of three types of styrene butadiene rubber

Yi Li[a,b], Youping Wu[a], Yanlong Luo[a], Tung W. Chan[c], Liqun Zhang[a], Sizhu Wu[a,*]

[a] Beijing Engineering Research Center of Advanced Elastomers, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] SINOPEC Beijing Research Institute of Chemical Industry, Beijing 100013, PR China
[c] Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg VA24061, USA

ARTICLE INFO

Article history:
Received 13 April 2015
Accepted 21 April 2015
Available online 27 May 2015

Keywords:
Styrene butadiene rubber
Molecular dynamics simulation
Hysteresis

ABSTRACT

The styrene/butadiene ratio of styrene butadiene rubber (SBR) greatly affects the inherent characteristics and material performance of the rubber. In this study, SBR vulcanizates comprising the same amount of carbon black and other additives were prepared with raw rubbers with different styrene/butadiene ratios. The mechanical and viscoelastic properties of the vulcanizates were investigated experimentally to analyze their performance as tire tread materials.

Besides, atomistic molecular dynamics (MD) simulation of the three SBRs in the bulk amorphous state were performed to study the effect of microstructure on material performance. The free volume, cohesive energy density (CED), mean square displacement (MSD), and glass transition temperature (T_g) of SBR models were simulated. The simulated free volume and T_g were consistent with the experimental results. Importantly, a high correlation between the simulated micro-structural characteristics and macro-performance was obtained by a linear fit of the calculated F_{sim} and loss factor tan δ values of the vulcanizates at 0 and 60 °C from the dynamic mechanical thermal analysis (DMTA) spectrum. The present study hopes to provide theoretical guidance to the chain structure design of SBR for tire tread applications.

1. Introduction

Styrene butadiene rubber (SBR), when protected by additives, is an elastomer with high wear resistance and aging stability. A large amount of automobile tires have been made from SBR [1,2]. The features of elastomers important for tire tread applications include excellent wet skid resistance, low rolling resistance, high wear resistance, and good general performance [3]. It is widely believed that the hysteresis of tread rubber, characterized by tan δ, at low temperatures is related to its wet skid resistance. Meanwhile, the hysteresis of tread composites at high temperatures is a parameter highly correlated with the rolling resistance of tires. Therefore, the wet skid resistance and rolling resistance of tread rubbers are generally characterized by the tan δ values of the rubber vulcanizates at a low temperature (0 °C) and high temperature (60 °C), respectively, obtained from the dynamic mechanical thermal analysis (DMTA) spectrum. It is favorable for a material to show a high tan δ at a low temperature (0 °C) for a high wet skid resistance, but a low tan δ at a high temperature (60 °C) for a low rolling resistance [4,5]. To date, many researchers have tried to improve the performance of tread rubbers by changing either the polymer structure [5,6] or the composition of the composites [1,7,8].

Although many factors affect the performance of rubber vulcanizates, the chemical structure of the rubber is the basic controlling factor. For SBR, the contents of the vinyl butadiene and styrene groups in the polymer chain affect the inherent elastomer characteristics such as glass transition temperature (T_g), hysteresis, and strength, thereby greatly influencing the performance of the rubber vulcanizates [9]. Hence, studies on the microstructure-inherent characteristics-macroscopic performance relationship of SBR are needed to better understand the mechanism behind the material performance and to provide theoretical guidance for material design.

Molecular simulation is one of the most promising methods to investigate the microstructure and to predict the properties of materials. Atomistic molecular dynamics (MD) simulation is of particular importance because it can provide direct quantitative information on both the microstructure and the dynamic

* Corresponding author. Tel.: +86 10 64444923.
E-mail address: wusz@mail.buct.edu.cn (S. Wu).

http://dx.doi.org/10.1016/j.mtcomm.2015.04.007
2352-4928/

properties of the materials [10]. MD simulation has been employed to complement experiments in the study of the structure of polymers and their composites. The simulation results indicate that with proper methods, the microstructure and properties of the models in the simulation are similar to those of the samples used by the experiments [11–16].

In this study, the atomistic models of three SBRs with different styrene/butadiene ratios (SBR1723N, SBR1756 and SBR1769E) were built. With the aid of MD simulation, the free volume, cohesive energy density (CED), mean square displacement (MSD), and T_g of the simulation models of these SBRs were calculated. Besides, three SBR compounds comprising the same amount of carbon black and other additives but with different styrene/butadiene ratios were prepared. The mechanical and viscoelastic properties of the rubber vulcanizates were measured and the experimental results of free volume and T_g were compared with the simulation results. To further study the effect of microstructure on material performance, attempts were made to establish a quantitative relationship between the microstructural characteristics of the simulation models and tan δ values of the vulcanizates at 0 and 60 °C in the DMTA spectrum.

2. Materials and methods

2.1. Experimental methods

2.1.1. Materials

The raw SBRs (SBR1723N, SBR1756, and SBR1769E) were supplied by the Research Institute of Petrochemical Technology (China), with styrene contents of 23.5%, 32.0%, and 40.0% by weight, respectively. The raw SBRs had already been extended with 37.5 phr of naphthenic oil. Table 1 summarizes the characteristics of the SBRs used in this study. For simplicity, the raw rubber, the compound, the vulcanizate, and the simulation model for SBR1723N are all denoted by SBR-1 in this paper, and those for SBR1756 and SBR1769E are denoted by SBR-2 and SBR-3, respectively. Carbon black (IRB 8) was purchased from Balentine Enterprises Inc. The other rubber additives were of commercial grade.

2.1.2. Sample preparation

The formulation used to prepare the rubber compounds was as follows: SBR 100 phr, naphthenic oil 37.5 phr, IRB 8 65.0 phr, zinc oxide (ZnO) 3.0 phr, stearic acid (SA) 2.0 phr, N-isopropyl-N'-phenyl-p-phenylenediamine (4010NA) 2.0 phr, paraffin 1.5 phr, accelerator CZ 1.5 phr, and sulfur 1.7 phr.

A rubber vulcanizate was prepared according to the following procedure: (1) The raw rubber which had already been extended with naphthenic oil was kneaded on a two-roll mill (Shanghai Rubber Machinery Works No. 1, Shanghai, China), (2) ZnO, SA, 4010NA, paraffin, and CZ were mixed into the rubber, (3) IRB 8 was mixed into the rubber, (4) sulfur was added into the mixtures for further mixing, and (5) the rubber compound was hot-pressed and vulcanized at 150 °C by an XLB-D350 × 350 Automatic Operation Vulcanizing Press (Huzhou Dongfang Machinery Co., Ltd. Zhejiang, China) for different curing times. The vulcanizing conditions for the compound were determined by an MR-C3 rotorless rheometer (Beijing Ruidayuchen Instrument Co., Ltd., Beijing, China).

2.1.3. Characterization

Positron annihilation lifetime spectroscopy (PALS) measurements were performed using a conventional fast–slow coincident spectrometer (EG&G ORTEC Co., USA) with BaF_2 as detector at room temperature. A 13 μCi ^{22}Na positron source sealed between aluminum foils was placed between two identical pieces of the sample. In each case, two million counts under each spectrum were recorded. The measured resolution of the lifetime spectrometer was found to be 194 ps. Samples for PALS measurements were the vulcanizates in the form of small disks with a diameter of 10 mm and a thickness of 1 mm.

The dynamic mechanical properties (temperature sweep) of the vulcanizates were determined by a VA3000 Dynamic Mechanical Thermal Analyzer (01dB-Metravib, France). The test area of the samples was 10 mm × 10 mm (length × wide). The thickness of the samples was 2 mm. The testing temperatures were from −80 °C to 80 °C, the heating rate was 3 °C/min, the frequency was 10 Hz, and the strain amplitude was 0.1% (operated in the tension mode).

The mechanical properties of the vulcanizates were measured according to ASTM D638 by a CMT4204 Electromechanical Universal Testing Machine (MTS Systems Co., Ltd., China). The crosshead speed was 500 mm/min. The test areas of a dumbbell-shaped tensile specimen and a nicked tear specimen were 25 mm × 6 mm and 100 mm × 19 mm (length × wide), respectively. The thickness of the samples was 2 mm. The hardness of the vulcanizates was measured with a HPE Shore AM/M Digital Hardness Tester (Bareiss, Germany).

The wear resistance of the vulcanizates was measured by an MZ-4061 Akron Abrader (Mingzhu Testing Machinery Co., Ltd., Jiangsu, China) according to Chinese standard GB/T 1689-82. The rotational speed of the rubber wheel spindle was 76 rpm, the acting force on the rubber wheel was 26.7 N, and the tilt angle between the rubber roll spindle and the grinding wheel spindle was 15°. The test was conducted at room temperature.

The dynamic compression heat of the vulcanizates was determined by a YS-III Compression Heat Built-up Tester (Aoqima Technological Development Co., Ltd., Beijing, China). The preheating temperature was 55 °C, the preheating time was 30 min, the compression time was 25 min, the frequency was 30 Hz, the stroke was 4.45 mm, and the load was 25 kg.

2.2. Molecular simulation method

For the MD simulations, the Amorphous cell and Discover modules of the Material Studio® suite software developed by Accelrys Software Inc., were used. All theoretical calculations were performed by using the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. COMPASS has been widely used to support the optimization and prediction of the structural, conformational, and thermo-physical condensed-phase properties of molecules including macromolecules [17,18]. The initial velocities of the atoms were set by using the Maxwell-Boltzmann profiles at 298 K [19].

Table 1
Structural parameters of raw SBRs.

	M_n (g/mol)	M_w (g/mol)	MWD	St[a] (mol%)	Bv[b] (mol%)	Cis-1,4[c] (mol%)
SBR-1	2.86×10^5	8.61×10^5	3.02	13.8	22.5	10.0
SBR-2	1.93×10^5	5.73×10^5	2.97	19.5	21.6	13.1
SBR-3	3.02×10^5	6.45×10^5	2.13	25.8	15.5	19.6

[a] Styrene content.
[b] Content of 1,2 butadiene.
[c] Content of cis-1,4 butadiene.