DEVELOPMENT OF PETROLEUM INDUSTRY BYPRODUCT SULFUR TO BE USED IN RUBBER VULCANIZATION

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ABSTRACT

In this research, the chemical structure of petroleum-based sulfur received from IRPC Plc. Co., Ltd. was investigated using various characterization techniques. Moreover, efficiency of petroleum-based sulfur as vulcanizing agent in 3 types of rubber matrices (i.e., NR, SBR, and NBR) was examined and compared with commercial natural-based sulfur and commercial petroleum-based sulfur coming from various manufacturers. Finally, in order to add value to the IRPC petroleum-based sulfur, a masterbatch of sulfur with TDAE oil as carrier was developed and then determined for its properties after being used in different rubber matrices. Enhancement in sulfur dispersion was focused and compared with uncoated petroleum-based sulfur.

The results measured from various techniques such as FT-IR, TGA, DSC, XRD, XRF, and XANES revealed that the chemical structure of petroleum-based sulfur possesses similarity to that of commercial natural-based sulfur with rhombic structure. Furthermore, the sulfur content of the petroleum-based sulfur was analogous compared with that of the commercial natural-based sulfur. The apparent quantity was approximately 97% as determined by SEM-EDX technique.

As a vulcanizing agent in different rubbers, the processability, mechanical properties, and dynamic properties of rubbers incorporated with the petroleum-based sulfur remained comparable to those incorporated with both the commercial natural-based and petroleum-based sulfurs. As a result, the petroleum-based sulfur received from IRPC Plc. Co., Ltd. possessed potential utilization as the vulcanizing agent in rubber as substitution for the commercial natural-based sulfurs.

Finally, the TDAE oil was used to coat the petroleum-based sulfur as dispersing agent. The ratio of sulfur:oil was kept constant at 80:20 %wt. The obtained results revealed the enhancement in dispersion of sulfur in rubber matrices. The crosslink density was increased leading to improvement in mechanical properties of vulcanizates whereas the processability remained unchanged. Therefore, development of TDAE oil-coated petroleum-based sulfur as a new product for the rubber industry is possible, which would be beneficial to IRPC Plc. Co., Ltd. as manufacturer of the TDAE oil and the petroleum-based sulfur.

KEY WORDS: SULFUR / VULCANIZATION / RUBBER / PETROLEUM / MECHANICAL AND DYNAMIC PROPERTIES

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การพัฒนากำมะถันที่เป็นผลิตภัณฑ์เหลือใช้จากกระบวนการกลั่นปิโตรเลียมในอุตสาหกรรมยาง

DEVELOPMENT OF PETROLEUM INDUSTRY BYPRODUCT SULFUR TO BE USED IN RUBBER VULCANIZATION

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บทคัดย่อ

ในงานวิจัยนี้ ได้ทำการศึกษาโครงสร้างทางเคมีของกำมะถันที่เป็นผลิตภัณฑ์เหลือใช้จากกระบวนการกลั่นปิโตรเลียมจากบริษัท ไออาร์พีซี จำกัด (มหาชน) ด้วยเทคนิคต่างๆ นอกจากนี้ยังทำการศึกษาสมบัติของกำมะถันจากปิโตรเลียมเมื่อถูกใช้เป็นสารเชื่อมขวางในยาง 3 ชนิด (ยางธรรมชาติ, ยางเอสบีอาร์, และยางไนไตรล์) โดยเปรียบเทียบกับกำมะถันจากธรรมชาติและกำมะถันที่มาจากการกลั่นปิโตรเลียมที่ขายในท้องตลาดจากหลากหลายผู้ผลิต ท้ายที่สุด ได้ทำการพัฒนากำมะถันจากปิโตรเลียมโดยเคลือบด้วยน้ำมันทีดีเออี (TDAE oil) เพื่อช่วยเพิ่มประสิทธิภาพในการกระจายตัวของกำมะถันในยาง และทำการศึกษาสมบัติของกำมะถันดังกล่าวที่ทำหน้าที่เป็นสารเชื่อมขวางเปรียบเทียบกับกำมะถันที่ไม่ได้ทำการเคลือบด้วยน้ำมันทีดีเออี

ผลการวิเคราะห์ด้วยเทคนิคต่างๆ เช่น FTIR, TGA, DSC, XRD, XRF, และ XANES พบว่ากำมะถันจากปิโตรเลียมมีโครงสร้างทางเคมีเหมือนกันกับกำมะถันที่ขายในท้องตลาดคือโครงสร้างแบบรอมบิก นอกจากนี้ ปริมาณของกำมะถันจากปิโตรเลียมก็มีปริมาณใกล้เคียงกันกับกำมะถันที่ขายในท้องตลาดคือประมาณ 97% ซึ่งวัดได้จากเทคนิค SEM-EDX

ในการทำหน้าที่เป็นสารเชื่อมขวางในยางแต่ละชนิด พบว่าสมบัติการขึ้นรูป สมบัติเชิงกล และสมบัติเชิงพลวัตของยางที่ใช้กำมะถันจากปิโตรเลียมเป็นสารเชื่อมขวาง มีค่าใกล้เคียงกันกับสมบัติของยางที่ใช้กำมะถันที่ขายในท้องตลาด (ทั้งกำมะถันจากธรรมชาติและกำมะถันจากปิโตรเลียม) เป็นสารเชื่อมขวาง จากผลการทดลองดังกล่าวสามารถสรุปได้ว่า กำมะกันจากปิโตรเลียมของบริษัท ไออาร์พีซี จำกัด (มหาชน) มีศักยภาพเพียงพอที่จะใช้ทดแทนกำมะถันเชิงการค้าชนิดอื่นในฐานะที่เป็นสารเชื่อมขวางในอุตสาหกรรมยางได้

ในส่วนท้าย ได้ทำการศึกษากำมะถันจากปิโตรเลียมที่เคลือบด้วยน้ำมันทีดีเออีเพื่อเป็นสารช่วยในการกระจายตัวในยาง โดยสัดส่วนของกำมะถันต่อน้ำมันที่ใช้คือ 80:20 เปอร์เซ็นต์โดยน้ำหนัก ผลการทดลองพบว่า การกระจายตัวของกำมะถันในยางดีขึ้นและความหนาแน่นเชื่อมขวางเพิ่มขึ้น ทำให้คุณสมบัติเชิงกลของยางวัลคาไนซ์สูงขึ้น ในขณะที่สมบัติการขึ้นรูปไม่เปลี่ยนแปลง ดังนั้นการพัฒนากำมะถันจากปิโตรเลียมเคลือบด้วยน้ำมันทีดีเออี เพื่อเป็นผลิตภัณฑ์ใหม่ในอุตสาหกรรมยางสามารถทำได้ ซึ่งเป็นประโยชน์ต่อบริษัท ไออาร์พีซี จำกัด (มหาชน) อย่างยิ่ง ในฐานะผู้ผลิตทั้งกำมะถันจากปิโตรเลียมและน้ำมันทีดีเออี

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LIST OF ABBREVIATIONS

α-S_8	Orthorhombic sulfur
β-S_8	Monoclinic sulfur
γ-S_8	Monoclinic sulfur
H_2S	Hydrogen sulfide
O_2	Oxygen
H_2O	Water
SO_2	Sulfur dioxide
CV	Conventional vulcanization
EV	Efficient vulcanization
Semi EV	Semi-efficient vulcanization
XANES	X-ray absorption near-edge spectroscopy
NEXAFS	Near-edge x-ray absorption fine structure spectroscopy
TEY	Total electron yield
PEY	Partial electron yield
AEY	Auger electron yield
FY	Fluorescence yield
I	Intensity of transmitted photons
I_0	Intensity of incident photons
PC	Polycarbonate
PBT	Poly(butylene terephtharate)
ZDEC	Zinc diethyldithiocarbamate
NR	Natural rubber
SBR	Styrene-butadiene rubber
NBR	Nitrile rubber
ZnO	Zinc oxide
TBBS	*N*-tert-butyl-2-benzothiazolesulfenamide
TDAE	Treated distillate aromatic extract oil

LIST OF ABBREVIATIONS (cont.)

IRPC-PS	Petroleum-based sulfur
RS	Elemental Sulfur
M101	Elemental Sulfur
M105	Elemental Sulfur
SGS	Elemental Sulfur
SP-400	Elemental Sulfur
DF325	Elemental Sulfur
DF5(325)	Elemental Sulfur
SM-400	Elemental Sulfur
FT-IR	Fourier transform infrared spectrometer
DRIFT	Diffuse reflectance infrared fourier transform
DSC	Differential scanning calorimeter
TGA	Thermogravimeter
XRD	X-ray diffractometer
XRF	X-ray fluorescence
SEM-EDX	Scanning electron microscope equipped with energy dispersive x-ray fluorescence spectrometer
SXRMB	Soft x-ray microcharacterization beam-line
MDR	Moving die rheometer
t_{s2}	Scorch time
t_{c90}	Cure time
RPA	Rubber process analyzer
G’	Storage shear modulus
G”	Loss shear modulus
Tan δ	Loss factor
DMA	Dynamic mechanical analyzer
E’	Elastic modulus
E”	Loss modulus

LIST OF ABBREVIATIONS (cont.)

S	Swelling ratio
w_1	Mass of rubber before swelling
w_2	Mass of the swollen rubber
ρ_d	Rubber density before swelling
ρ_s	Solvent density
υ_r	Volume fraction of rubber in the swollen network
υ_e	Network chain density
υ_1	Molar volume of solvent
χ_1	Flory–Huggins interaction parameter between rubber and solvent
OC	TDAE oil-coated petroleum-based sulfur
OA	Conventional petroleum-based sulfur in which TDAE oil is added directly during the mixing cycle

CHAPTER I
INTRODUCTION

Generally, raw rubber cannot be used as received because of its unstable shape, low elasticity, and poor mechanical properties. Thus, the raw rubber needs to be transformed to vulcanized rubber through vulcanization process before being used [1–13].

The vulcanization process results in crosslink structure of rubber molecules giving high elasticity and high stability at ambient temperature [1–13]. Typically, the vulcanization process originates from adding vulcanizing agents such as sulfur or peroxide into rubber compounds and then heating together with giving pressure to initiate chemical reaction [1–17]. Generally, the vulcanization process can be divided into two main systems depending on types of vulcanizing agent, i.e., sulfur, and peroxide [1–6, 8–19]. The sulfur system is preferential only for unsaturated rubbers, whereas the peroxide system is functional for both unsaturated and saturated rubber [1, 3-5, 8-9, 11-14]. The sulfur system, nevertheless, offers low investment cost, good mechanical properties as well as ease of curing behavior adjustment compared with the peroxide system [1–6, 8–11, 14–21]. These are the reasons why the sulfur vulcanization is widely used in rubber industry.

The sulfur used in industry originates from two main sources, i.e., natural resource and petroleum refinery [22 – 34]. The sulfur coming from the former is a major source of sulfur widely used in rubber industry while that from the latter is generally treated as by-product from refinery process. In the view of petroleum refinery, sulfur containing in crude oil has to be eliminated because such sulfur causes corrosion in machine as well as environmental pollution such as acid rain [23, 25–29, 32–39].

In Thailand, main products of large refinery companies include gas and oil used as fuel in car engine. Nevertheless, the sulfur gained from refinery process is still treated as by-product, and usually sold at low price for preparing sulfuric acid as reagent. In the view of rubber technology, the petroleum-based sulfur may possess a potential utilization as vulcanizing agent in rubber. The objectives of this research are therefore to increase value and make full use of petroleum-based sulfur by physical modification with different techniques to suit the rubber application. Also, attempts to modify the petroleum-based sulfur to practically match the vulcanization in rubber industry are carried out. The research focuses on the study of chemical structure and properties of petroleum-based sulfur compared with commercial rhombic sulfurs as vulcanizing agent in natural rubber as well as synthetic rubbers.

CHAPTER II
OBJECTIVES

The objective of this research aims to study the potential utilization of petroleum-based sulfur as vulcanizing agent compared with commercial rhombic sulfurs in rubber industry. The study is divided into 3 main parts; (i) characterization of petroleum-based sulfur, and (ii) investigation of capability of petroleum-based sulfur as vulcanizing agent in rubber, and (iii) the development of oil-coated petroleum-based sulfur as a new product.

CHAPTER III
LITERATURE REVIEW

This chapter is primarily concerned with reviews of 3 major areas. The first section is a general introduction of the sulfur used in the present study. Sources of sulfur and chemical structure are also included. The second section provides a role of sulfur in rubber industry’s view point. The vulcanization systems of sulfur are described. The last section is the principle of X-ray absorption near-edge spectroscopy (XANES) applied in rubber research. The previous works related to the use of XANES to characterize sulfur in rubber are required.

3.1 Sulfur

Sulfur is classified as non-metal element in VIA group having yellow crystal structure [22–25, 27–31, 40–41]. Generally, the sulfur possesses several allotropes, but S_8 ring structure is abundant in nature called cyclooctasulfur [22–25, 27–28, 30–31, 40–41]. The S_8 molecule has a crown-shaped, puckered conformation as illustrated in Figure 3.1. Also, the sulfur can be found in other forms such as sulfide or sulfate [22–25, 27–32]. Typically, the sulfur is very beneficial in commerce, for example, as an ingredient in gunpowder, match, insecticide, and especially rubber industry [22–25, 27–32].

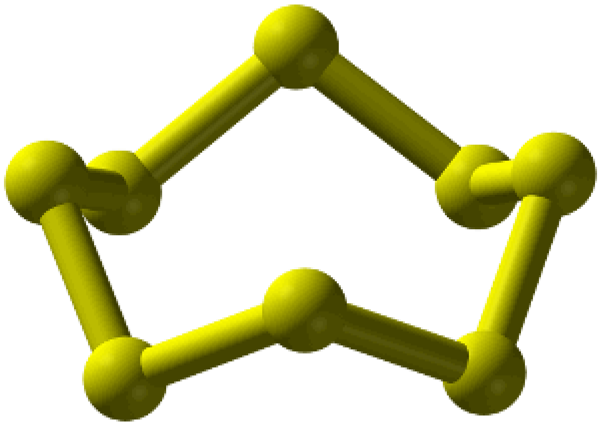


Figure 3.1 Crown-shaped of S_8 molecule [22]

3.1.1 General knowledge on sulfur

As aforementioned, the sulfur has several allotropes, but natural abundance is found in the form of S_8 ring structure. Moreover, the S_8 ring structure can be categorized based on its crystal structure including orthorhombic (α-S_8), monoclinic (β-S_8), and monoclinic (γ-S_8) [23–25, 27–32, 40]. Generally, the α-S_8 is easily found in nature more than other forms because of its high stability at ambient temperature [23–25, 27–32, 40]. Furthermore, the α-S_8 can transform to the β-S_8 at the temperature of 96^{o}C which is stable up to melting temperature of approximately 120^{o}C, and the transformation is reversible [23–25, 27–32, 40]. Geometry of three types of sulfur is almost the same, although bond lengths and bond angles are influenced by the different packing environments as tabulated in Table 3.1.

Table 3.1 Molecular structure parameters of the S_8 molecule [30]

Allotrope	α-S_8	β-S_8[a]		γ-S_8[b]	
		o	d	I	II
Bond lengths (pm)	204.6±3	204.8±2	204.2±4.4	204.6±9	204.5±9
Bond angles (^{o})	108.2±6	107.7±7	108.3±1.6	108.0±4	107.5±4
Torsion angles (^{o})	98.5±19	99.1±1.7	98.3±2.2	98.6±5	99.4±5
Temperature (^{o}C)	25	-55[c]		~27	

[a] The letter “o” and “d” represent molecules of β-S_8 at ordered and disordered positions, respectively

[b] I and II refer to the two independent molecules of γ-S_8

[c] Data for the disordered structure above the transition temperature of $T_c \approx -75^oC$

3.1.2 Sources of sulfur

Typically, the sulfur widely used in industry originates from two main sources; i.e., natural source and natural gas or petroleum refinery [22–34]. The sulfur coming from the former is a major source of sulfur widely used in industry while that the latter is generally treated as by-product and sold at low price for preparing sulfuric acid as reagent.

3.1.2.1 Natural-based sulfur

Elemental sulfur is found easily in nature such as underground. It is believed that such sulfur is a by-product from decomposition of sulfur compound elements by anaerobic bacteria for a long time. Process used to recover sulfur from the natural source is the Frasch Process as shown in Figure 3.2 [22–25, 27–31, 41]. Brief explanation of this process is as follows: superheated water and compressed air are passed through a long pipe to sulfur deposit. The sulfur is melted by hot water and pushed to the ground surface via another huge pipe together with the hot water. In addition to the underground source, the sulfur is found in volcanic area.

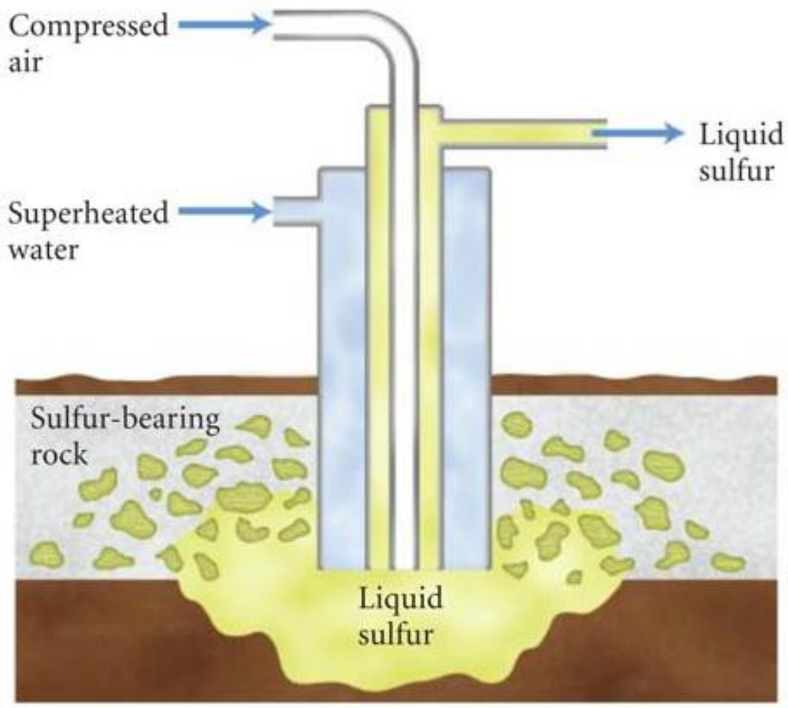


Figure 3.2 The Frasch Process [41]

3.1.2.2 Petroleum-based sulfur

The sulfur coming from this process is treated as by-product. Reagent is hydrogen sulfide (H_2S) is a component of natural gas [26, 32–38]. H_2S can dissolve in organic solvent, and can react with oxygen (O_2) or water (H_2O) in atmosphere resulting in acid rain if released to the air [26, 32–38]. Therefore, there is a regulation in order to forbid refinery companies releasing the H_2S into the atmosphere. For solving such a problem, there is a process to transform H_2S into sulfur called sulfur recovery via Claus Process [22, 34–38, 41–43].

The Claus Process consists of 2 steps; thermal step and catalytic step. First, the H_2S is burned with air in a furnace at the temperature of 1300^{o}C to form sulfur dioxide (SO_2). Then, hot gas from the combustion chamber is quenched to from liquid sulfur which is collected in container at the temperature of 130^{o}C for shipment to end users. The remaining gases are then sent to catalyst beds undergoing SO_2 to form the elemental sulfur. More than 2 stages are used in this series to ensure that all gases are completely converted to elemental sulfur. The chemical reaction of both thermal and catalytic steps are exhibited below.

Reaction of thermal step:

$$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$
$$2H_2S + SO_2 \longrightarrow 3/8S_8 + 2H_2O$$

Reaction of catalytic step:

$$2H_2S + SO_2 \longrightarrow 3/8S_8 + 2H_2O$$

Example of plant layout of sulfur recovery unit is illustrated in Figure 3.3. This layout is the plant layout of IRPC (Public) Co., Ltd. located at Rayong Province, Thailand.

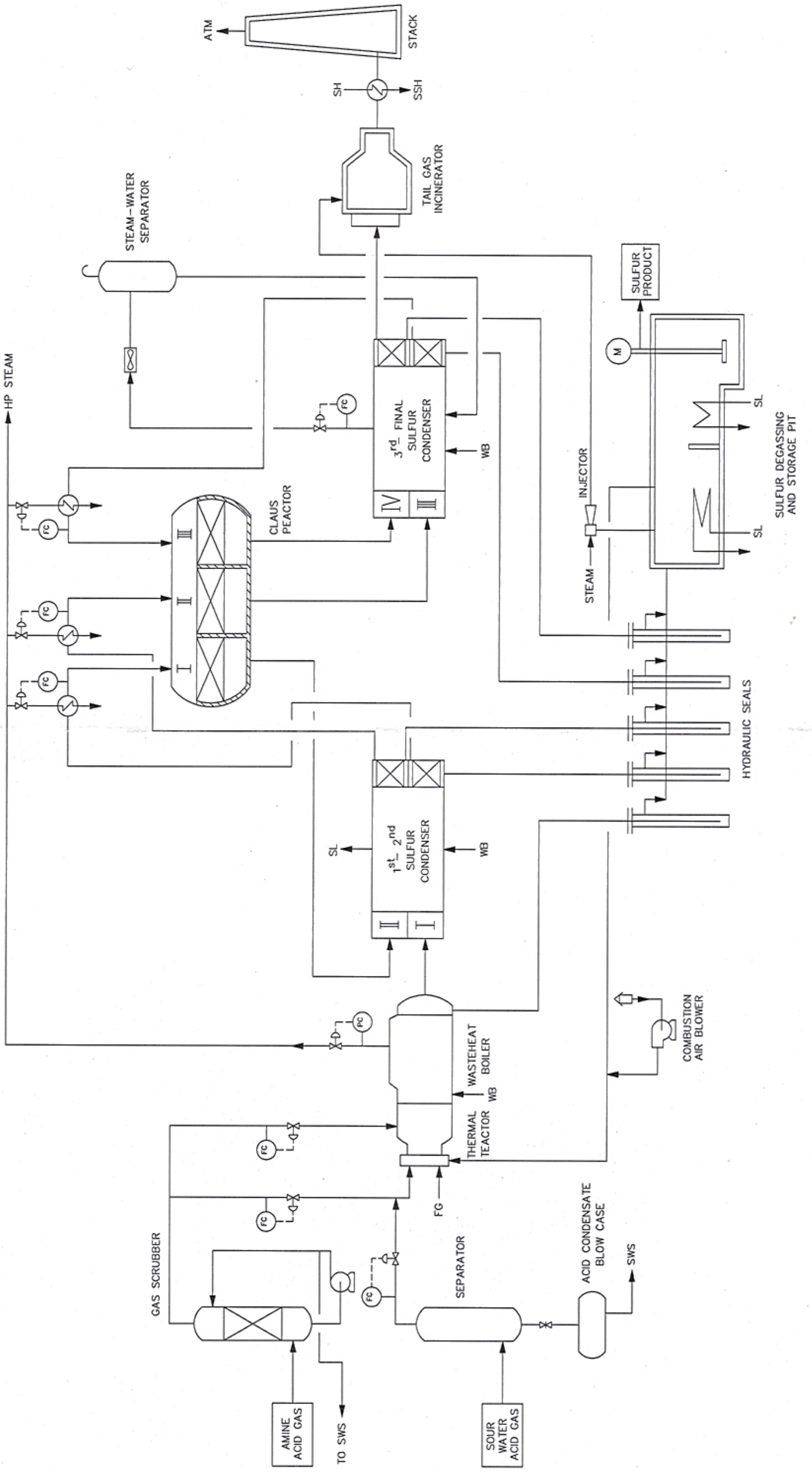


Figure 3.3 Example of plant layout of sulfur recovery unit of IRPC (Public) Co., Ltd

3.2 Vulcanization process

Generally, raw rubber is not usable as received without passing through a vulcanization process due to its low strength and poor shape recovery after deformation [1–13]. The vulcanization is the chemical reaction resulting in chemical bonds between rubber molecules called crosslink. The crosslink causes changing of rubber molecules from random coil to three-dimensional network which possesses high strength and good elasticity. Regularly, there is chemical added to the raw rubber, giving the crosslink. Such a chemical is known as curing agent or vulcanizing agent. There are many types of vulcanizing agent used in rubber industry; however, sulfur and peroxide are widely used [1–21]. Nevertheless, in most rubber industries, the sulfur is preferential to peroxide, because of good vulcanizate mechanical properties, and ease of cure adjustment of compounds. Therefore, this research is merely focused on sulfur vulcanization.

3.2.1 Sulfur vulcanization

As mentioned above, sulfur possesses many advantages to industry, especially rubber industry. It is used as vulcanizing agent through vulcanization process usually known as sulfur vulcanization.

The sulfur vulcanization was first discovered by Charles Goodyear. He found that rubber mixed with sulfur, and then aired under suitable pressure about 2 – 4 hours gave a rubber vulcanizate [7]. Therefore, there has been development of vulcanization techniques. On the first step of vulcanization research, there was only sulfur added leading to a long cure time. Then, there was a development by the use of accelerators together with sulfur offering shortened time in vulcanization process [1–6, 8–19, 44–45]. The amount of added accelerators plays a significant role in properties of rubber compounds and products depending on the ratio of sulfur to accelerator [1–6, 8–21, 44–46].

Presently, sulfur vulcanization is typically divided into 3 major systems; i.e., Conventional vulcanization (CV), Efficient vulcanization (EV), and Semi-efficient vulcanization (Semi EV) [1–6, 8–14, 17, 20, 44–45]. The difference between such systems is the ratio of sulfur to accelerator added. The ratio plays important role in sulfidic linkage structure in rubber vulcanizate including crosslink density and thus product properties. The ranges of the ratio in each system are summarized in Table 3.2, and the influences of crosslink density on vulcanizate properties are shown in Figure 3.4.

Table 3.2 Ratios of accelerator to sulfur of CV, EV, and Semi EV vulcanization systems [14]

System	Sulfur (S, phr*)	Accelerator (A, phr*)	A/S ratio
CV	2.0-3.5	1.2-0.4	0.1-0.6
Semi EV	1.0-1.7	2.4-1.2	0.7-2.5
EV	0.4-0.8	5.0-2.0	2.5-12.0

*part per hundred of rubber

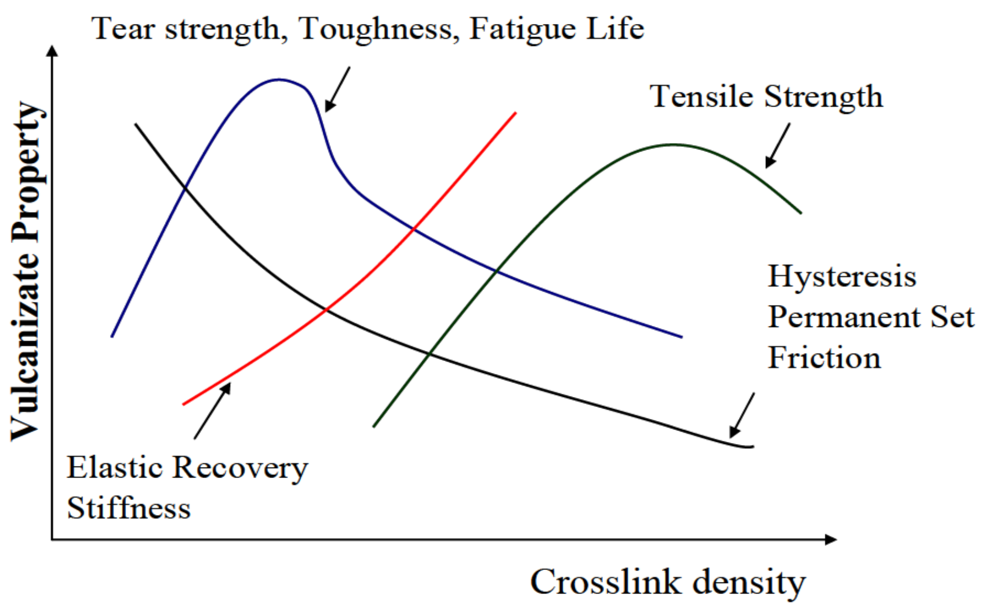


Figure 3.4 The influences of crosslink density on vulcanizate properties [3, 12]

3.2.1.1 Conventional vulcanization (CV)

Referred to Table 3.2, the CV system has sulfur content higher than accelerator giving dominantly the polysulfidic linkage in rubber vulcanizates. The polysulfidic linkage offers the rubber vulcanizate with good mechanical properties because of its flexibility of S-S bond [1, 3–5, 8–9, 11–14, 44–45].

3.2.1.2 Efficient vulcanization (EV)

In the case of EV system, accelerator content is higher than sulfur resulting dominantly in mono- and disulfidic linkages. The advantage of such linkages is good heat resistance, due to the high bond energy of C-S bond [1, 3–5, 8–9, 11–14, 44–45].

3.2.1.3 Semi-efficient vulcanization (Semi EV)

The ratio of sulfur to accelerator in this system is somewhat kept equal. The sulfidic linkages obtained are combination of mono-, di-, and polysulfidic linkages. The properties of vulcanizates received from this system are therefore in between those vulcanized with CV and EV systems [1, 3–5, 8–9, 11–14, 44–45].

3.2.2 Previous works on sulfur vulcanization

As aforementioned, the curing systems (CV, EV, and Semi-EV) play a significant role in properties of vulcanizates. Study on cure characteristics prepared with different systems is capable of predicting the properties of vulcanizates. For example, González et al [20] studied effect of curing systems in natural rubber, and found that the CV system gave cure reversion whereas the EV system showed cure plateau (normal curve) characteristics as represented in Figure 3.5. However, CV system gave higher mechanical properties than EV system. Similar results were reported by Rohanayahya et al [21] investigating the effect of curing systems on thermal degradation of natural rubber. The results of vulcanizates with CV system revealed, before thermal aging, superior mechanical properties to those with the EV system. On the contrary, after thermal aging, the results were in the other way round.

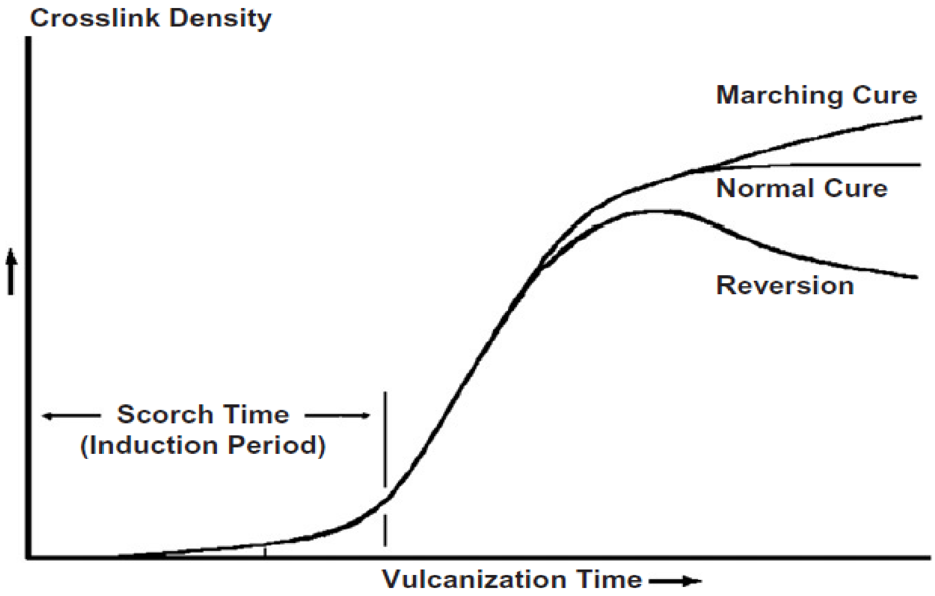


Figure 3.5 Rheometer cure curve [3]

3.3 X-ray absorption near-edge spectroscopy (XANES)

X-ray absorption near-edge spectroscopy (XANES), also known as Near-edge X-ray absorption fine structure spectroscopy (NEXAFS), is one of the very useful synchrotron-based techniques. It is used to investigate the absorption of electromagnetic radiation by excitation of core electrons into unoccupied bound or continuum states [47–52]. The XANES is widely used in many fields of research such as biological, agricultural, and environmental research [48–49, 51, 53–56]. In addition, this technique is applied presently in material research [39, 48–49, 54, 57–59]. For better understanding, the principle of the XANES is described as follows:

Absorption process is a major phenomenon of this technique. Such a process occurs when a sample is subjected to X-ray irradiation. An electron at core level can absorb the X-ray and then is excited to the upper level such as Rydberg state or is ionized resulting in a core hole. Subsequently, the core hole is refilled by an electron. The excess energy can be carried away by another electron (Auger decay) or by photon emission (Fluorescence) as illustrated in Figure 3.6. Measurement of Auger or Fluorescence decay can be used to measure the XANES spectra.

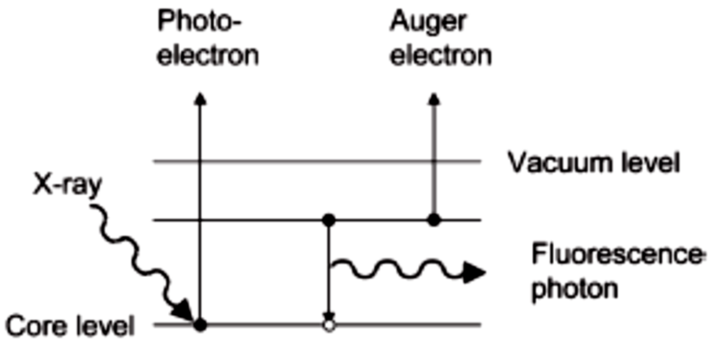


Figure 3.6 Energy diagram of photo absorption process [48–49]

As mentioned, XANES measures X-ray absorption of X-ray resulting from changing of energy state from core level to other states such as Rydberg state as exhibited in Figure 3.7. Such a change is a characteristic of an element, depending significantly on chemical environment of atom. Therefore, XANES is a very useful tool for analyzing the atomic fingerprint as well as chemical composition [50–52].

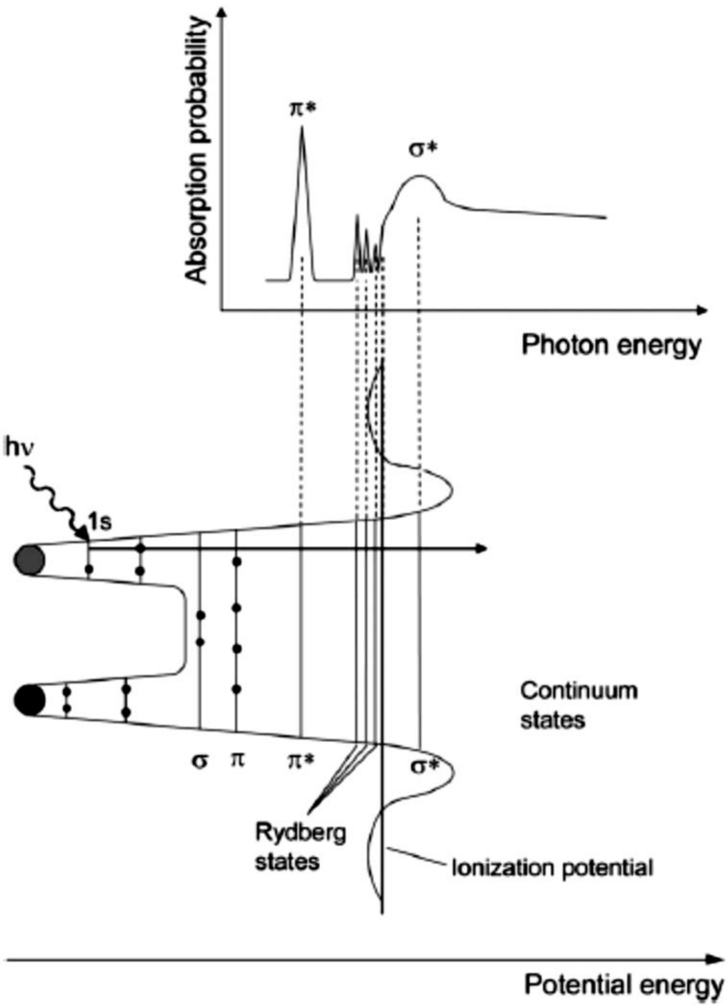


Figure 3.7 Schematic potential and corresponding XANES K-shell spectrum of a diatomic molecular (sub) group [48]

XANES spectra can be obtained in several ways depending on detection. Generally, the detection includes transmission detection and fluorescence detection or electron detection. As for the electron detection, it can be divided into Total Electron Yield (TEY), Partial Electron Yield (PEY), and Auger Electron Yield (AEY) detection schemes based on the measured energy regime of the electrons. For transmission detection, the sample is subjected between an X-ray source and a detector. The intensity of transmitted photons (I) is measured compared to that of incident photons (I_0). This method requires a thin layer sample in which the photons can penetrate easily. On the other hand, fluorescence detection or fluorescence yield (FY) is based on the secondary fluorescence process occurring as a result of core-hole relaxation. However, thick sample is not appropriate for this detection owing to the self-absorption resulting in the loss of fluorescence intensity. In addition to transmission or fluorescence detection, the electron detection resulting from ejection of electrons after the relaxation of the core hole can be tracked to measure the XANES spectra. Total electron yield (TEY) is a very simple technique because all electrons having enough energy to overcome the work function of ejection from the surface are measured using the sample drain current. Regarding the partial electron yield (PEY), this technique is a detection of low kinetic energy electrons coming from the substrate as well as the more energetic electrons created at the very top layers of the surface. In Auger electron yield (AEY), the Auger electrons are detected with an energy analyzer detector. This technique possesses the highest surface sensitivity. In this dissertation, FY and TEY detection are used to measure the XANES spectra as represented in Chapter V.

In the view of polymer technologists, the XANES is one of the advantageous techniques for characterizing chemical sensitivity, orientational sensitivity, and quantitative analysis. For instance, the XANES can be used to determine the composition of polycarbonate (PC) blended with poly(butylene terephtharate) (PBT) as depicted in Figure 3.8.

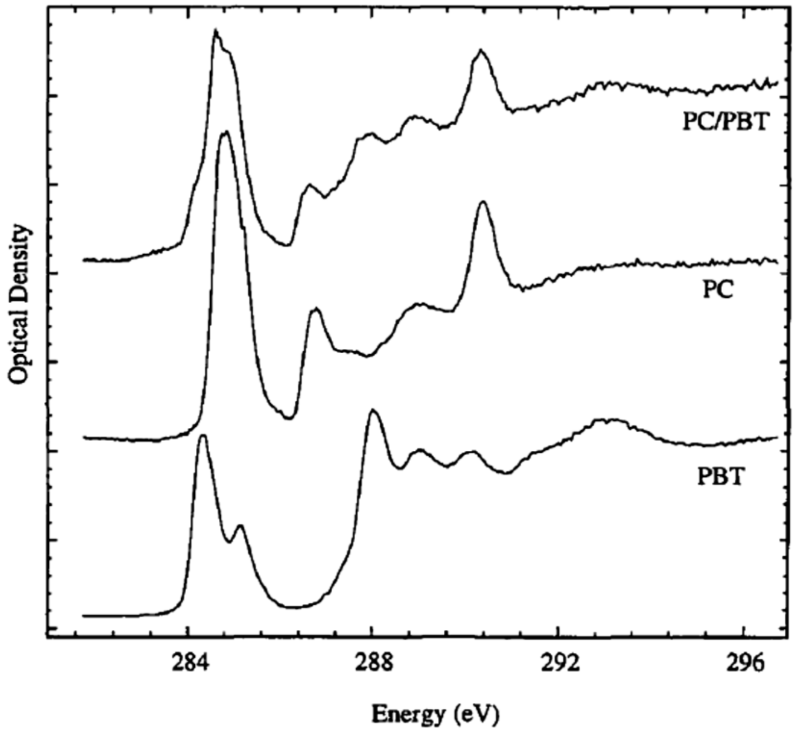


Figure 3.8 C 1s XANES spectrum of PC/PBT blend in comparison to the C 1s XANES spectra of PC and PBT homopolymer [47]

Moreover, the XANES plays an important role in rubber research. It can be applied to reveal the type of sulfidic linkage formed, or the degree of sulfur crosslinking in rubber. For example, the XANES is used to determine the degree of sulfur crosslinking in natural rubber filled with silica [60]. The results reveal that the sulfur crosslinking in the system with higher silica content shows lower absorption peak than that with lower silica content as illustrated in Figure 3.9. This is because the silica can absorb sulfur on its surface resulting in decreased degree of crosslinking [60].

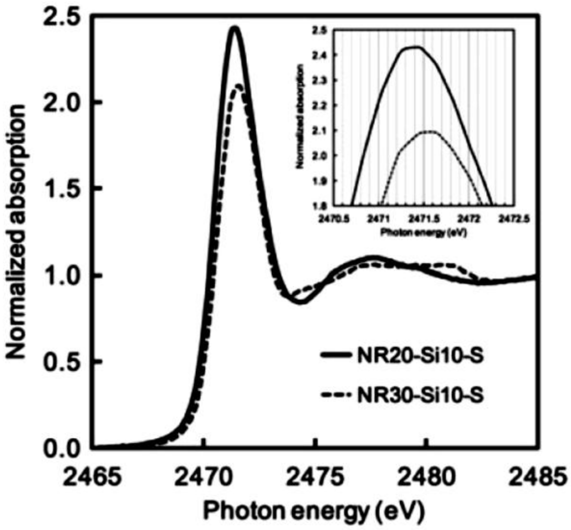


Figure 3.9 Sulfur K-shell XANES spectra of NR filled with different silica contents [60]

3.4 Previous works of XANES on study of sulfur vulcanization

Recently, there have been a number of research studied sulfur structure in rubber by the use of XANES technique [46, 61–63]. The obtained results reveal good sensitivity and reproductivity of the sulfur K-shell in both rubber compound and vulcanizate [46, 61–63]. In the case of oxidative degradation of NR, the XANES technique possesses good capability [64]. It is found that XANES could be used to monitor oxidative degradation by ozone. The physico-chemical properties correlated with mechanical properties of NR film also gave high strength in the case of using zinc diethyldithiocarbamate (ZDEC). Similar findings were reported elsewhere [62–63]. With thermal degradation of sulfur crosslink in SBR, there was appearent reversion together with production of cyclic sulfanes. In addition, the presence of carbon black and the amount of S_8 / *N*-tert-butyl-2-benzothiazolesulfenamide (TBBS) affected such degradation in SBR. By this means, the XANES technique offers good sensitivity and possesses capability to study the sulfur structure in rubbers.

CHAPTER IV
MATERIALS AND METHODS

4.1 Materials

Rubbers and the chemical ingredients used in the present work are tabulated in Table 4.1.

Table 4.1 Lists of rubbers and chemical ingredients used in this study

Chemical name	Abbreviation	Grade/Supplier
Natural rubber	NR	STR 5L /Union Rubber Product Co., Ltd., Thailand
Styrene-butadiene rubber (23.5% Styrene)	SBR	SBR 1502 /BST Elastomers Co., Ltd., Thailand
Nitrile rubber (35% Acrylonitrile)	NBR	JSR 230SL /JSR Co., Ltd., Japan
Zinc oxide	ZnO	Chemmin Co., Ltd., Thailand
Stearic acid	-	Chemmin Co., Ltd., Thailand
N-tert-butyl-2-benzothiazolesulfenamide	TBBS	Reliance Technochem (Flexsys) Co., Ltd., Thailand
Treated Distillate Aromatic Extract oil	TDAE	IRPC Plc., Thailand
Petroleum-based sulfur	IRPC-PS	IRPC Plc., Thailand
Elemental Sulfur (99.94% Sulfur)	RS	Chemmin Co., Ltd., Thailand
Elemental Sulfur; MIDAS 101 (99% Sulfur; 0.99% Oil)	M101	Miwon Commercial Co., Ltd., Korea
Elemental Sulfur; MIDAS 105 (95.36% Sulfur; 4.64% Oil)	M105	Chem-Lube Intertrade Co., Ltd., Thailand

Table 4.1 Lists of rubbers and chemical ingredients used in this study (Cont.)

Chemical name	Abbreviation	Grade/Supplier
Elemental Sulfur; SULFUR GOLDEN STAR (99.9% Sulfur)	SGS	Cosan Co., Ltd., Thailand
Elemental Sulfur; MIDAS SP-400 (99.9% Sulfur)	SP-400	Miwon Commercial Co., Ltd., Korea
Elemental Sulfur; SAMU-DF (325 Coated Oil) (98.5% Sulfur; 1% Oil)	DF325	Saemwoo Chemical Mfg. Corp., Philippines
Elemental Sulfur; SAMU-DF5 (325 Coated Oil) (94.5% Sulfur; 5% Oil)	DF5(325)	Saemwoo Chemical Mfg. Corp., Philippines
Elemental Sulfur; SAMU-400 (99.9% Sulfur)	SM-400	Saemwoo Chemical Mfg. Corp., Philippines

4.2 Equipment

The equipment used in this work is detailed in Table 4.2.

Table 4.2 List of the equipment used in this study

Equipment	Model
Fourier transform infrared spectrometer (FT-IR)	Bruker Equinox 55, USA
Differential scanning calorimeter (DSC)	Universal V4.7A TA Instruments model Q200 V24.4 Build 116, USA
Thermogravimeter (TGA)	Mettler Toledo model TGA/SDTA851^{e}, USA
X-ray diffractometer (XRD)	Bruker AXS Model D8 Discover, USA

Table 4.2 List of the equipment used in this study (Cont.)

Equipment	Model
X-ray fluorescence spectrometer (XRF)	Bruker AXS S4 EXPLORER WDS, USA
Scanning electron microscope equipped with energy dispersive x-ray fluorescence spectrometer (SEM-EDX)	JSM-5800LV, Japan
X-ray absorption near-edge spectrometer (XANES)	Soft X-ray Microcharacterization Beam-line (SXRMB), Canada
Two-roll mill	LabTech model LRM 150, Thailand
Moving die rheometer (MDR)	TechPro MD+, USA
Rubber process analyzer (RPA)	RPA2000, Alpha Technologies, USA
Hydraulic hot press	Carver, Inc., USA
Hardness tester	Wallace Shore A durometer, UK
Dynamic Mechanical Analyzer (DMA)	GABO EPLEXOR 25N, Germany
Universal testing machine	Instron (Model 5566), USA
Goodrich flexometer Model II	Alpha Technologies, USA

4.3 Experimental

4.3.1 Characterization of sulfur characteristics

The techniques used to characterize the chemical structure of sulfur are detailed below.

4.3.1.1 Fourier transform infrared spectroscopy (FT-IR)

The petroleum-based sulfur was determined for its chemical structure by the use of FT-IR under a Diffuse Reflectance Infrared Fourier Transform (DRIFT) mode at 25^oC.

4.3.1.2 Differential scanning calorimetry (DSC)

The DSC technique was used to investigate melting behavior of sulfurs. Temperature was scanned from 40^oC to 160^oC under nitrogen atmosphere at heating rate of 10^oC/min.

4.3.1.3 Thermogravimetry (TGA)

Thermal behavior of petroleum-based sulfur was examined using TGA. Temperature was scanned from ambient temperature to 600^oC under nitrogen atmosphere. After 600^oC, the atmosphere was switched to oxygen, and the test was carried out until 800^oC. The heating rate used was 20^oC/min.

4.3.1.4 X-ray diffraction spectroscopy (XRD)

The XRD technique was utilized to determine the crystal structure of both sulfurs. The test was carried out at 25^oC, and the scanned angle (2θ) was varied from 5^o to 60^o.

4.3.1.5 X-ray fluorescence spectroscopy (XRF)

This technique was used to investigate the characteristics of sulfurs. The test was conducted at 25^oC, and the binding energy was measured. The results obtained were analyzed qualitatively and quantitatively.

4.3.1.6 Scanning electron microscopy equipped with energy dispersive x-ray fluorescence spectroscopy (SEM-EDX)

Sulfurs were examined for determining the quantity and quality of their elemental composition. The test was carried out at ambient temperature under vacuum.

4.3.1.7 X-ray absorption near-edge spectroscopy (XANES)

This technique was used to characterize chemical structure of all sulfurs by TEY detection, and to investigate network structure of sulfur in vulcanized rubbers by FY detection. The test was carried out at ambient temperature using vacuum system with energy range of 1.7 – 10 keV. A Si(111) double-crystal monochromator was used for selecting the photon energy, and the energy resolution ($\Delta E/E$) was around $1x10^{-4}$. The sulfur powders were placed on carbon tape on the sample holder while the vulcanized sheets were cut into 10 mm x 5 mm before placing on a sample holder. The photon beam size was 5 mm x 1 mm. All XANES spectra were recorded around the sulfur K-edge in vacuum environment, and were averaged as well as normalized using ATHENA software version 0.8.056. [65] The XANES technique was conducted at the Soft x-ray microcharacterization beam-line (SXRMB Beam-line), Canadian Light Source, and the beam-line layout was illustrated in Figure 4.1.

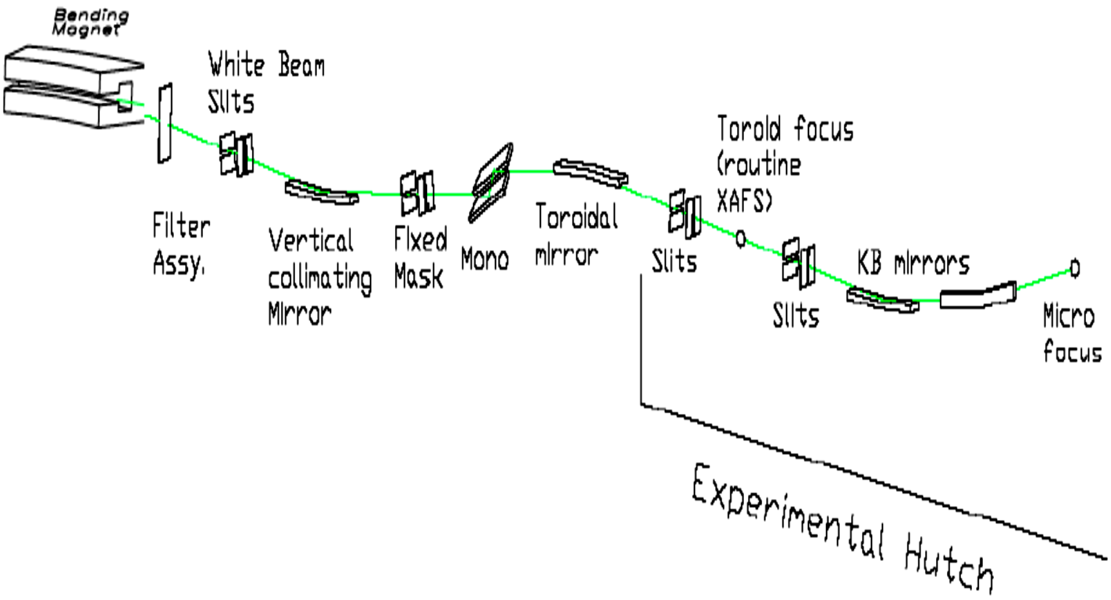


Figure 4.1 Layout of SXRMB Beam-line located at Canadian Light Source [66]

4.3.2 Preparation of oil-coated petroleum-based sulfur (OC)

The IRPC-PS was mixed with TDAE oil at the ratio of IRPC-PS:TDAE oil ratio of 80:20 %wt (denoted as OC).

4.3.3 Preparation of rubber compounds

The rubber compounds were prepared using two-roll mill at 50^{o}C. The mixing time was kept constant at 10 min, and the compound formulations were tabulated in Table 4.3 and Table 4.4. The rubber used in this research consisted of natural rubber (NR), nitrile rubber (NBR), and styrene-butadiene rubber (SBR). In the case of Part 2, types of sulfur used were also varied as mentioned previously. In Part 3, only 2 types of sulfur, namely, IRPC-PS and OC were used.

Table 4.3 Compound formulations used in Part 2

Chemical ingredients	**Loading (phr*)**
Rubber	100
ZnO	3
Stearic acid	1
TBBS	1
Sulfur	1.75

*phr =part per hundred of rubber

Table 4.4 Compound formulations used in Part 3

Chemical ingredients	Loading (phr)	
	General recipe	Oil-coated recipe
Rubber	100	100
ZnO	3	3
Stearic acid	1	1
TBBS	1	1
Sulfur (IRPC-PS)	1.40	-
TDAE oil	0.35	-
Oil-coated sulfur (OC)	-	1.75*

*Active sulfur content was equivalent to 1.40 phr

4.3.4 Measurement of rubber compound properties

4.3.4.1 Viscoelastic properties

The viscoelastic properties of the rubber compounds were investigated using Rubber Process Analyzer (RPA). Storage modulus (G'), loss modulus (G"), and loss factor (tan δ) of the rubber compounds were measured as a function of strain (from 0.56 to 1200%) at test frequency and temperature of 1 Hz and 100^{o}C, respectively.

4.3.4.2 Cure characteristics

The vulcanization properties of the rubber compounds were monitored using Moving Die Rheometer (MDR) at 150^{o}C as per ASTM D 5289. Scorch time (t_{s2}) and cure time (t_{c90}) of the rubber compounds were determined.

4.3.5 Vulcanization of the rubber compounds

The rubber compounds were vulcanized by hydraulic hot-press at 150^{o}C under molding pressure of 150 kg/cm^2. The vulcanization time used was the optimum cure time (t_{c90}) as pre-determined from the MDR. The vulcanizates prepared were used for further measurement of properties.

4.3.6 Measurement of vulcanizate properties

The properties of the rubber vulcanizates were measured as follows.

4.3.6.1 Determination of crosslink density

The vulcanizates were cut into rectangles with dimensions of 10x10x2 mm^3, and then weighed before and after immersing in good solvent of rubber for 7 days. Toluene was used as solvent in the cases of NR and SBR, while acetone was used in the case of NBR. According to Eq. 1, volume fraction of rubber in the swollen network (υ_r) was calculated. The Flory-Rehner equation as expressed in Eq. 2 was used to calculate the crosslink density. [67]

$$v_r = \frac{\left(\frac{w_1}{\rho_d}\right)}{\left(\frac{w_1}{\rho_d} + \frac{(w_2 - w_1)}{\rho_s}\right)} \tag{1}$$

where w_1 is the mass of rubber before swelling, w_2 is the mass of the swollen rubber, ρ_d is the rubber density before swelling, and ρ_s is the solvent density.

$$v_e = \frac{-\left[\ln(1 - v_r) + v_r + \chi_1 v_r^2\right]}{\left[v_1\left(v_r^{1/3} - \frac{v_r}{2}\right)\right]} \tag{2}$$

where υ_e is the network chain density, υ_1 is molar volume of solvent, and χ_1 is the Flory–Huggins interaction parameter between rubber and solvent. The swelling ratio (S) could be calculated from Eq. 3.

$$S = \frac{(w_2 - w_1)}{w_1} \tag{3}$$

4.3.6.2 Hardness

The hardness of the specimens was measured by Shore A hardness tester (Wallace Shore A durometer, UK) as per ASTM D2240.

4.3.6.3 Tensile properties

Tensile properties were measured according to ASTM D412 Die C at crosshead speed and load cell of 500 mm/min and 1 kN, respectively. The samples were dumbbell-shape having thickness of approximately 2 mm and dimensions as shown in Figure 4.2. Average values of tensile strength, and elongation at break were reported.

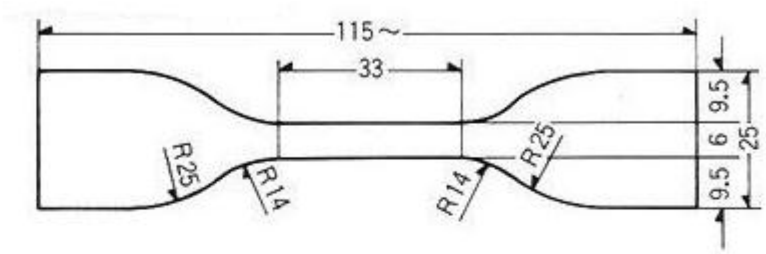


Figure 4.2 Dimensions (in the millimeter unit) of the tensile specimen as per ASTM D412 Die C

Tensile strength (TS) is calculated as follows:

$$TS = F_{(BE)}/A$$

where:	TS	=	tensile strength or the stress at rupture, MPa
	$F_{(BE)}$	=	force magnitude at rupture, N
	A	=	cross-sectional area of unstrained specimen, mm^2

Calculation the elongation (at any degree of extension) is shown as follows:

$$E = 100[L - L_0]/L_0$$

where: E = elongation in percent (of original benchmark distance)

L = observed distance between benchmarks on the extended specimen (m)

L_0 = original distance between benchmarks (m)

4.3.6.4 Tear properties

Tear resistance was determined as per ASTM D624 Die B exhibited in Figure 4.3 at crosshead speed and load cell of 500 mm/min and 1 kN, respectively. Thickness of specimens was of approximately 2 mm, and the average value was reported.

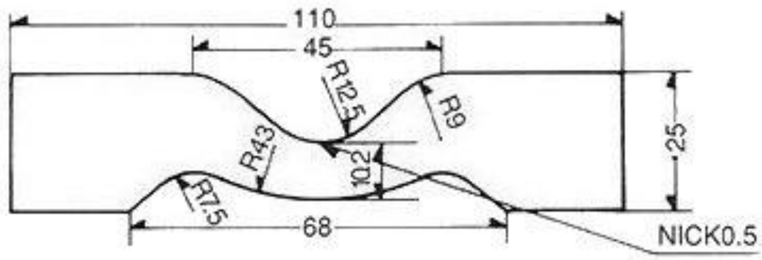


Figure 4.3 Dimension of standard test specimen (in millimeter unit) of ASTM D624 Die B

Calculation the tear strength (Ts) of thickness is shown as follows:

$$Ts = F/d$$

where: F = maximum force, N

d = median thickness of each test specimen, mm

4.3.6.5 Dynamic mechanical properties

Dynamic mechanical properties of vulcanizates were examined using dynamic mechanical analyzer under temperature sweep test mode at frequency of 5 Hz under static and dynamic strains of 1 and 0.1%, respectively. The test temperature was scanned from -80°C to 60°C at a heating rate of 2°C/min. Elastic (E') and loss (E") moduli as well as damping factor (tan δ) of vulcanizates were determined.

4.3.6.6 Determination of temperature rise under cyclic deformation (Heat build-up test)

Heat build-up test of cured specimens was measured in terms of temperature rise as per ASTM D623 Method A using BF Goodrich Flexometer (Model II), USA. The test specimen with cylindrical shape, having diameter of 17.8±0.1 mm with height of 25.4±0.2 mm was used. Test temperature was set at 100°C, and temperature rise at the specimen base was measured as a function of test duration. The value of temperature rise at the test time of 25 min was reported as heat build-up.

4.3.6.7 Static compression set

The measurement of compression set was carried out in accordance with ASTM D 395 Method B specimen type 2 as illustrated in Figure 4.4. First, the specimen thickness was measured for their initial thickness, and then the test specimens were placed between spacers in the compression device, kept for 22 hours, and then measured for their thickness after load removal. Temperatures used in this test were 25°C and 100°C. Finally, the percentage of compression set was calculated as follows.

$$\text{Compression set (\%)} = 100[(t_0 - t_i)/(t_0 - t_n)]$$

where: t_0 = original specimen thickness, mm

t_i = specimen thickness after testing, mm

t_n = spacer thickness, mm

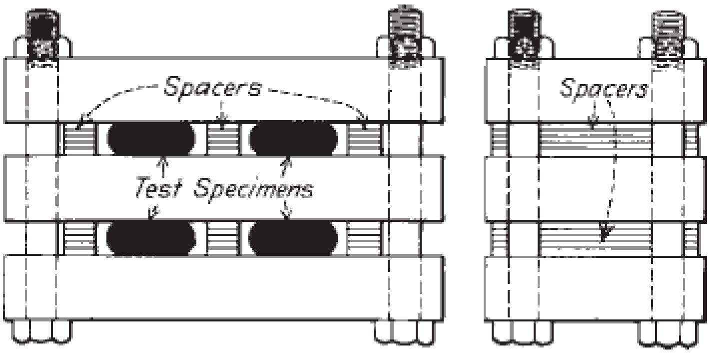


Figure 4.4 Device for compression set test under constant deflection of ASTM D 395 Method B

CHAPTER V
RESULTS AND DISCUSSION

The results and discussion in this research are divided into 3 major parts. The first part concerns comparison of chemical structure of IRPC-PS and RS with the various techniques both qualitatively and quantitatively. The second part involves the use of IRPC-PS as vulcanizing agent in various types of raw rubbers, and its performance was compared with commercial sulfurs. The final part is focused on development of oil-coated PS (OC-PS) as a new product in rubber industry. Properties of compounds and vulcanizates prepared with OC-PS are compared with those prepared with IRPC-PS.

5.1 Chemical structure of petroleum-based sulfur

In order to understand the chemical structure of IRPC-PS, a number of characterization techniques are used. Firstly, FT-IR is conducted under a diffuse reflectance infrared fourier transform mode (DRIFT). The spectra of IRPC-PS as well as RS are illustrated in Figure 5.1. It can be seen that the spectrum of the RS shows characteristic peak of sulfur at the wavenumbers of 1,101, 845, and 468, respectively, which are also observed in that of IRPC-PS [68]. The wavenumber of 468 is assigned to S-S stretching whereas that of 845 and 1,101 are difficult to identify due to the large number of modes in orthorhombic S_8 resulting in a manifold of overtones and combination bands in the vibrational spectra [40, 68]. Nevertheless, owing to the resemblance of the wavenumbers, the results thus suggest similarity in functional groups in RS and IRPC-PS.

Moreover, thermal properties of both RS and IRPC-PS determined from DSC and TGA are displayed in Figures 5.2 and 5.3, respectively. The DSC spectra of IRPC-PS and RS are similar as far as the peak positions are concerned. There are two peak positions observed. The first peak at temperature of around 104 - 107^{o}C contributes to the transformation of sulfur crystal from orthorhombic to monoclinic whereas the second peak found at 120°C attributes to the melting temperature of sulfur [30–31]. Likewise, both sulfurs demonstrate similarity in TGA thermograms, supporting FT-IR and DSC results that the chemical structure of both RS and IRPC-PS are in common with the decomposition temperature of approximately 370°C.

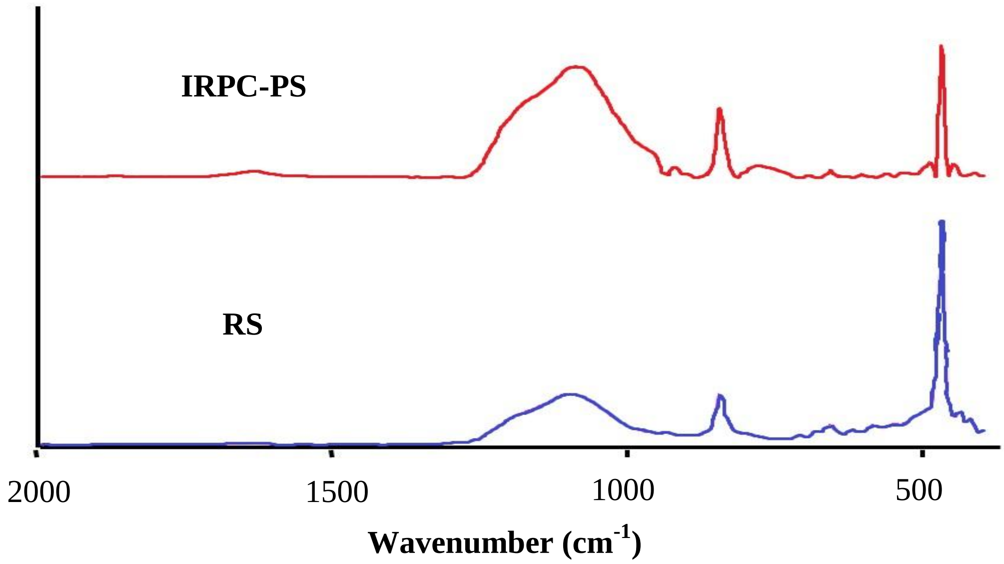


Figure 5.1 FT-IR spectra of RS and IRPC-PS

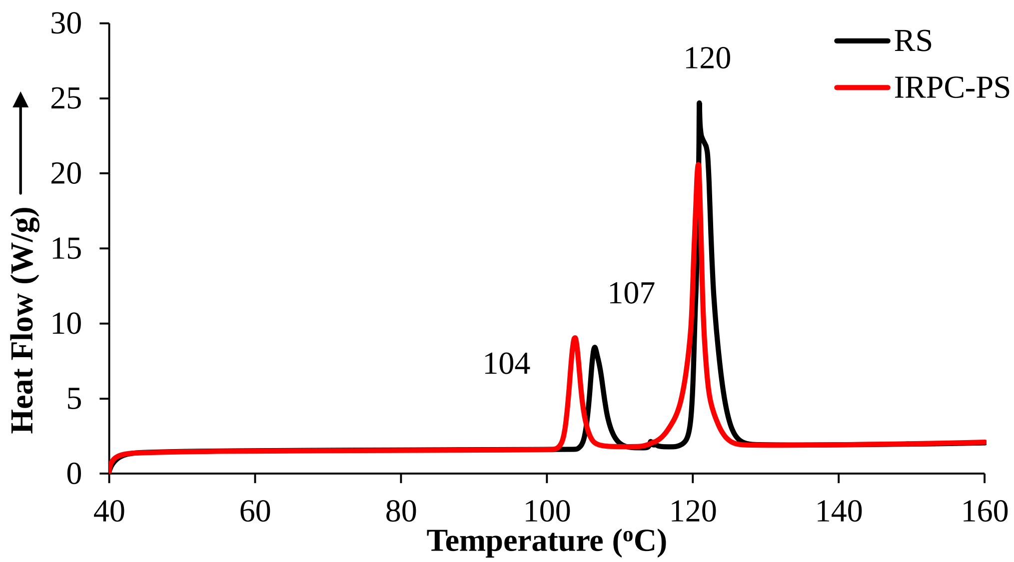


Figure 5.2 DSC spectra of RS and IRPC-PS

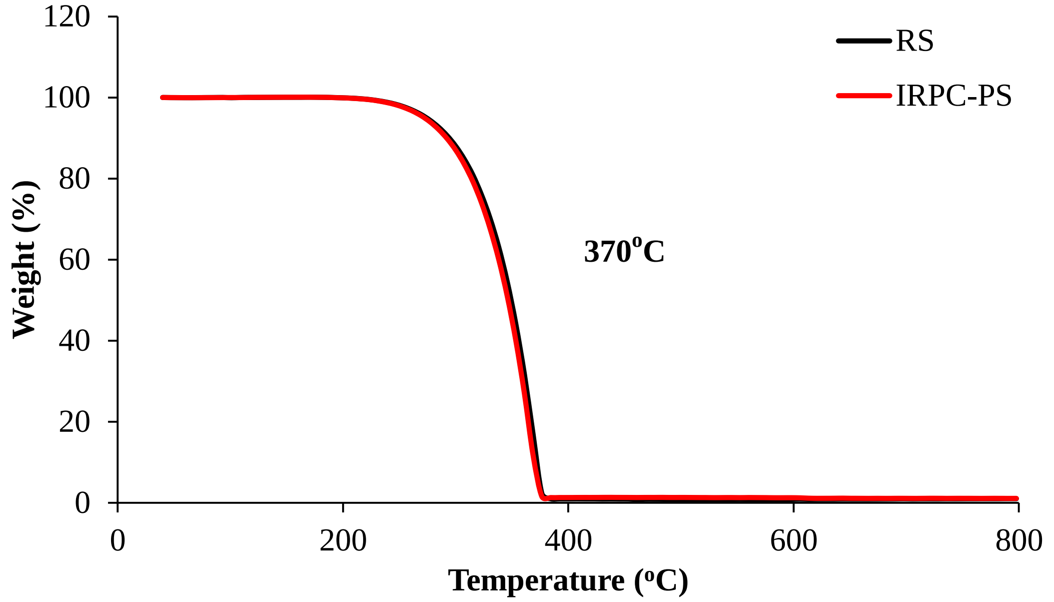


Figure 5.3 TGA thermograms of RS and IRPC-PS

Figure 5.4 illustrates XRD pattern comparison of RS and IRPC-PS. It is obvious that both RS and IRPC-PS give similar XRD pattern. Strong peak can be observed at 2θ of 23^{o}, implying similarity in their orthorhombic structure. Furthermore, the XRF results are in good agreement with the XRD results as shown in Figure 5.5. Evidently, both RS and IRPC-PS exhibit no significance in binding energy characteristics. In addition to XRD and XRF results, XANES spectra agree well with those as exhibited in Figure 5.6. The main absorption peak appears at approximately 2472 eV for both RS and IRPC-PS, referring to elemental sulfur. However, the peak of RS is broader than that of IRPC-PS, which is probably because the RS consists of more sulfur allotropes (S_n; n = 2, 3, 4,…) [30]. Although rhombic sulfur (S_8) is a stable form, the existence of other forms is possible [30]. Also, the IRPC-PS is generally produced from chemical reaction called the Clause Process giving the sulfur product mainly in the form of S_8 [35–37, 42]. From XRD, XRF and XANES results, it is suggested that the chemical structure of IRPC-PS and RS is similar with the rhombic structure.

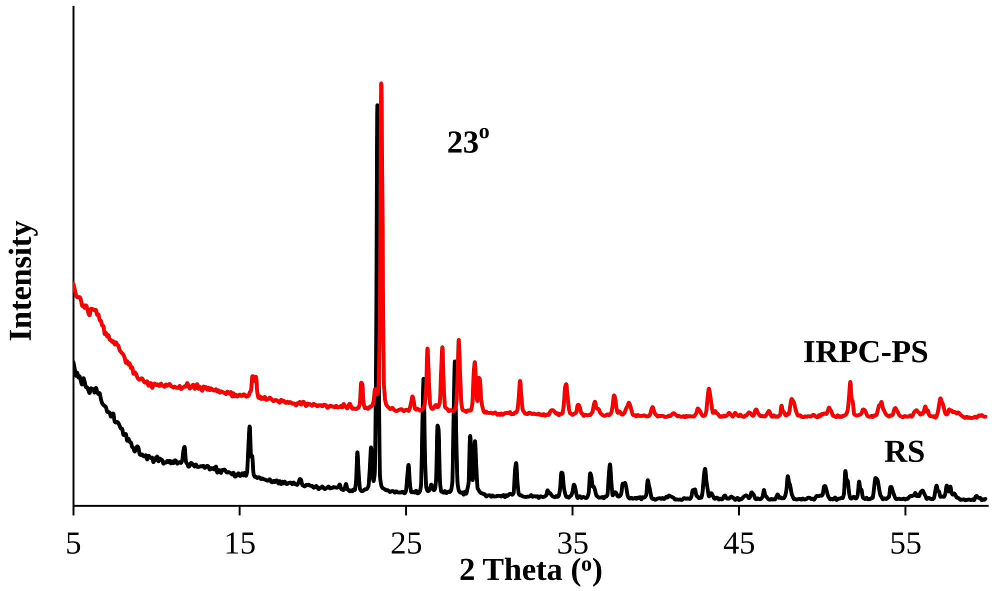


Figure 5.4 XRD patterns of RS and IRPC-PS

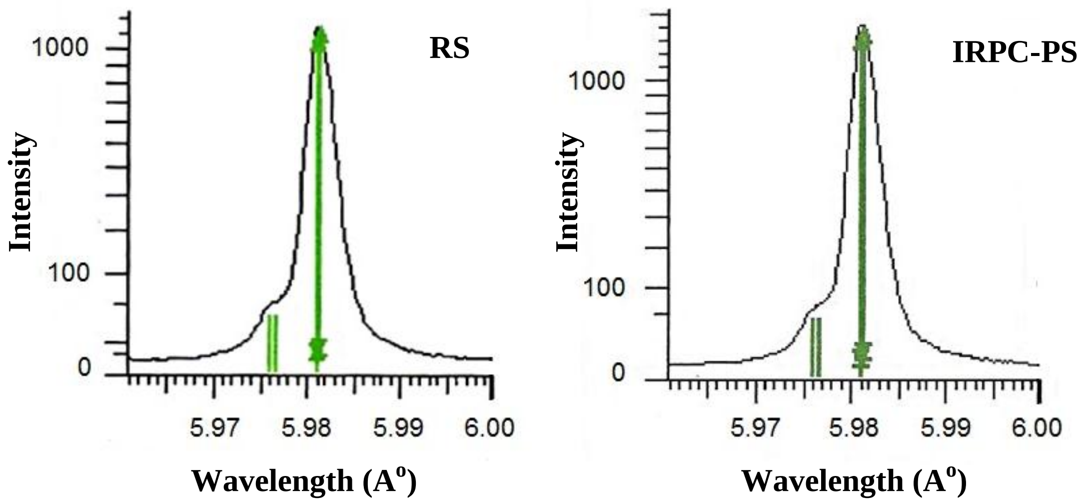


Figure 5.5 XRF spectra of RS and IRPC-PS

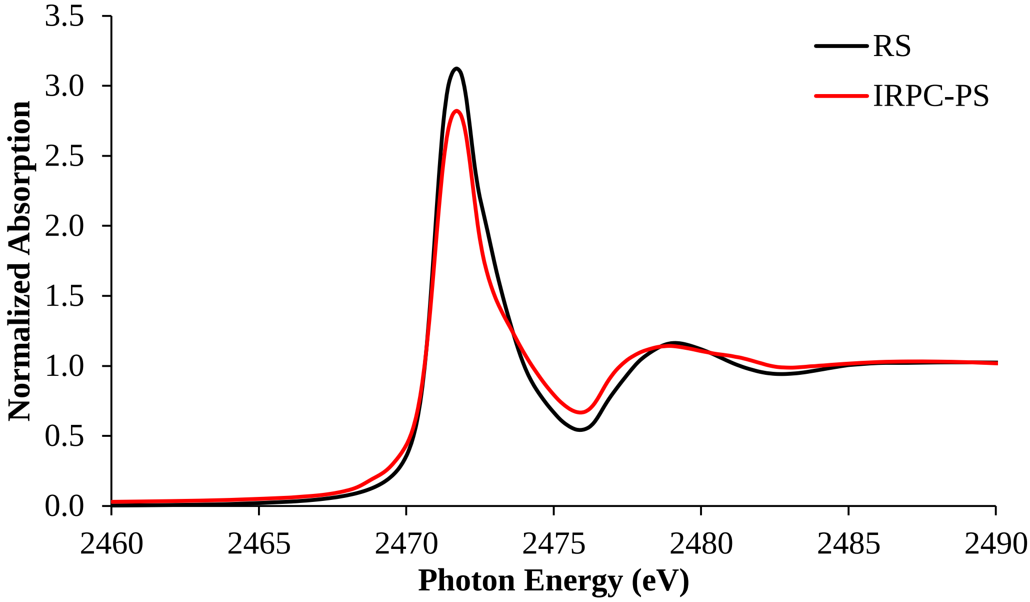


Figure 5.6 TEY Sulfur K-edge XANES spectra of sulfur powders (RS and IRPC-PS) [68]

SEM-EDX spectra of both RS and IRPC-PS are illustrated in Figure 5.7. Obviously, the IRPC-PS demonstrates similar peak characteristics to RS, implying similarity in chemical composition, i.e., the sulfur content of approximately 97%. As a result, it can be summarized that the IRPC-PS classified as by-product from petroleum refinery and the commercial RS are similar in chemical structure and composition.

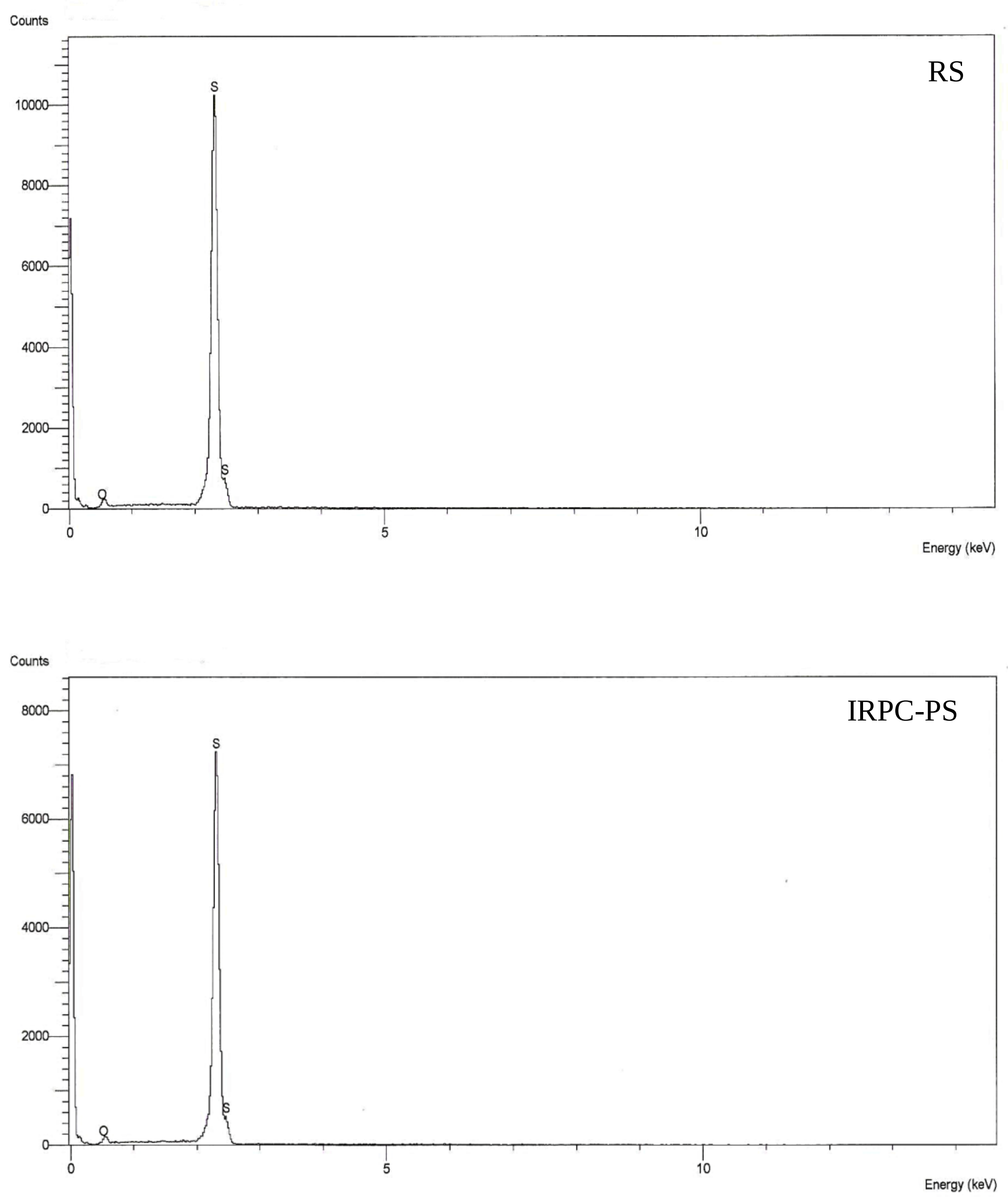


Figure 5.7 SEM-EDX spectra of RS and IRPC-PS

5.2 Efficiency of petroleum-based sulfur as vulcanizing agent in rubbers

In this part, IRPC-PS is used as vulcanizing agent in rubbers, and is compared with commercial sulfurs produced from many manufacturers. There are 2 major groups of commercial sulfurs depending on their resources; natural source and petroleum refinery. For better understanding, this part is thus divided into 2 parts, i.e., (i) comparison of IRPC-PS with commercial natural-based sulfurs and (ii) such comparison with commercial petroleum-based sulfurs.

5.2.1 Property comparison of IRPC-PS with commercial natural-based sulfurs

Properties of rubbers using IRPC-PS as vulcanizing agent are determined and compared with those of rubbers using commercial rhombic sulfurs. The results obtained are reported below.

5.2.1.1 Cure characteristics

Cure characteristics including scorch time (t_{s2}) and cure time (t_{c90}) of NR, SBR, and NBR are tabulated in Table 5.1. It can be seen that both scorch time and cure time of IRPC-PS in all rubbers are comparable with those of commercial sulfurs. Remarkably, both scorch time and cure time of IRPC-PS in NBR are somewhat faster than those of other sulfurs except for M105 sulfur. However, such discrepancies in scorch and cure time do not play significant role in other properties of rubbers to be discussed later.

Table 5.1 Cure characteristics of rubber vulcanizates cured with different sulfurs

Type of sulfur	**NR**		**SBR**		**NBR**	
	t_{s2} (min)	**t_{c90} (min)**	**t_{s2} (min)**	**t_{c90} (min)**	**t_{s2} (min)**	**t_{c90} (min)**
IRPC-PS	12.4±0.3	14.1±0.3	29.3±0.1	43.0±0.1	10.2±0.1	16.1±0.3
RS	11.5±0.5	13.4±0.2	28.1±0.3	42.3±0.1	15.1±0.4	22.3±0.3
M101	12.0±0.2	13.4±0.2	28.5±0.4	42.3±0.0	15.3±0.2	21.4±0.3
M105	12.5±0.4	14.3±0.0	30.1±0.1	43.5±0.4	11.1±0.1	17.1±0.0
SGS	12.0±0.1	13.5±0.5	29.4±0.5	42.5±0.4	14.1±0.2	20.3±0.3
SP400	12.0±0.1	13.4±0.1	29.2±0.4	43.1±0.1	14.3±0.0	20.3±0.0

5.2.1.2 Swelling ratio and crosslink density

Swelling ratio (S) and crosslink density (υ_e) of all vulcanized rubbers are tabulated in Table 5.2. It can be clearly seen that IRPC-PS as vulcanizing agent gives similar swelling results to other sulfurs in a given type of rubber. Because of similarity in swelling ratio and crosslink density in all rubbers, comparable mechanical properties of vulcanizates cured with natural-based and petroleum-based sulfur may be expected.

Table 5.2 Swelling ratio (S) and crosslink density (υ_e) of rubber vulcanizates cured with different sulfurs

Type of sulfur	NR		SBR		NBR	
	S	υ_e (x10^{-4} mol.cm^{-3})	S	υ_e (x10^{-4} mol.cm^{-3})	S	υ_e (x10^{-4} mol.cm^{-3})
IRPC-PS	3.94±0.01	1.23±0.02	4.54±0.03	0.94±0.03	2.88±0.05	2.40±0.06
RS	3.80±0.03	1.28±0.01	4.47±0.05	0.99±0.01	2.71±0.03	2.71±0.06
M101	3.81±0.01	1.21±0.02	4.55±0.00	0.94±0.03	2.76±0.01	2.59±0.02
M105	3.75±0.01	1.25±0.01	4.70±0.02	0.91±0.03	3.02±0.10	2.23±0.13
SGS	3.64±0.01	1.33±0.01	4.50±0.08	0.98±0.02	3.01±0.01	2.19±0.01
SP400	3.75±0.01	1.11±0.02	4.57±0.06	0.95±0.05	2.79±0.07	2.54±0.12

5.2.1.3 Viscoelastic properties

Figures 5.8 -5.10 show strain-dependent viscoelastic properties of rubber compounds incorporated with different sulfur types. It is clearly seen that storage modulus (G') of all compounds is superimposable. This means the sulfur types give no significant effect on rheological behavior of rubber compounds. In other words, the processability of all rubber compounds is comparable. All sulfurs exhibit no significant change in the onset of non-linearity regardless of sulfur types used demonstrating no significant effect of sulfur types on magnitude of change in molecular mobility of rubber compounds.

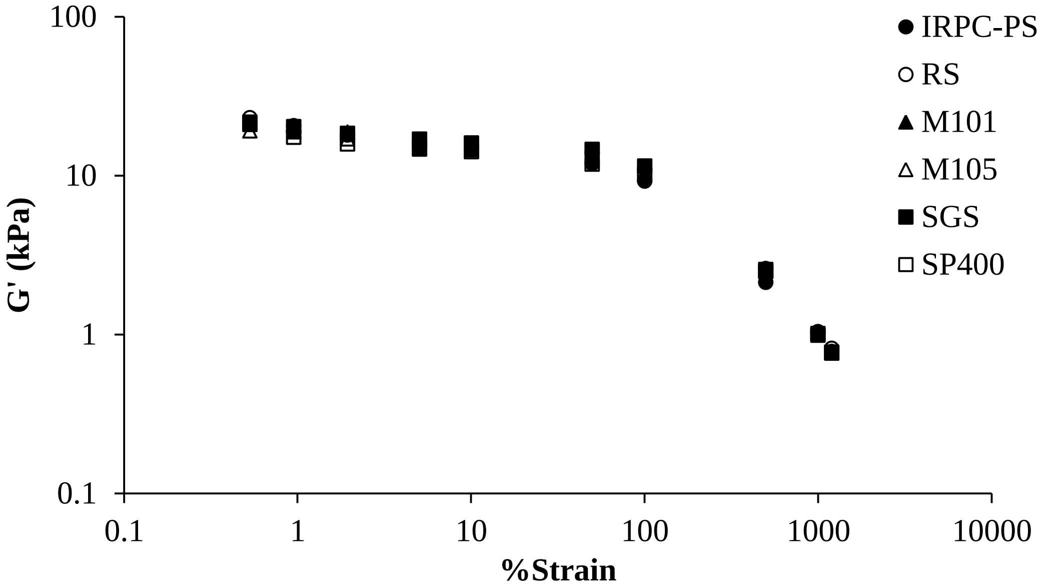


Figure 5.8 Storage modulus as a function of strain in NR compounds incorporated with different types of sulfur

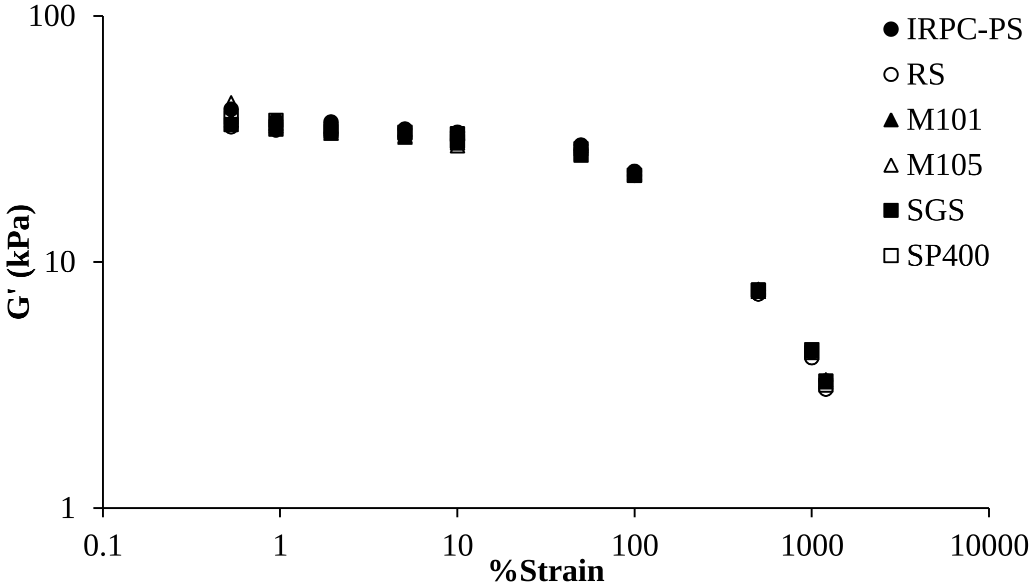


Figure 5.9 Storage modulus as a function of strain in SBR compounds incorporated with different types of sulfur

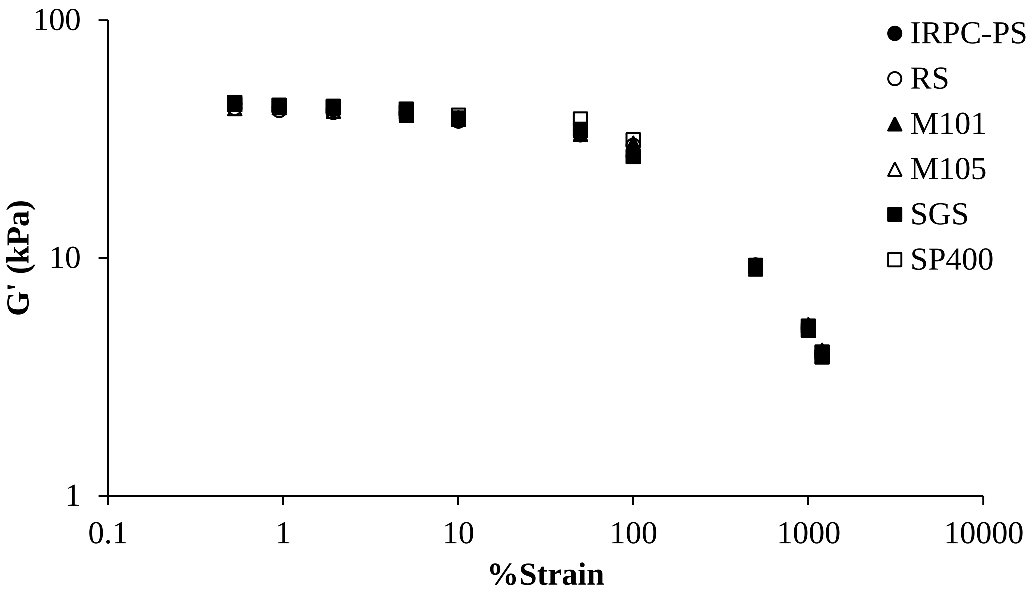


Figure 5.10 Storage modulus as a function of strain in NBR compounds incorporated with different types of sulfur

5.2.1.4 Mechanical properties

Tensile properties including tensile strength and elongation at break of rubber vulcanizates cured with different sulfurs are illustrated in Figures 5.11 – 5.12, respectively. It is noted that IRPC-PS as vulcanizing agent offers similarity in both tensile strength and elongation at break compared with other sulfurs in all rubbers. These findings are also true for the results of tear strength and hardness as exhibited in Figures 5.13 and 5.14, respectively. These results can be supported by the similarity in crosslink density as shown previously. From results of mechanical properties, it is evident that IRPC-PS possesses potential utilization in rubber vulcanization as vulcanizing agent.

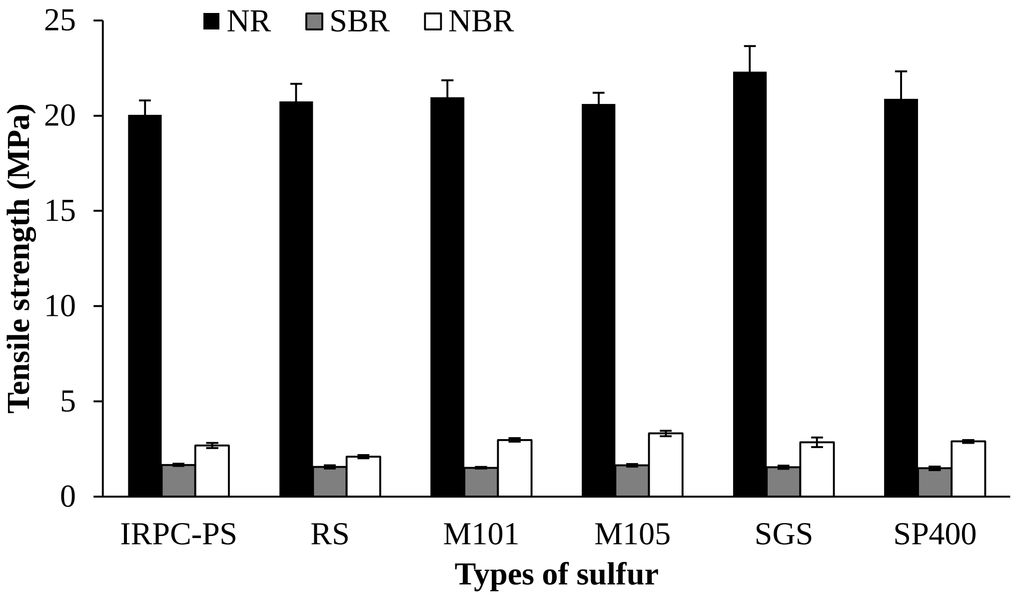


Figure 5.11 Tensile strength of rubber vulcanizates cured with different sulfurs

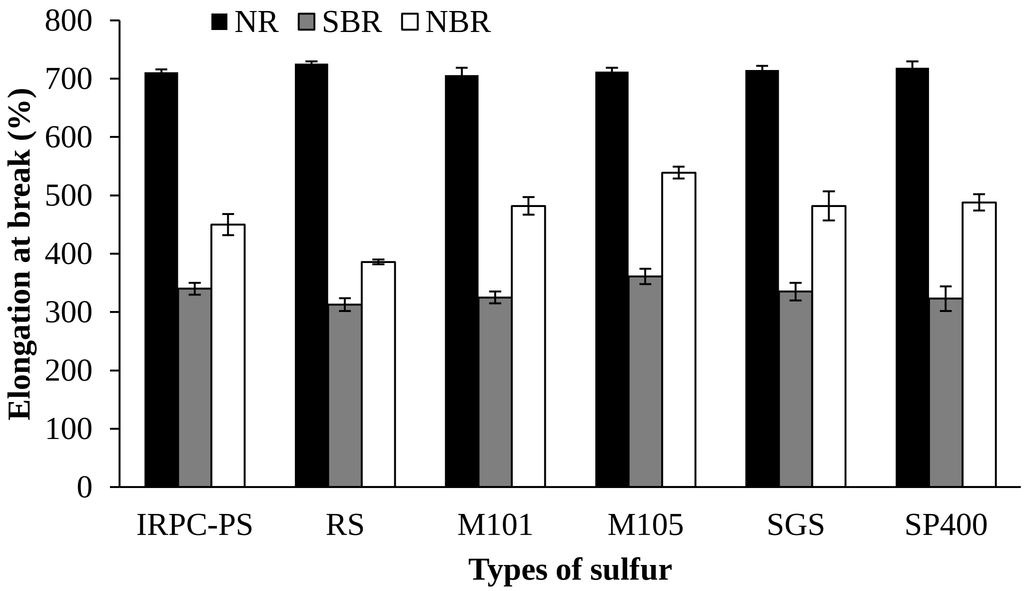


Figure 5.12 Elongation at break of rubber vulcanizates cured with different sulfurs

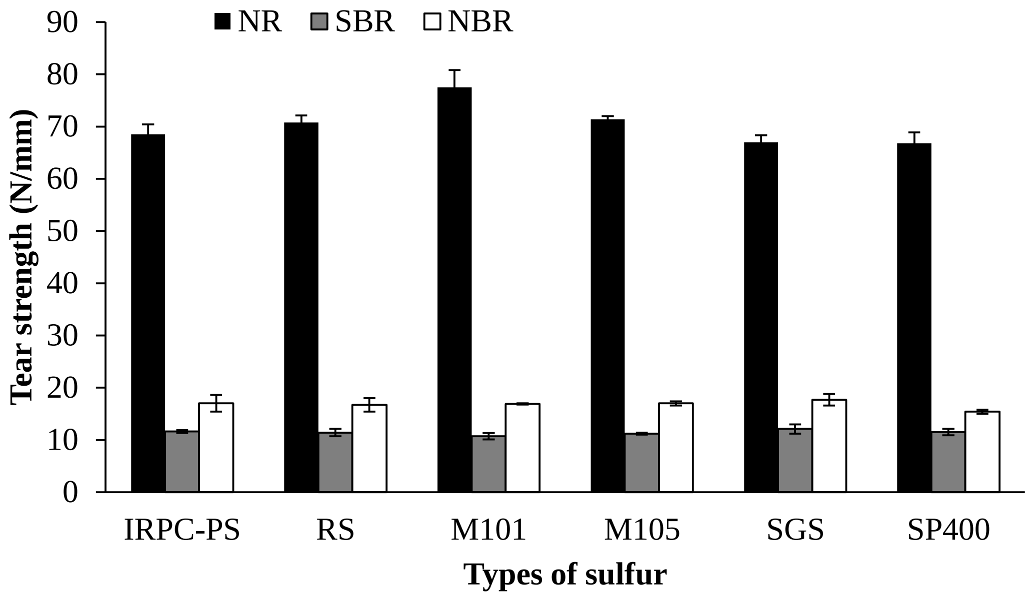


Figure 5.13 Tear strength of rubber vulcanizates cured with different sulfurs

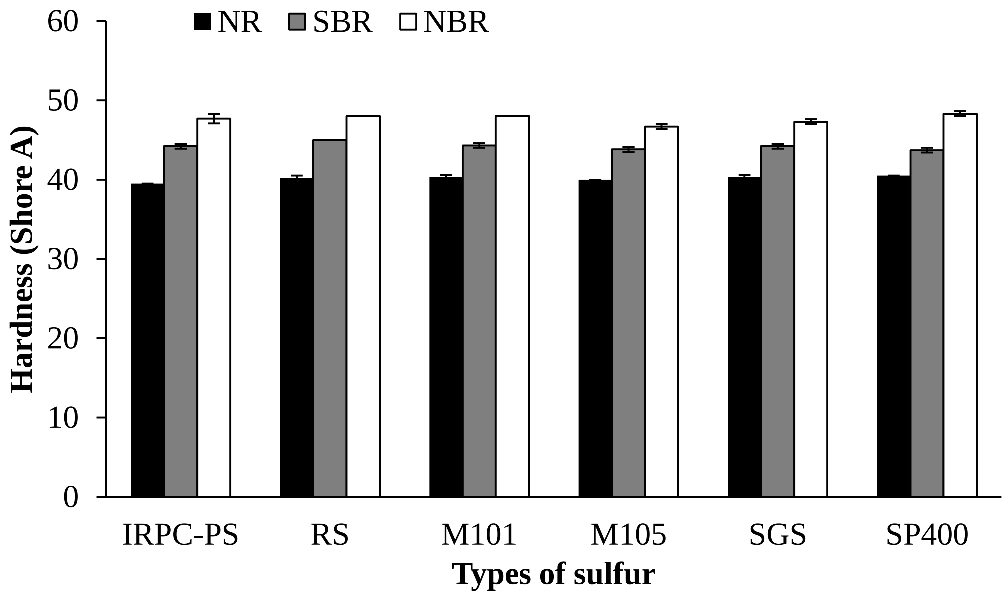


Figure 5.14 Hardness of rubber vulcanizates cured with different sulfurs

5.2.1.5 Dynamic mechanical properties

Figures 5.15 – 5.20 show dynamic mechanical properties as a function of temperature of vulcanizates cured with different types of sulfurs. Elastic modulus (E’) and tan δ of rubbers are investigated. Evidently, similar to the results of mechanical properties, there is no significant difference observed in all rubbers demonstrating no profound effect of sulfur types on dynamic mechanical properties of rubbers. This is attributed to the comparable crosslink density of rubbers regardless of sulfur type used.

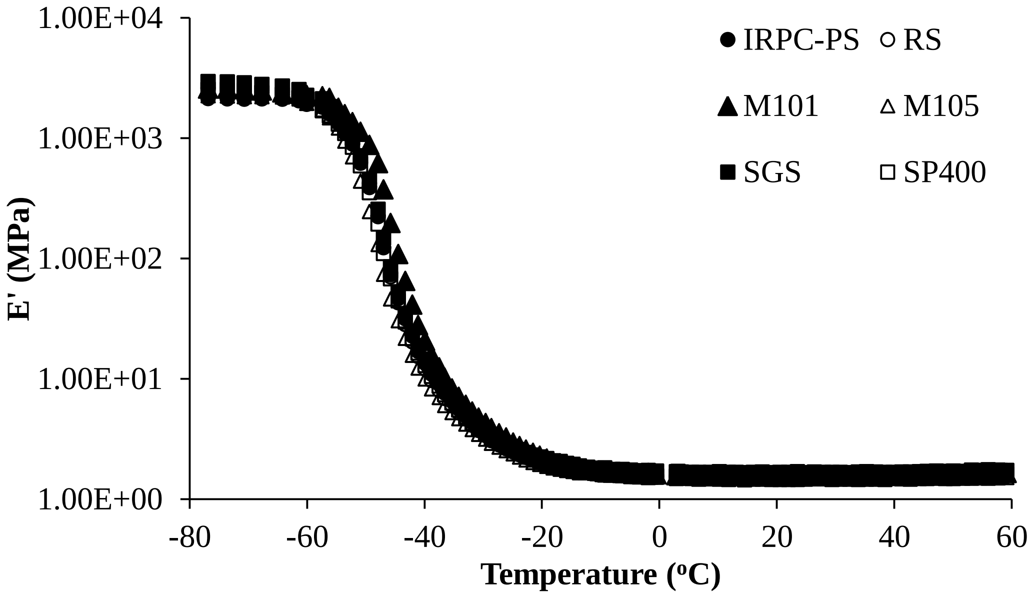


Figure 5.15 Elastic modulus as a function of temperature in NR vulcanizates cured with different types of sulfur

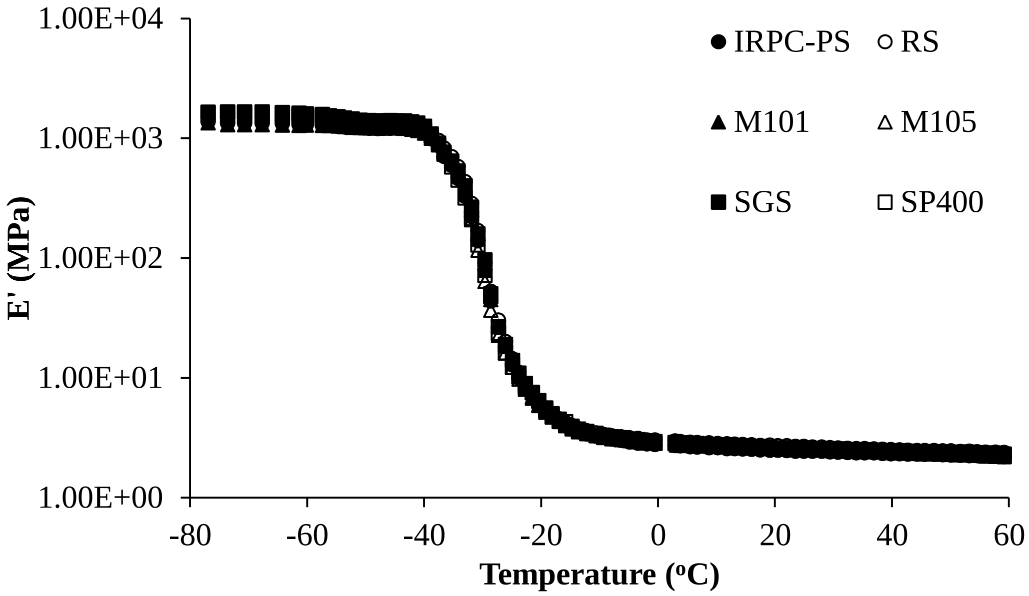


Figure 5.16 Elastic modulus as a function of temperature in SBR vulcanizates cured with different types of sulfur

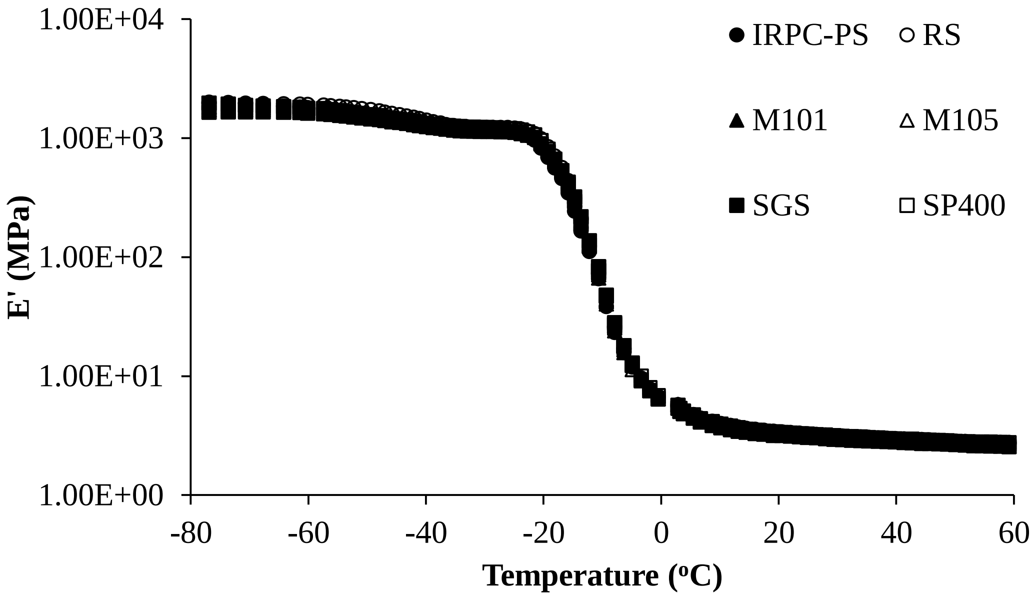


Figure 5.17 Elastic modulus as a function of temperature in NBR vulcanizates cured with different types of sulfur

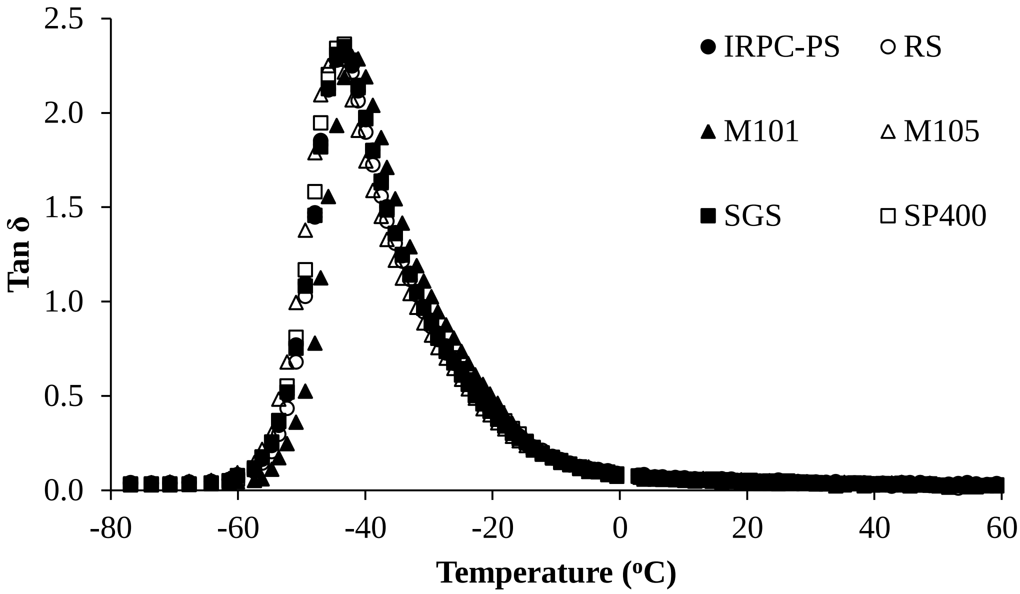


Figure 5.18 Tan δ as a function of temperature in NR vulcanizates cured with different types of sulfur

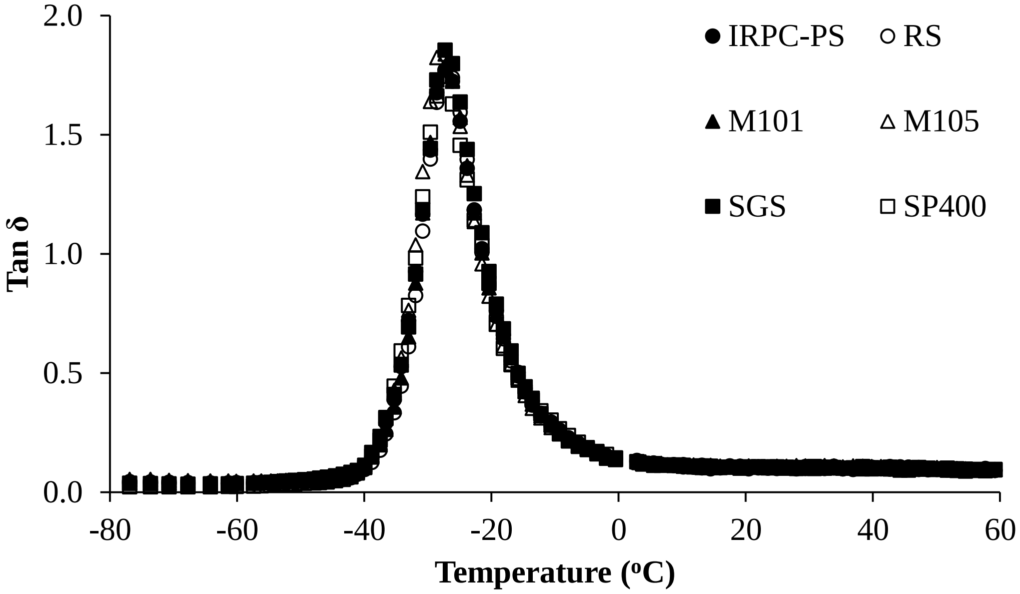


Figure 5.19 Tan δ as a function of temperature in SBR vulcanizates cured with different types of sulfur

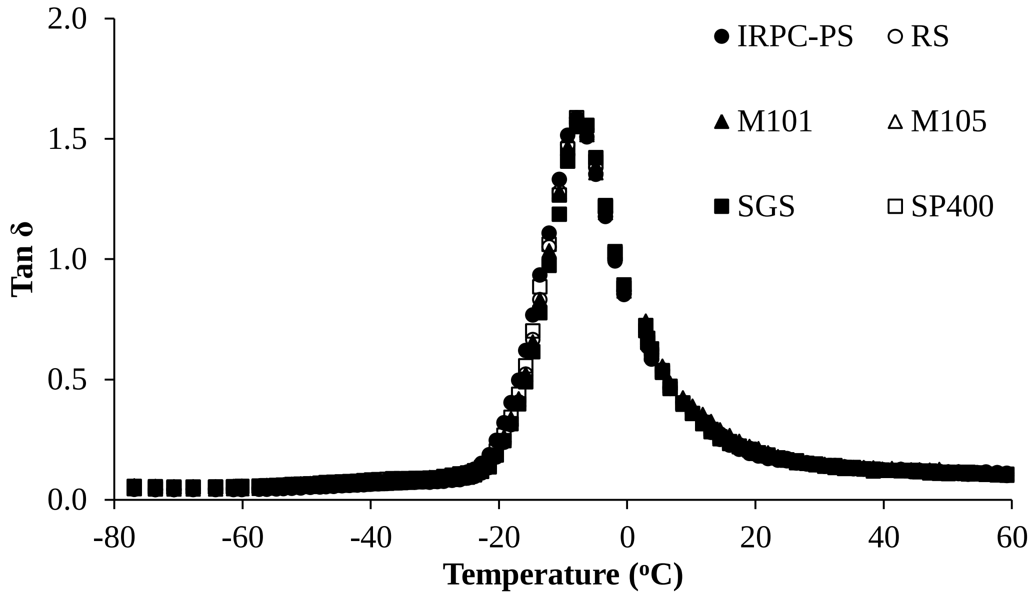


Figure 5.20 Tan δ as a function of temperature in NBR vulcanizates cured with different types of sulfur

5.2.1.6 Heat build-up

Heat build-up (or temperature rise) results of rubbers cured with different types of sulfur are illustrated in Figure 5.21. The temperature rise of the systems with IRPC-PS is similar to that of other sulfurs. As a result, IRPC-PS possesses potential utilization as vulcanizing agent in all types of rubber while dynamic mechanical properties of rubber compounds and vulcanizates remain as good as commercial sulfurs.

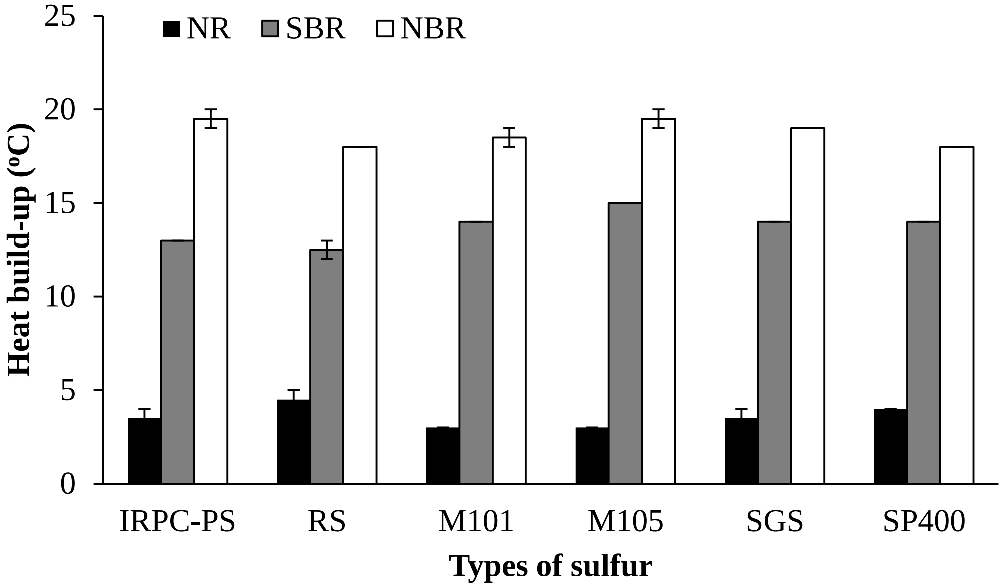


Figure 5.21 Heat build-up test of vulcanizates cured with different sulfurs

5.2.1.7 Static compression set

Figures 5.22 – 5.24 demonstrate results of static compression set of vulcanizates incorporated with different types of sulfur. Evidently, the vulcanizates cured with IRPC-PS give similar results compared with the other sulfurs. The similarity in crosslink density is considered as a key factor for such results. As mentioned previously, no significant disparity of crosslink density leads to the analogous properties of vulcanizates incorporated with IRPC-PS compared with commercial sulfurs. Moreover, the percentage of static compression set at 100^{o}C shows higher value than that at 25^{o}C. This is attributed to the devulcanization of polysulfidic linkages. It is known that the polysulfidic linkages possess relatively low bond energy and therefore are prone to be chain-scission at 100 ^{o}C. The results suggest that the IRPC-PS possesses potential to be used as vulcanizing agent in all types of rubber (i.e., NR, SBR, and NBR).

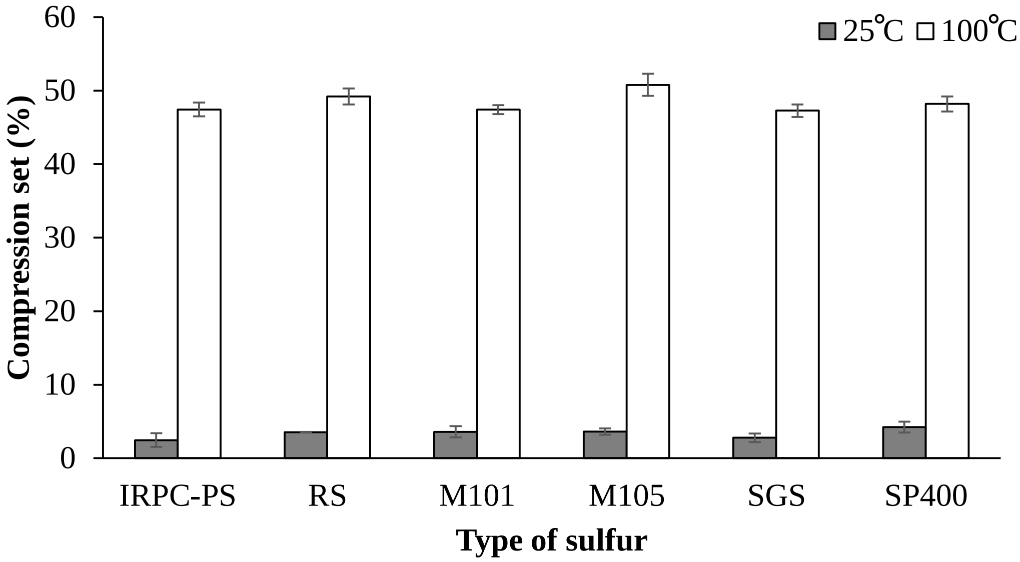


Figure 5.22 Compression set test of NR vulcanizates cured with different sulfurs

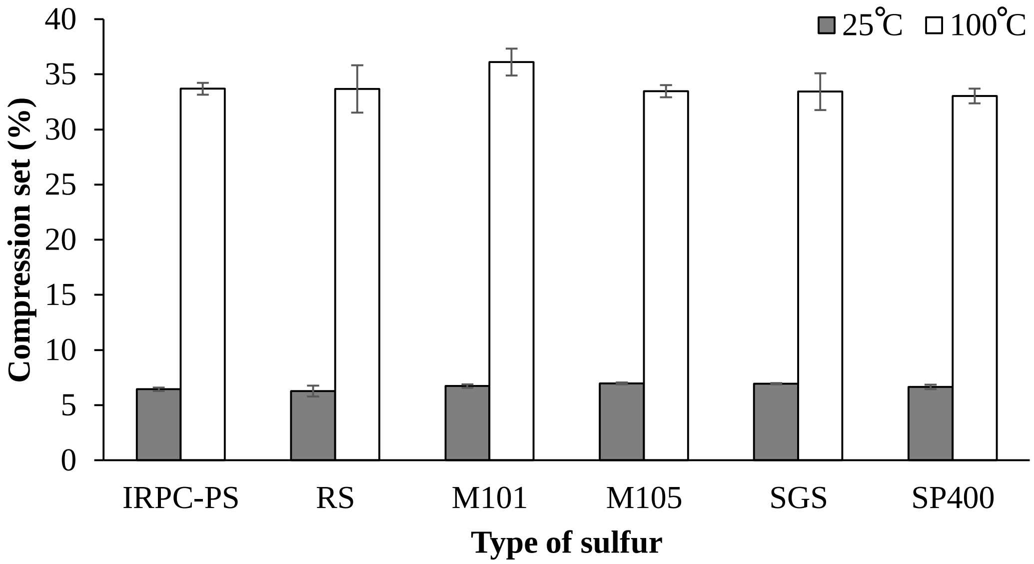


Figure 5.23 Compression set test of SBR vulcanizates cured with different sulfurs

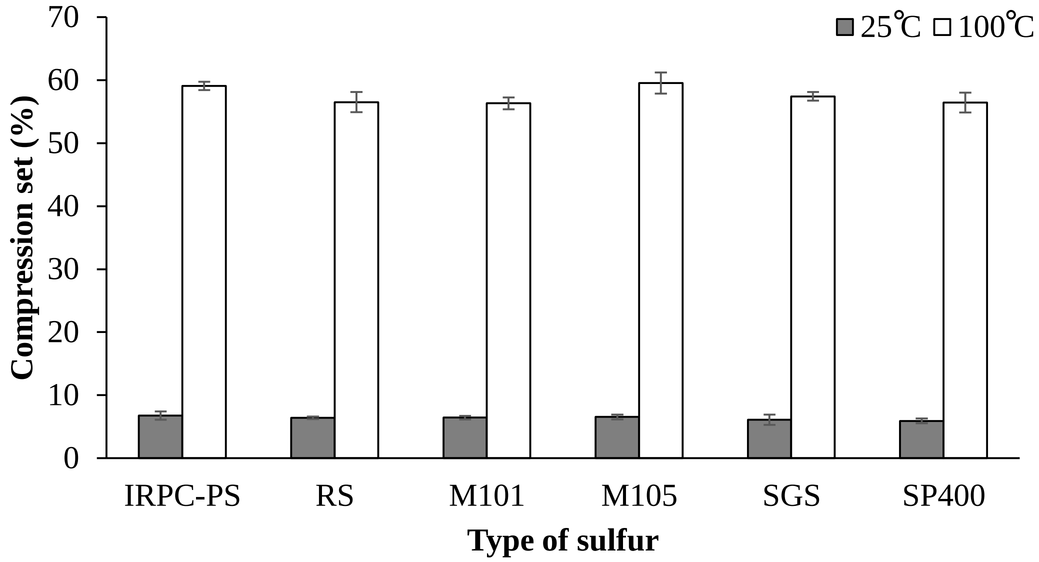


Figure 5.24 Compression set test of NBR vulcanizates cured with different sulfurs

5.2.2 Property comparison of IRPC-PS with commercial petroleum-based sulfurs

All properties of rubbers vulcanized by IRPC-PS are determined and compared with those of rubbers vulcanized by commercial petroleum-based sulfurs. The results obtained are discussed below.

5.2.2.1 Cure characteristics

Cure characteristics including scorch time (t_{s2}) and cure time (t_{c90}) of NR, SBR, and NBR are shown in Table 5.3. It can be seen that both t_{s2} and t_{c90} of IRPC-PS in all rubbers are comparable with those of other petroleum-based sulfurs.

Table 5.3 Cure characteristics of rubber vulcanizates cured with different sulfurs

Type of sulfur	NR		SBR		NBR	
	t_{s2} (min)	t_{c90} (min)	t_{s2} (min)	t_{c90} (min)	t_{s2} (min)	t_{c90} (min)
IRPC-PS	12.5±0.2	14.3±0.2	31.1±0.3	45.1±0.2	9.1±0.1	14.5±0.5
DF325	13.1±0.4	14.3±0.1	31.1±0.2	44.3±0.4	8.2±0.3	14.1±0.0
DF5(325)	12.5±0.0	14.4±0.4	31.3±0.4	44.2±0.3	11.2±0.2	16.4±0.4
SM400	12.5±0.2	14.1±0.2	31.0±0.3	44.4±0.1	10.5±0.3	16.0±0.3

5.2.2.2 Swelling ratio and crosslink density

Swelling ratio (S) and crosslink density (υ_e) of all vulcanized rubbers are tabulated in Table 5.4. Obviously, analogous results are found in all types of rubber regardless of sulfur types used.

Table 5.4 Swelling ratio (S) and crosslink density (υ_e) of rubbers cured with different sulfurs

Type of sulfur	NR		SBR		NBR	
	S	υ_e (x10^{-4} mol.cm^{-3})	S	υ_e (x10^{-4} mol.cm^{-3})	S	υ_e (x10^{-4} mol.cm^{-3})
IRPC-PS	4.03±0.06	1.22±0.03	4.52±0.00	0.96±0.02	2.49±0.03	3.12±0.08
DF325	4.04±0.06	1.23±0.03	4.50±0.06	0.95±0.02	2.45±0.04	3.18±0.05
DF5(325)	4.17±0.06	1.16±0.04	4.56±0.05	0.94±0.03	2.37±0.03	3.40±0.07
SM400	3.88±0.06	1.33±0.01	4.52±0.02	0.95±0.01	2.34±0.01	3.43±0.04

5.2.2.3 Viscoelastic properties

Figures 5.25 - 5.27 show strain-dependent viscoelastic properties of rubber compounds incorporated with different sulfur types. Evidently, storage modulus (G') of all compounds is superimposable suggesting that the sulfur types give no profound effect on rheological behavior of rubber compounds. In other words, there is no requirement for adjusting the processing conditions. Regardless of sulfur types used, all sulfurs exhibit no significant change in the onset of non-linearity demonstrating no significance of sulfur types on magnitude of molecular slippage of rubber molecules.

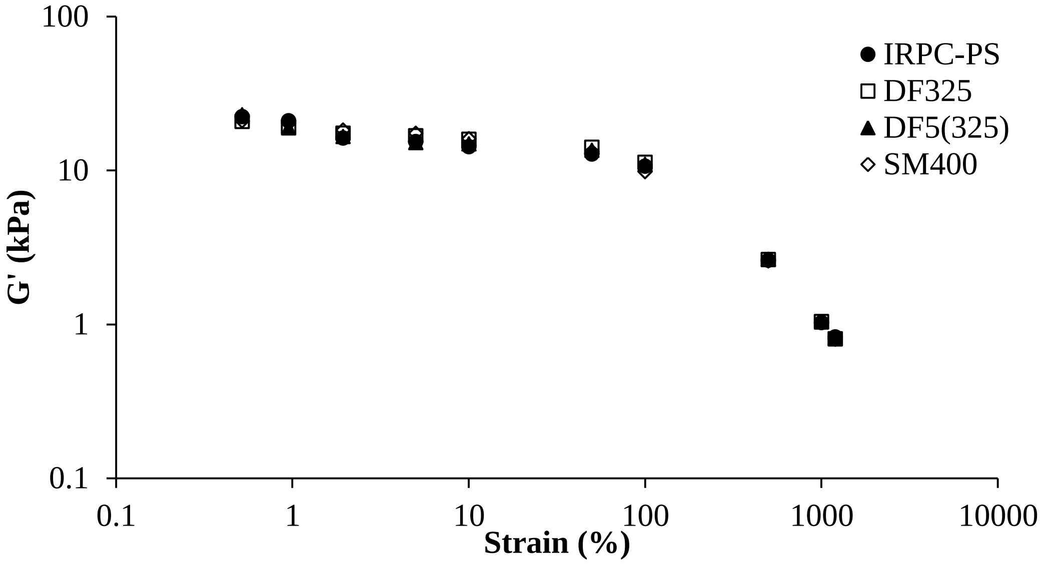


Figure 5.25 Storage modulus as a function of strain in NR compounds incorporated with different types of sulfur

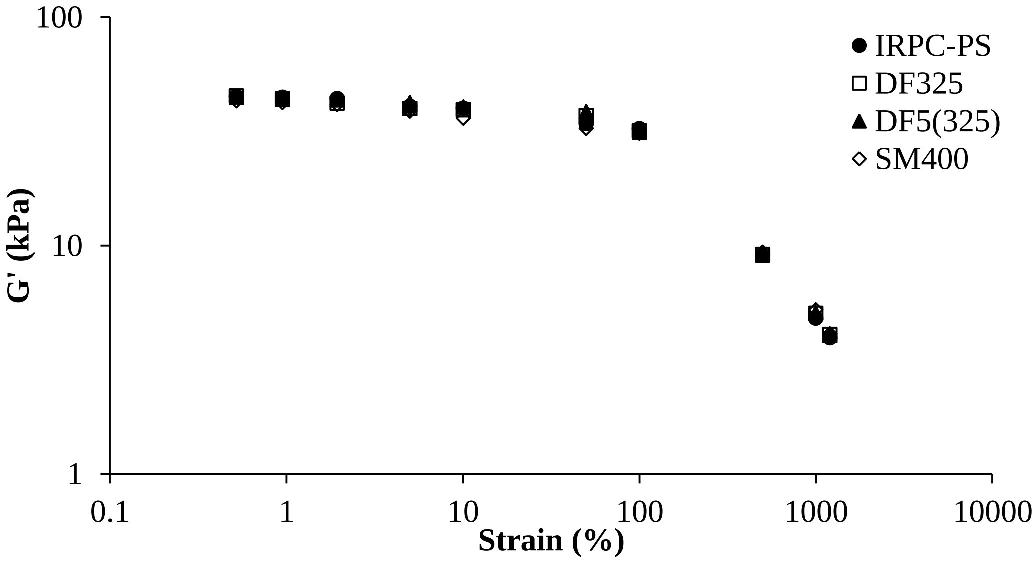


Figure 5.26 Storage modulus as a function of strain in SBR compounds incorporated with different types of sulfur

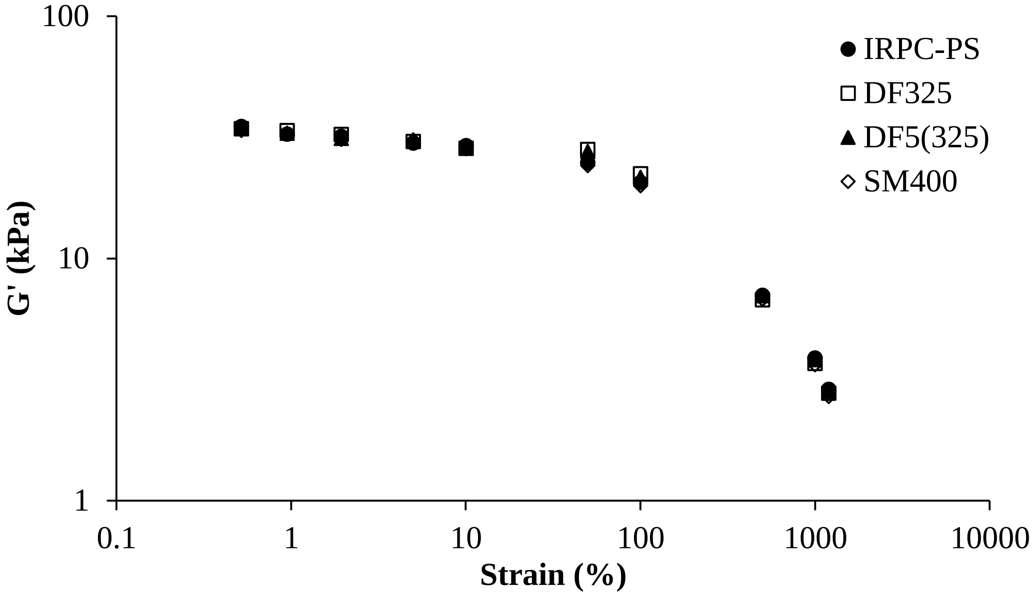


Figure 5.27 Storage modulus as a function of strain in NBR compounds incorporated with different types of sulfur

5.2.2.4 Mechanical properties

Results of tensile strength, elongation at break, tear strength, and hardness of rubbers cured with different sulfurs are exhibited in Figures 5.28 – 5.31, respectively. Evidently, IRPC-PS as vulcanizing agent in each rubber exhibits analogous results compared with other commercial petroleum-based sulfur. The reason contributed to these results is the crosslink density effect as discussed previously. The IRPC-PS offers similarity in crosslink density to other sulfurs. Hence, the mechanical properties of IRPC-PS-vulcanized rubbers shows similar trend to those of other petroleum-based sulfurs. In other words, the sulfur types affect neither rheological nor mechanical properties of rubbers regardless of rubber matrix type.

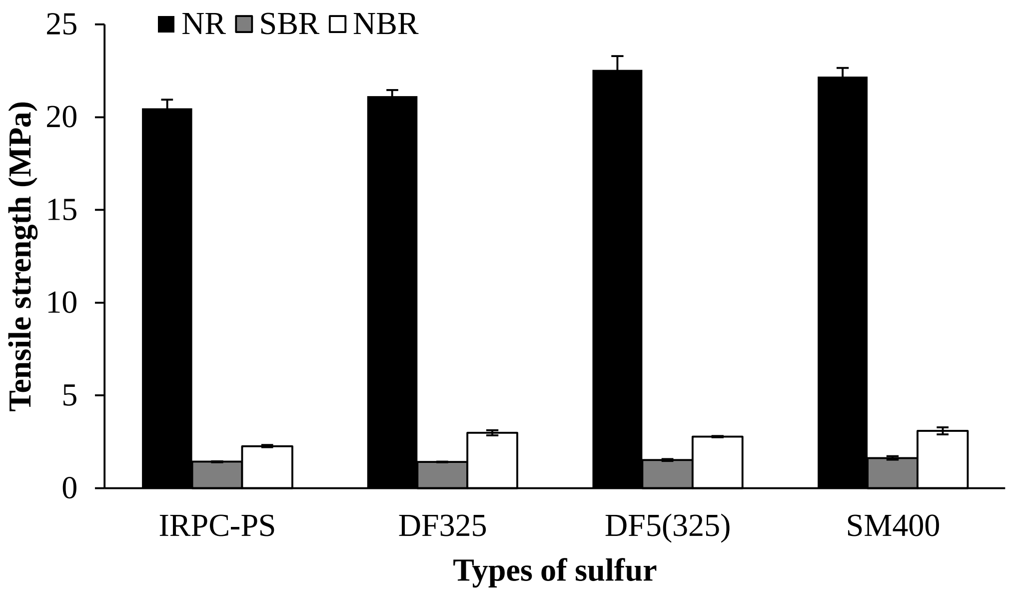


Figure 5.28 Tensile strength of rubber vulcanizates cured with different sulfurs

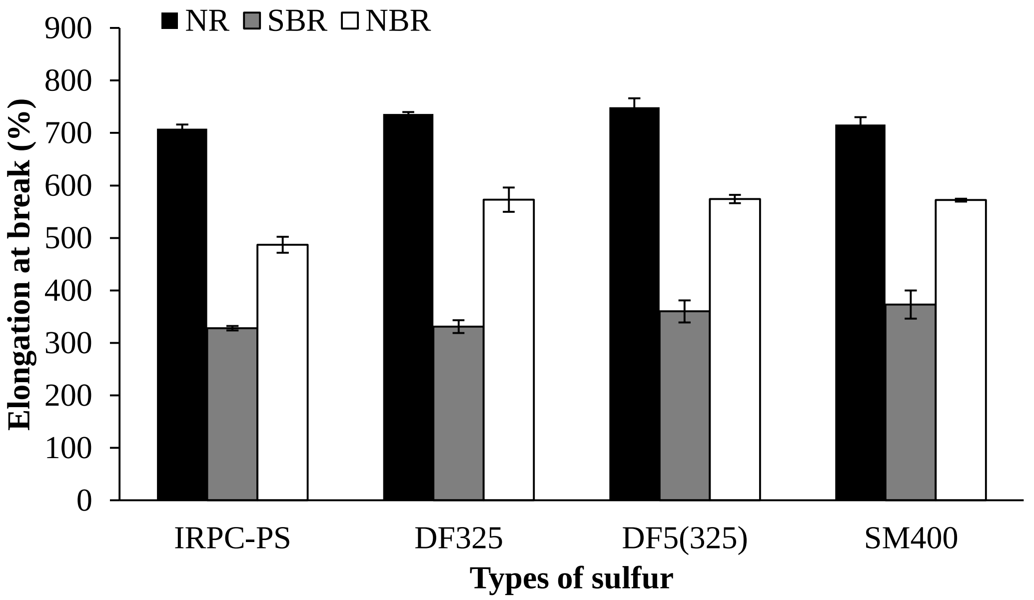


Figure 5.29 Elongation at break of rubber vulcanizates cured with different sulfurs

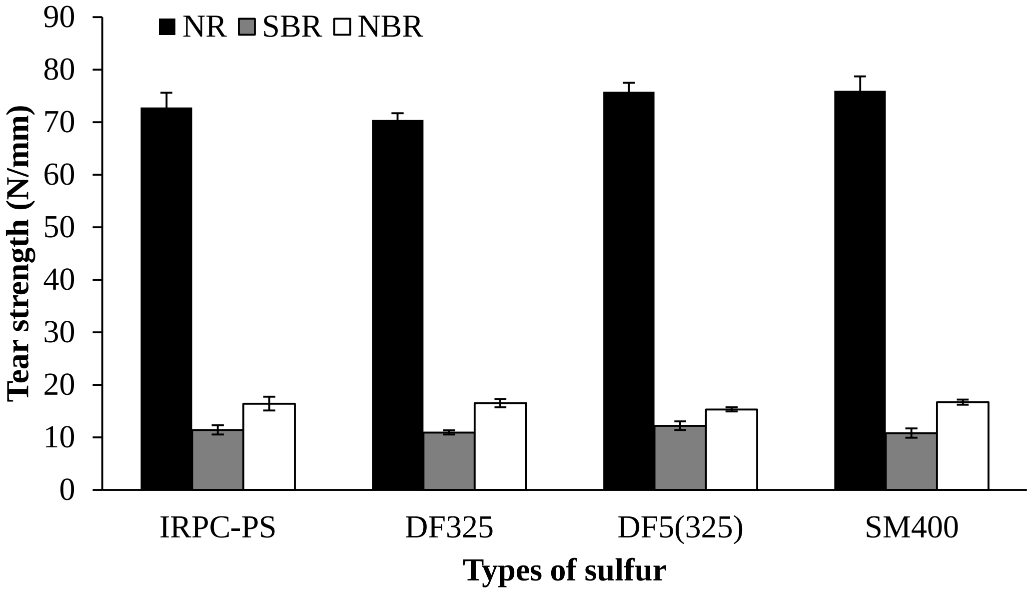


Figure 5.30 Tear strength of rubber vulcanizates cured with different sulfurs

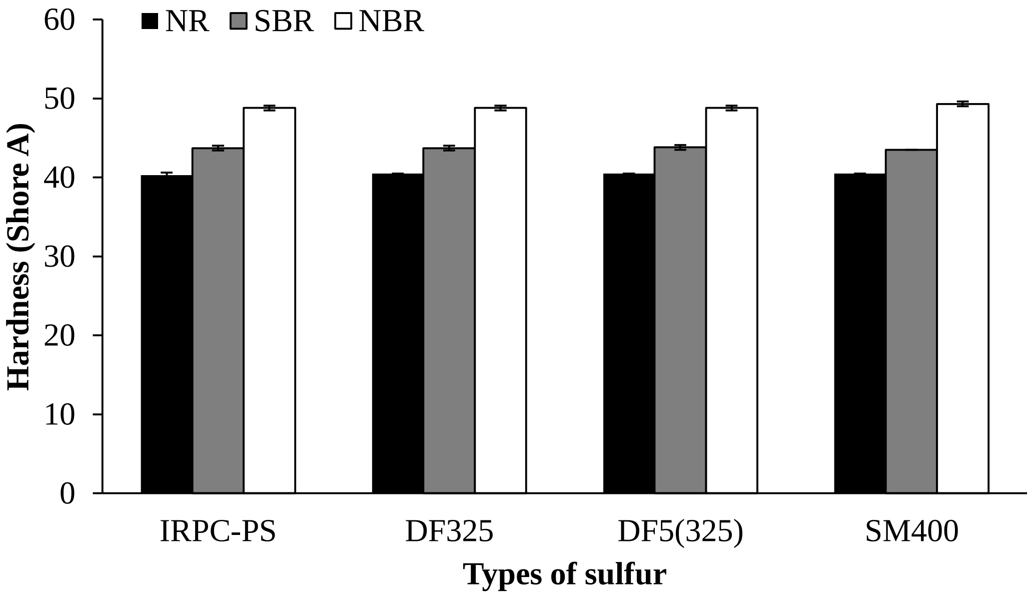


Figure 5.31 Hardness of rubber vulcanizates cured with different sulfurs

5.2.2.5 Dynamic mechanical properties

Dynamic mechanical properties including elastic modulus (E') and tan δ as a function of temperature of all rubbers incorporated with different sulfurs are illustrated in Figures 5.32 – 5.37. It can be seen that IRPC-PS as vulcanizing agent offers dynamic mechanical properties similar to other petroleum-based sulfurs. The elastic modulus and the tan δ of IRPC-PS also show the same result trend as those of other sulfurs.

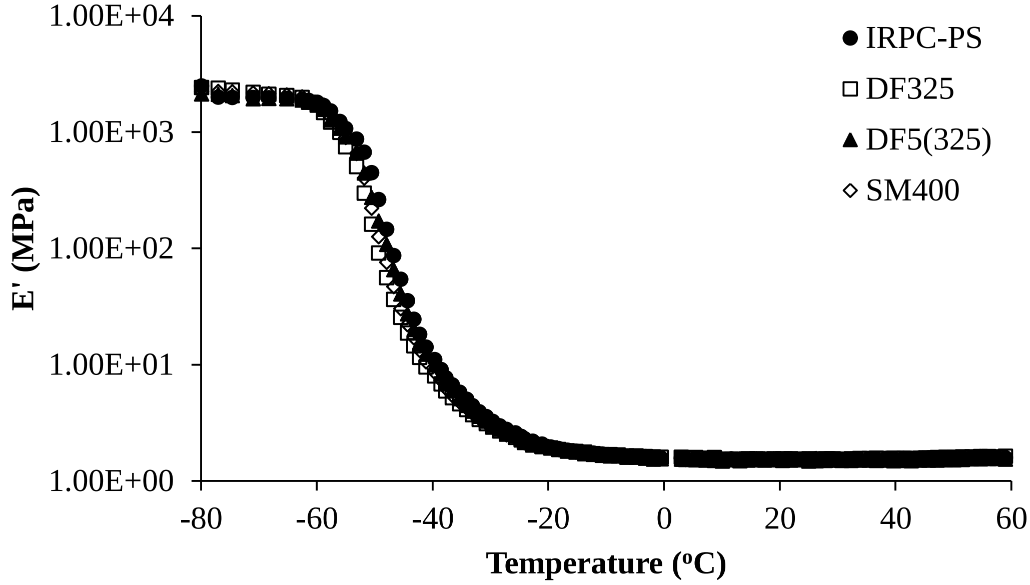


Figure 5.32 Elastic modulus as a function of temperature in NR vulcanizates cured with different types of sulfur

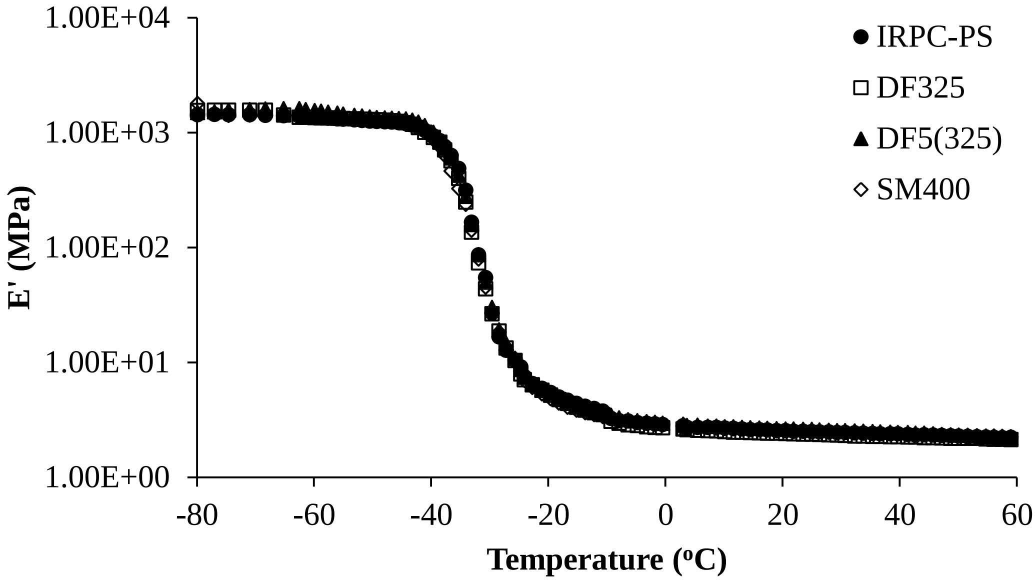


Figure 5.33 Elastic modulus as a function of temperature in SBR vulcanizates cured with different types of sulfur

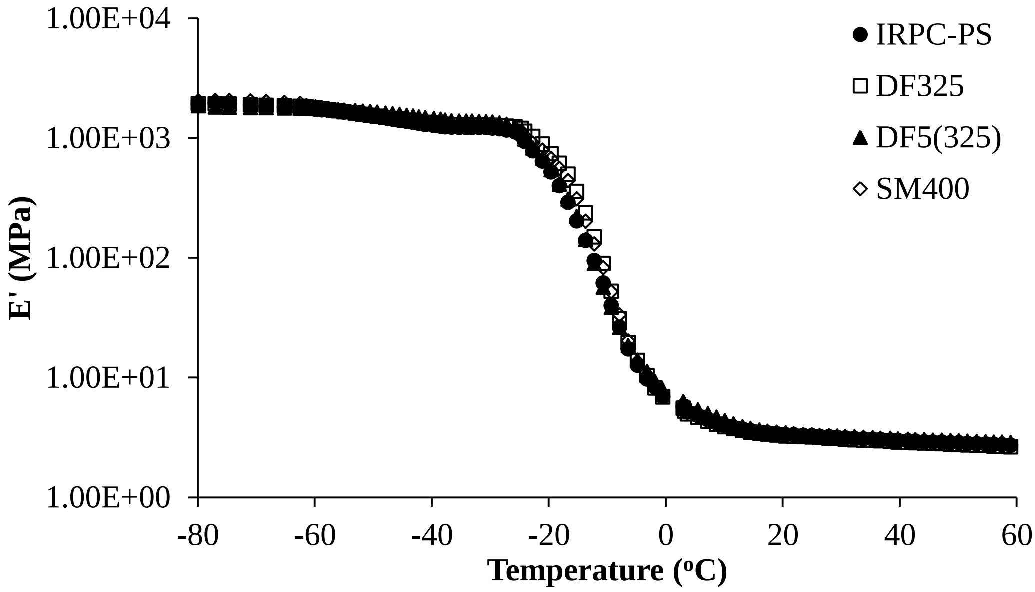


Figure 5.34 Elastic modulus as a function of temperature in NBR vulcanizates cured with different types of sulfur

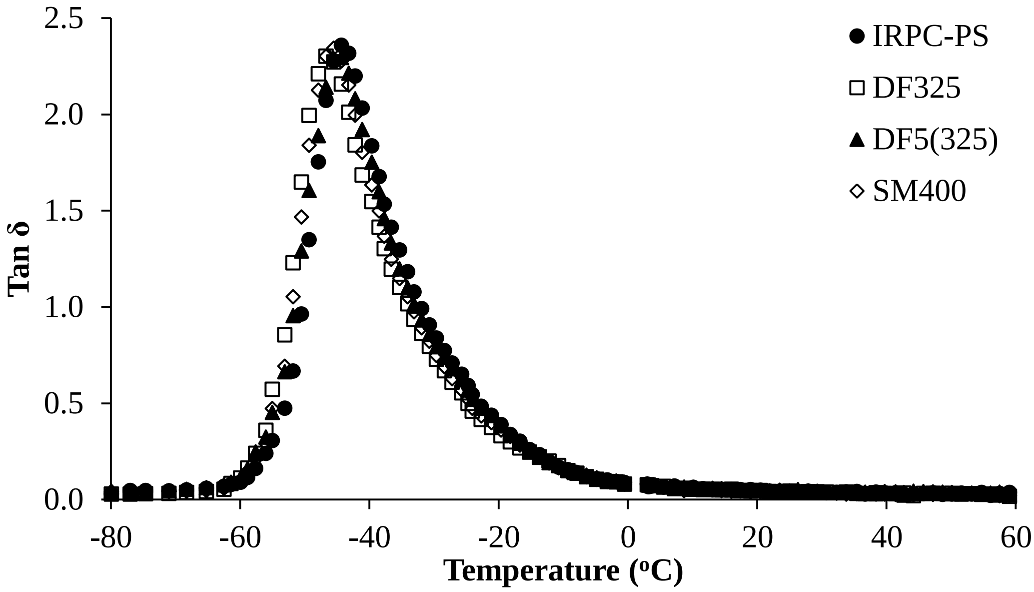


Figure 5.35 Tan δ as a function of temperature in NR vulcanizates cured with different types of sulfur

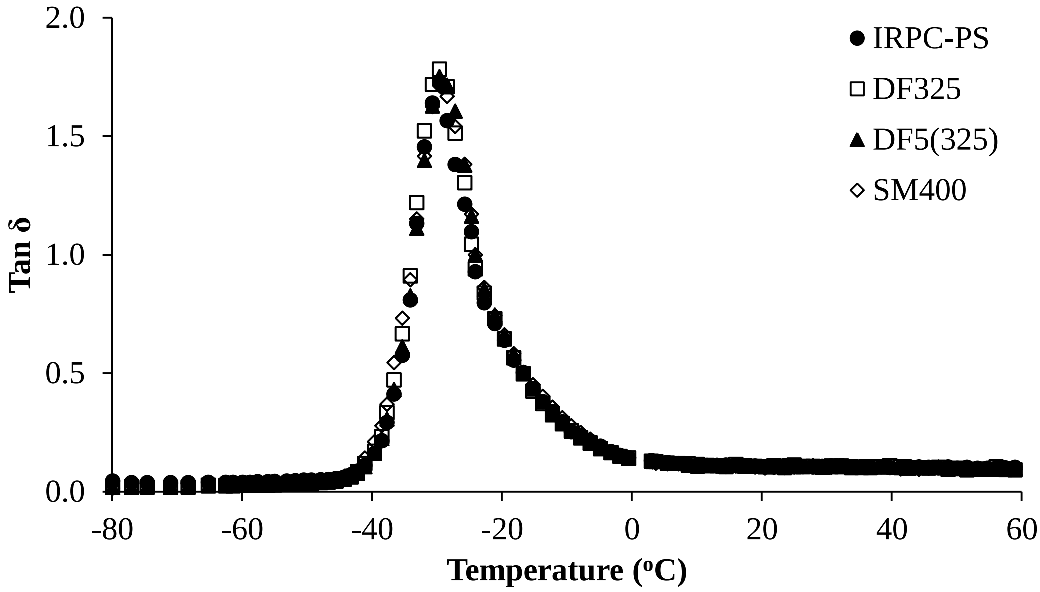


Figure 5.36 Tan δ as a function of temperature in SBR vulcanizates cured with different types of sulfur

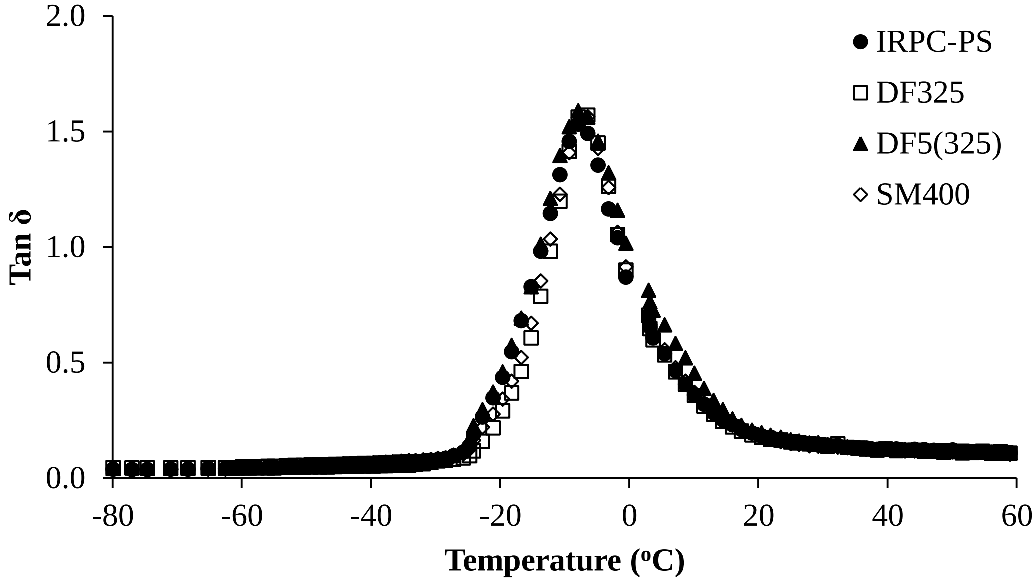


Figure 5.37 Tan δ as a function of temperature in NBR vulcanizates cured with different types of sulfur

5.2.2.6 Heat build-up

Heat build-up of rubbers cured with different types of sulfur is exhibited in Figure 5.38. Evidently, heat build-up magnitude of IRPC-PS in each rubber type is similar to that of other sulfurs. As a result, IRPC-PS can be used as vulcanizing agent in rubbers where its heat build-up are comparable to other commercial sulfurs.

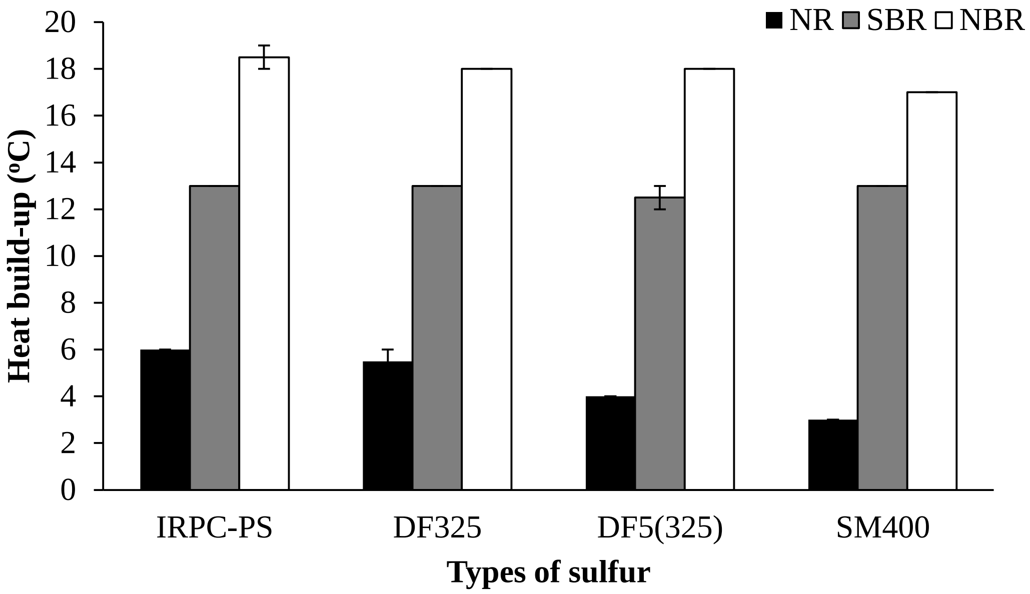


Figure 5.38 Heat build-up test of vulcanizates cured with different sulfurs

5.2.2.7 Static compression set

Figures 5.39 – 5.41 exhibit static compression set of all vulcanizates cured with different types of sulfur. Obviously, the IRPC-PS as vulcanizing agent shows analogous result to other sulfurs. Because of the similarity in crosslink density, there is no significant alteration of the static compression set observed in each rubber matrix. Furthermore, the results measured at 25^{o}C give lower static compression set than those at 100^{o}C which is in good accordance with the results shown in Figure 5.24. Similar explanation is thus applied.

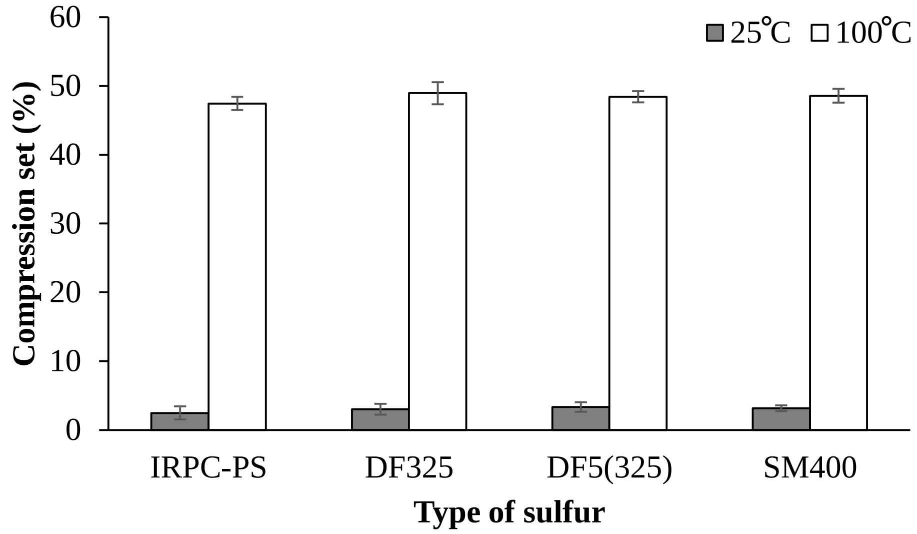


Figure 5.39 Compression set test of NR vulcanizates cured with different sulfurs

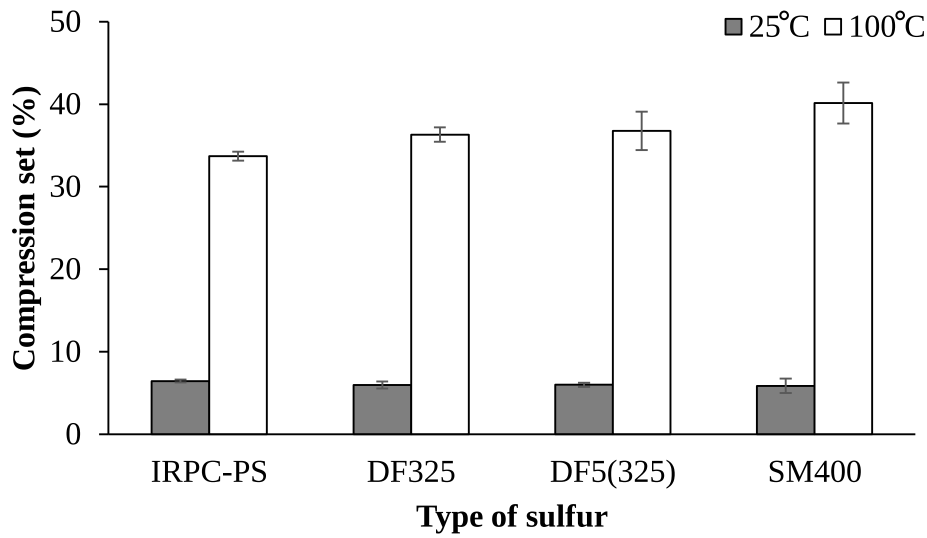


Figure 5.40 Compression set test of SBR vulcanizates cured with different sulfurs

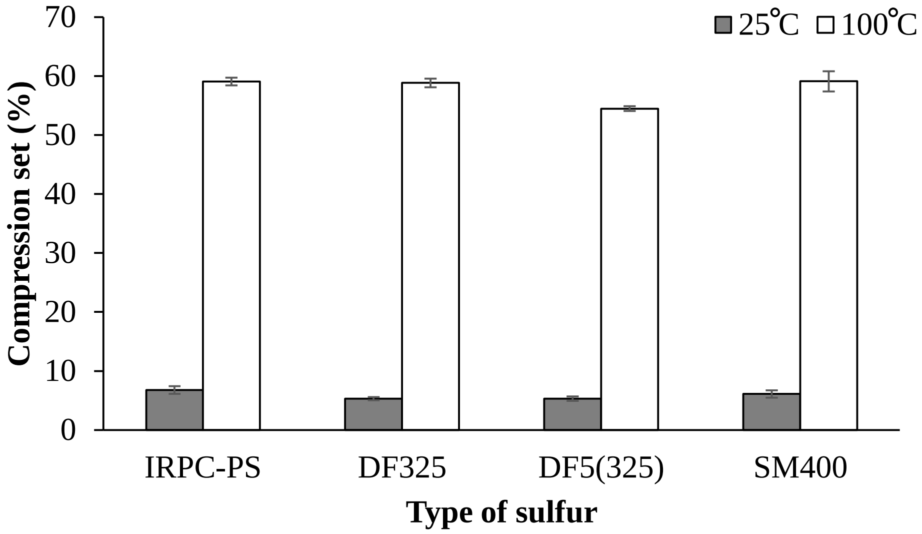


Figure 5.41 Compression set test of NBR vulcanizates cured with different sulfurs

5.2.3 Study of sulfur chemical structure in rubber vulcanizates

In order to study chemical structure of sulfur as vulcanizing agent in rubbers, XANES technique is used. All rubber vulcanizates are subjected to synchrotron radiation at the SXRMB station [66]. In this case, IRPC-PS- and RS-vulcanized rubbers are investigated, and the results are illustrated in Figures 5.42 – 5.44. The results obtained reveal similarity in the absorption peak of rubbers cured with either RS or IRPC-PS. The maximum absorption peak occurs at the photon energy of 2,472 eV (1s → σ* of S – C bond) referring to polysulfide crosslink [40, 61–63, 69–70]. Moreover, in the cases of SBR and NBR systems, there are weak peaks observed around 2,481 and 2,480 eV, respectively. For the peak at 2,481 eV of the SBR, this feature is attributed to the sulfate group while the peak at 2,480 eV of the NBR corresponds to the sulfonate group. These chemical groups are found in synthetic rubber because of oxidative process of sulfur during the crosslink reaction [62–63, 69]. The results from this technique, hence, confirm that the IRPC-PS is capable of being used as vulcanizing agent in rubbers by replacing commercial sulfurs with no marked adjustment in compounding recipe or processing conditions required while still giving comparable properties of compounds and vulcanizates. This finding is also true in all rubber matrices.

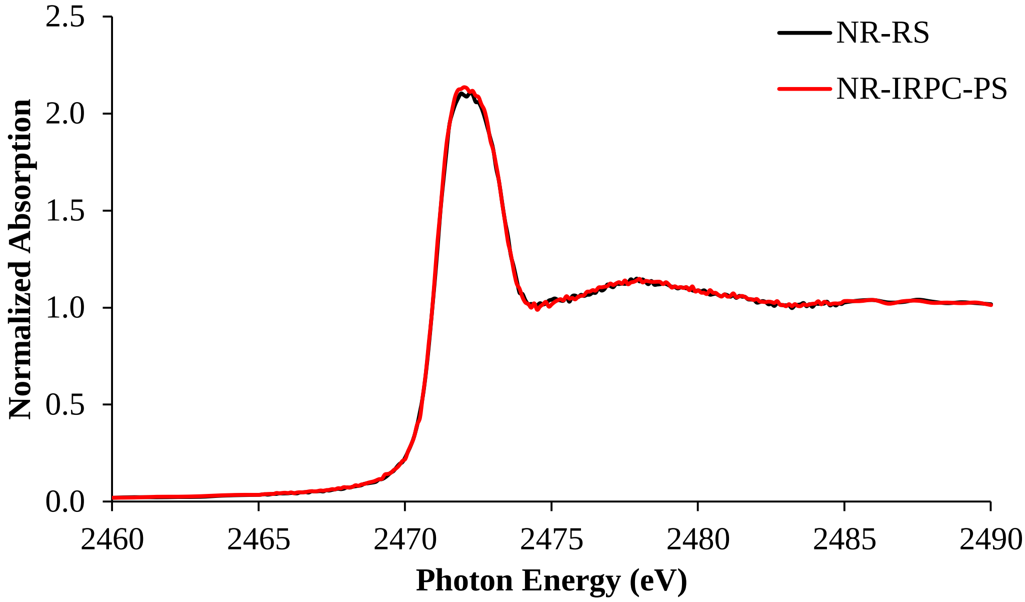


Figure 5.42 FY Sulfur K-shell XANES spectra of NR vulcanizates [69]

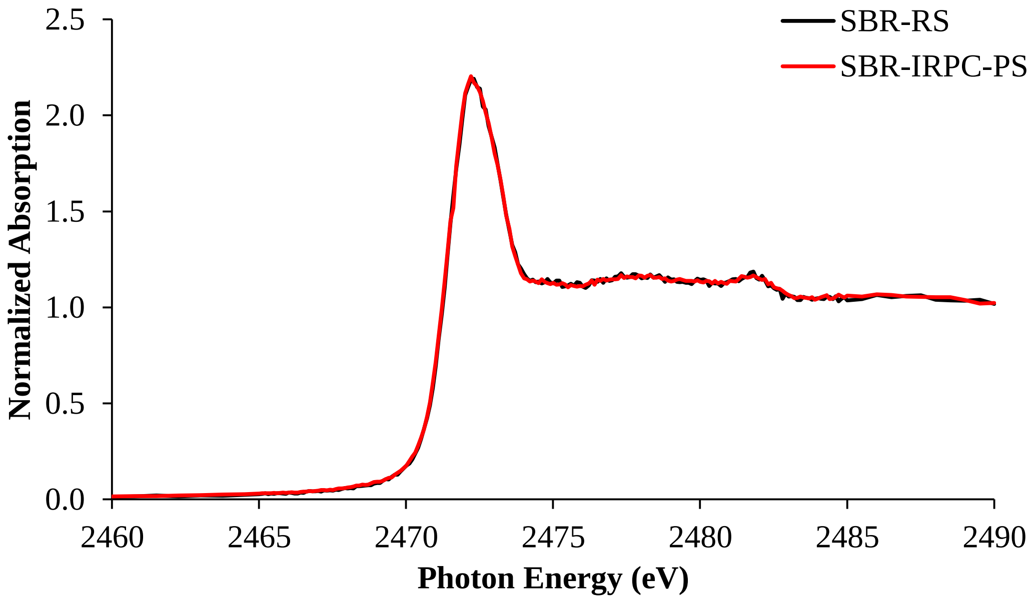


Figure 5.43 FY Sulfur K-shell XANES spectra of SBR vulcanizates [69]

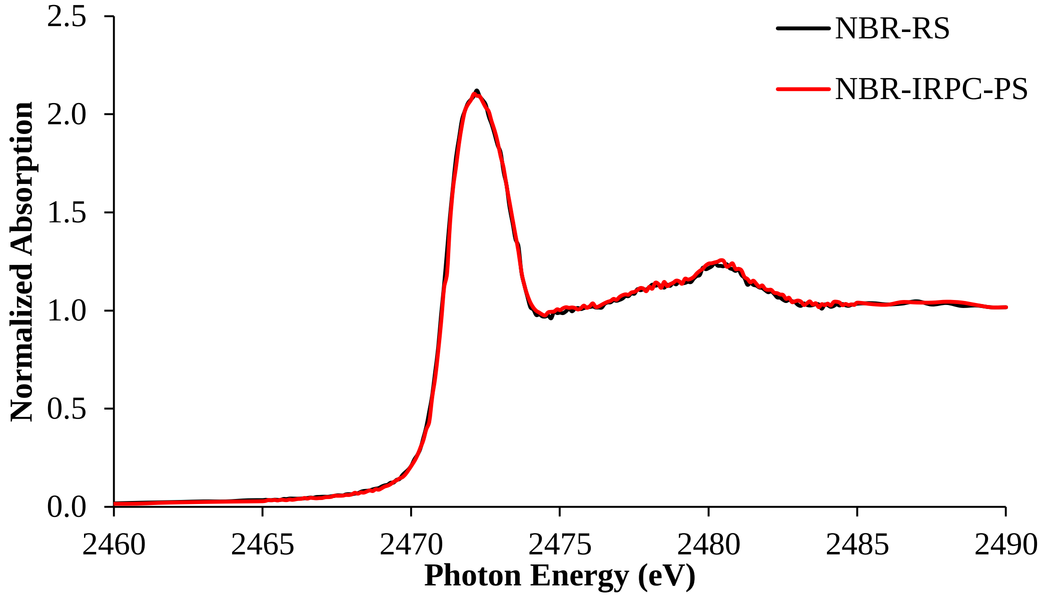


Figure 5.44 FY Sulfur K-shell XANES spectra of NBR vulcanizates [69]

5.3 Development of a new product from petroleum-based sulfur in rubber

In this section, properties of TDAE oil-coated petroleum-based sulfur (OC) as vulcanizing agent in rubbers are investigated and compared with conventional petroleum-based sulfur (OA) in which TDAE oil is added directly during the mixing cycle. The TDAE oil-coated petroleum-based sulfur (OC) is anticipated to offer superiority in sulfur dispersion in rubber matrix leading to improvement in vulcanizate properties.

5.3.1 Cure characteristics

Table 5.5 illustrates cure characteristics of compounds prepared with un-coated and oil-coated sulfurs. It can be seen that there are no significant discrepancies in cure behaviors of NR and SBR. On the other hand, there is slight difference observed in the case of NBR. Cure time of OC-NBR is somewhat shorter than that of OA-NBR. This is probably attributed to good dispersion of sulfur in NBR matrix leading to good cure efficiency [71].

Table 5.5 Cure characteristics of rubber vulcanizates cured with un-coated and oil-coated sulfurs

Sulfur and rubber systems	Cure characteristics	
	t_{s2} (min)	t_{c90} (min)
OA-NR	10.2±0.5	12.1±0.2
OC-NR	10.1±0.3	12.1±0.4
OA-SBR	34.2±0.1	50.0±0.0
OC-SBR	34.4±0.3	49.0±0.1
OA-NBR	3.4±0.2	11.3±0.2
OC-NBR	3.4±0.3	9.2±0.3

5.3.2 Swelling ratio and crosslink density

Swelling ratio (S) and calculated crosslink density (υ_e) are shown in Table 5.6. Obviously, rubbers cured with OC exhibit relatively low swelling ratio and thus relatively high crosslink density. It is believed that the OC yields superior dispersion in rubber matrices, and so the mechanical properties of vulcanizates to be discussed later.

Table 5.6 Swelling ratio (S) and crosslink density (υ_e) of rubbers cured with un-coated and oil-coated sulfurs

Sulfur and rubber systems	S	υ_e ($\times10^{-4}$ mol.cm^{-3})
OA-NR	3.92±0.05	1.26±0.02
OC-NR	3.82±0.16	1.37±0.07
OA-SBR	4.88±0.16	0.82±0.08
OC-SBR	4.75±0.02	0.90±0.03
OA-NBR	2.69±0.09	2.67±0.12
OC-NBR	2.49±0.07	3.11±0.16

5.3.3 Viscoelastic properties

Strain-dependent viscoelastic properties of rubber compounds incorporated with different sulfur types are displayed in Figures 5.45 -5.47. Evidently, there are no discrepancies observed in storage modulus (G') of all compounds. The onset of non-linearity of all compounds, regardless of types of sulfur, takes place at the strain of approximately 100% suggesting the commencing of molecular slippage. This means the TDAE oil used for coating the sulfur has no significant effect on rheological behavior of rubber compounds. In general, the oil added during the mixing stage acting as processing aid is expected to affect processability of rubber compounds. However, in these cases, there is no alteration in processability observed although TDAE oil is added in the compounds. This is attributed to the relatively small amount of TDAE oil used in this work.

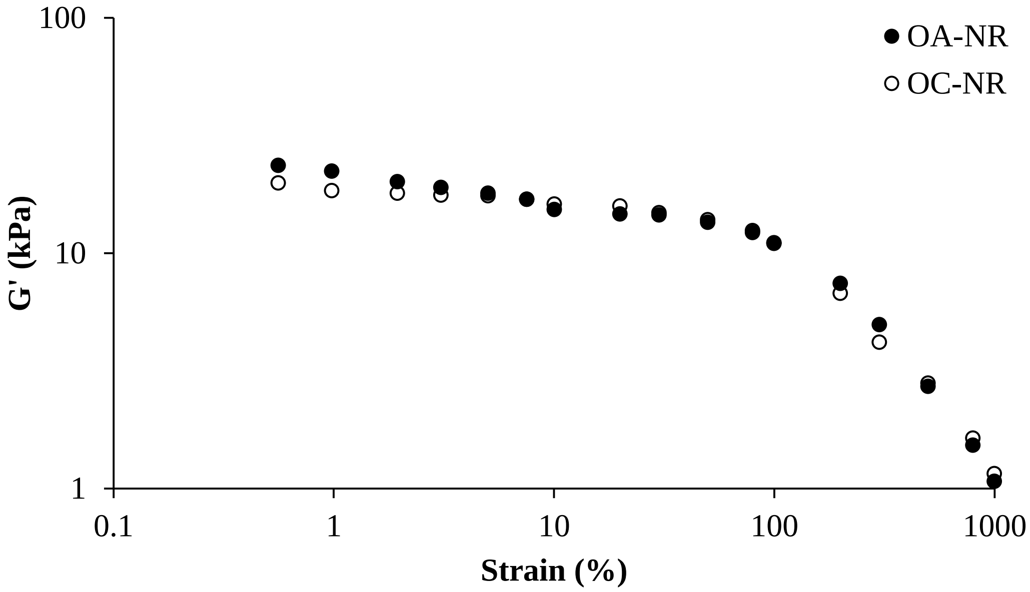


Figure 5.45 Storage modulus as a function of strain in NR compounds incorporated with different types of sulfur

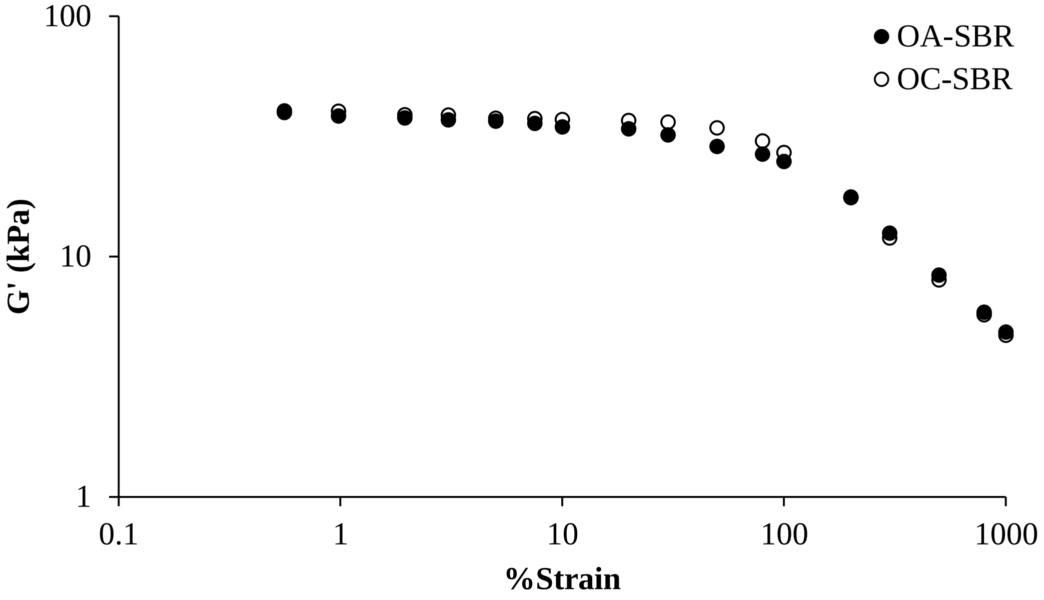


Figure 5.46 Storage modulus as a function of strain in SBR compounds incorporated with different types of sulfur

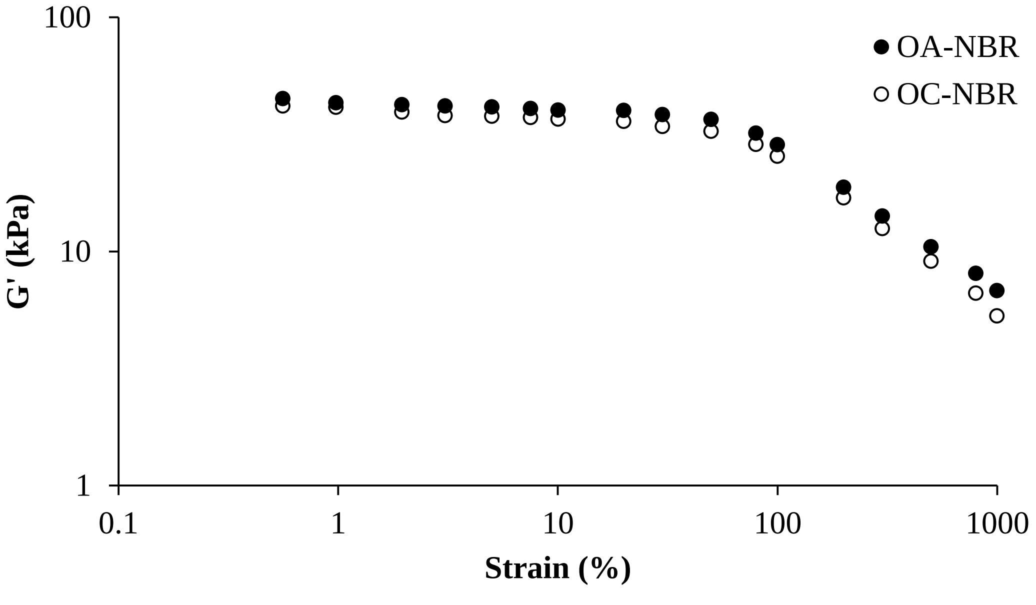


Figure 5.47 Storage modulus as a function of strain in NBR compounds incorporated with different types of sulfur

5.3.4 Mechanical properties

Figures 5.48 – 5.51 exhibit results of tensile strength, elongation at break, tear strength, and hardness of rubbers cured with different sulfurs, respectively. By considering the tensile strength, it is evident that rubbers vulcanized with the OC show greater properties than those with OA, especially in NR system. This is attributed to the enhancement in dispersion of the OC in rubber matrices and crosslink density as discussed previously. Moreover, the tensile properties of the NR are superior to those of SBR and NBR. Strain-induced crystallization of the NR is contributed to these results as reported elsewhere [72-74]. Therefore, despite the lower crosslink density of NR, its tensile properties are greater than NBR. Furthermore, as demonstrated in Figures 5.52 – 5.54, there are no dark spots observed in cured specimens of all rubbers prepared with oil-coated sulfur (OC). The results suggest that the OC offers enhanced degree of sulfur dispersion in rubber matrices resulting in good crosslink distribution along with increased crosslink density, which then leads to improved tensile strength of vulcanizates.

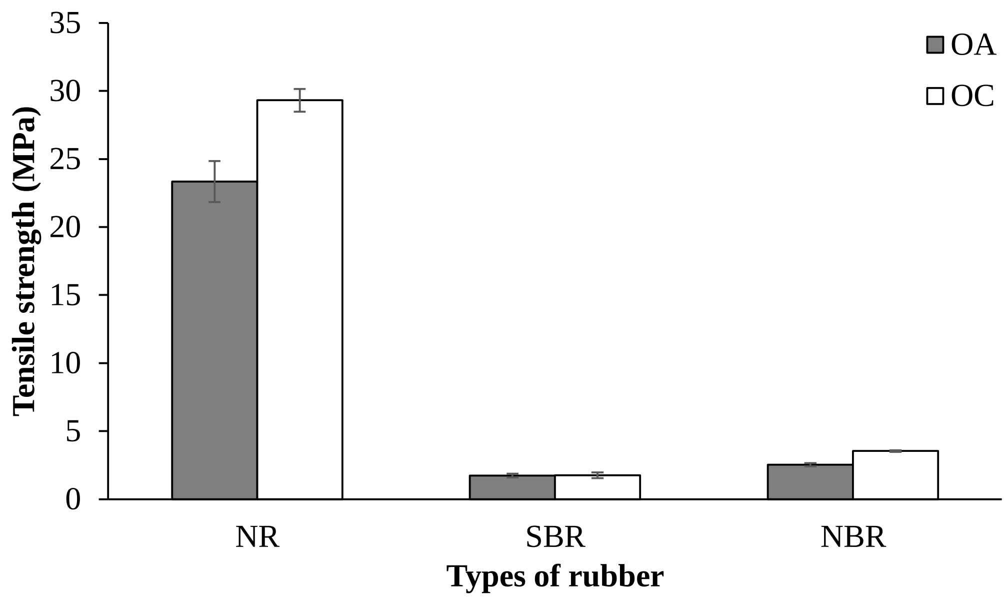


Figure 5.48 Tensile strength of rubber vulcanizates cured with different sulfurs

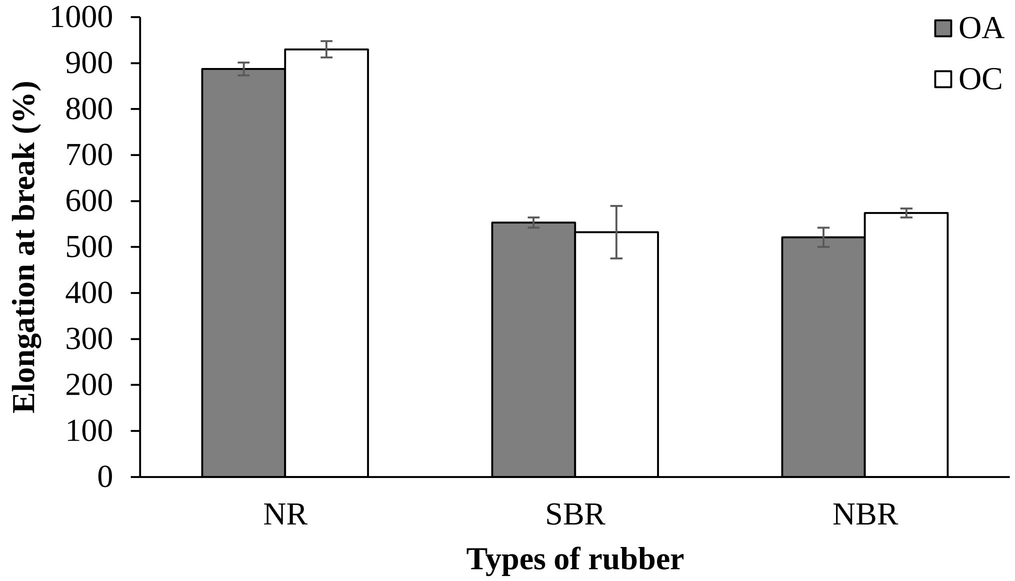


Figure 5.49 Elongation at break of rubber vulcanizates cured with different sulfurs

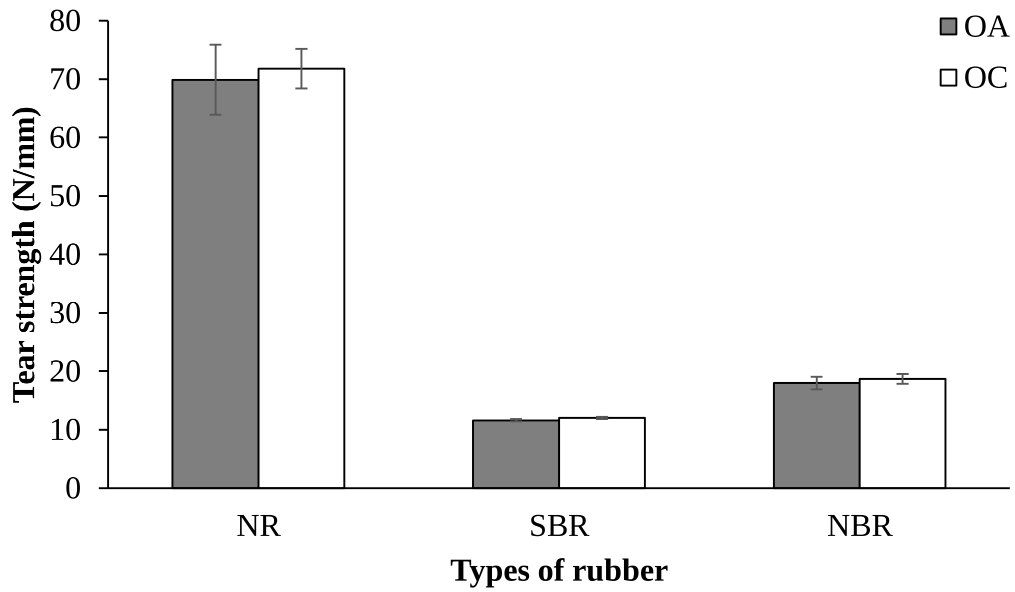


Figure 5.50 Tear strength of rubber vulcanizates cured with different sulfurs

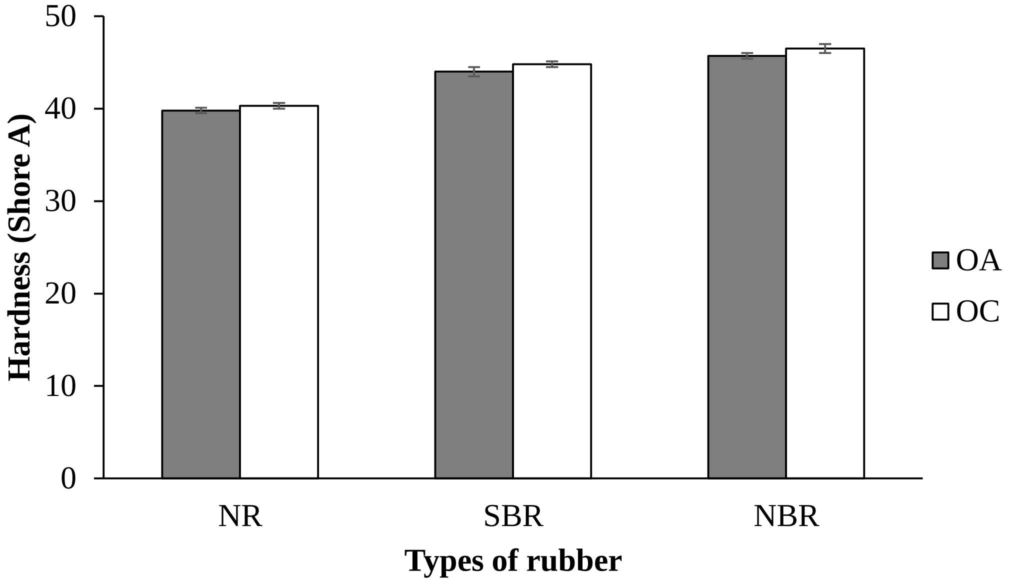
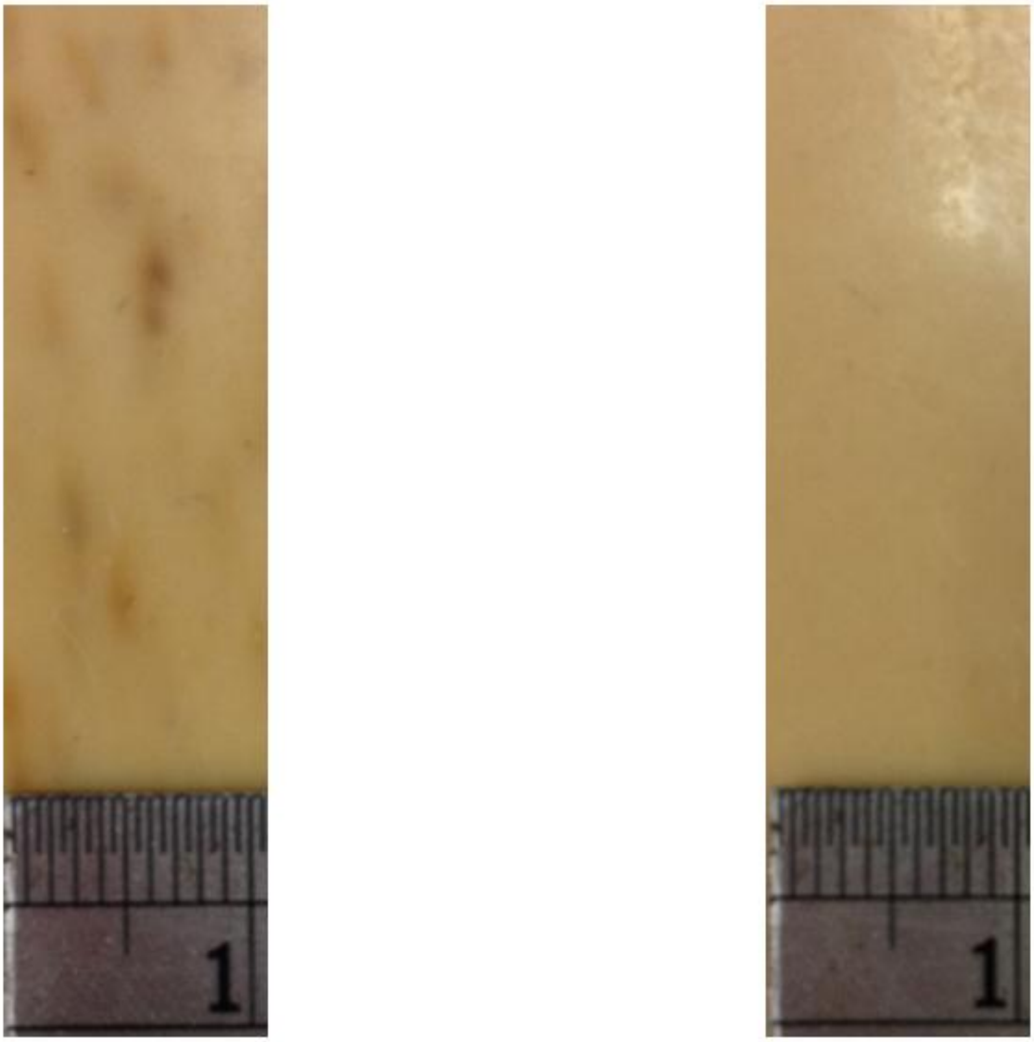
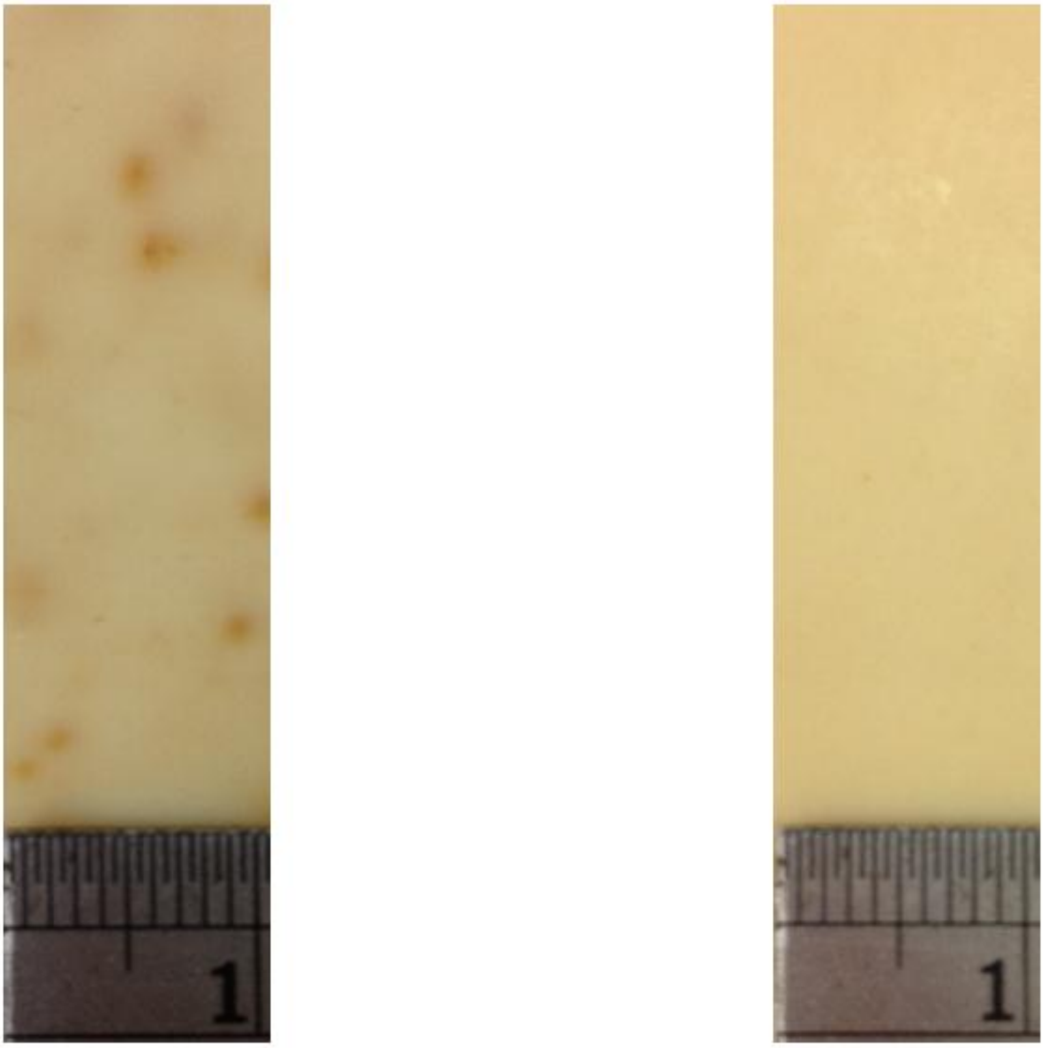


Figure 5.51 Hardness of rubber vulcanizates cured with different sulfurs



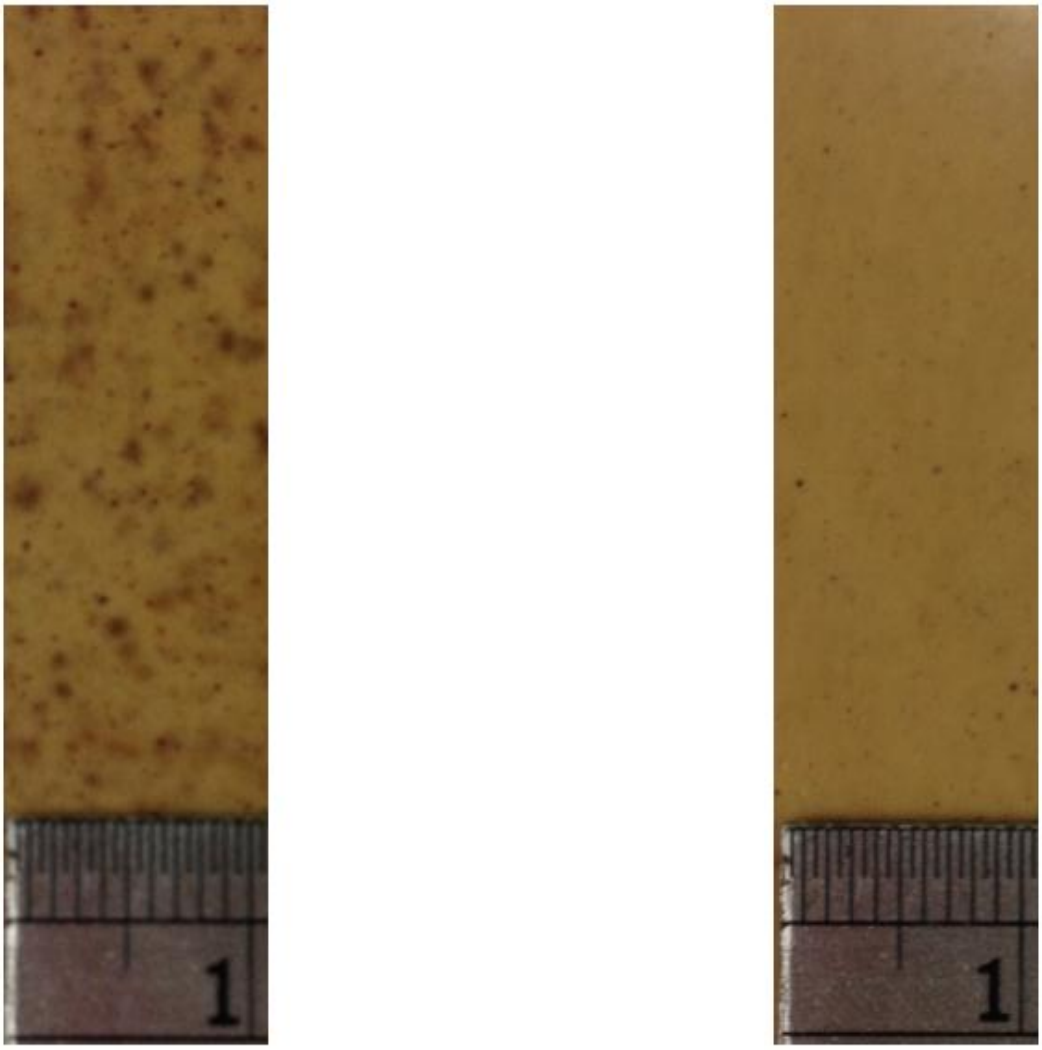
(a) (b)

Figure 5.52 Photographs of NR specimens prepared with different types of sulfurs: (a) OA and (b) OC



(a) (b)

Figure 5.53 Photographs of SBR specimens prepared with different types of sulfurs: (a) OA and (b) OC



(a) (b)

Figure 5.54 Photographs of NBR specimens prepared with different types of sulfurs: (a) OA and (b) OC

5.3.5 Dynamic mechanical properties

Dynamic mechanical properties including elastic modulus (E’) and tan δ as a function of temperature of all rubbers vulcanized with different sulfurs are shown in Figures 5.55 – 5.60. Clearly, the NR and SBR cured with OC offer similar magnitude of dynamic mechanical properties to those with OA. The E’ and the tan δ of the systems with OC exhibit the same trend as those of OA. Nevertheless, in the case of NBR, there are significant differences observed both in the elastic modulus and the tan δ. The onset of E’ softening of NBR cured with the OC shifts to higher temperature (i.e., broader glassy temperature region). This is attributed to increased crosslink density leading to high molecular restriction [3, 12]. This finding is supported by the temperature shift to the high temperature at the damping peak.

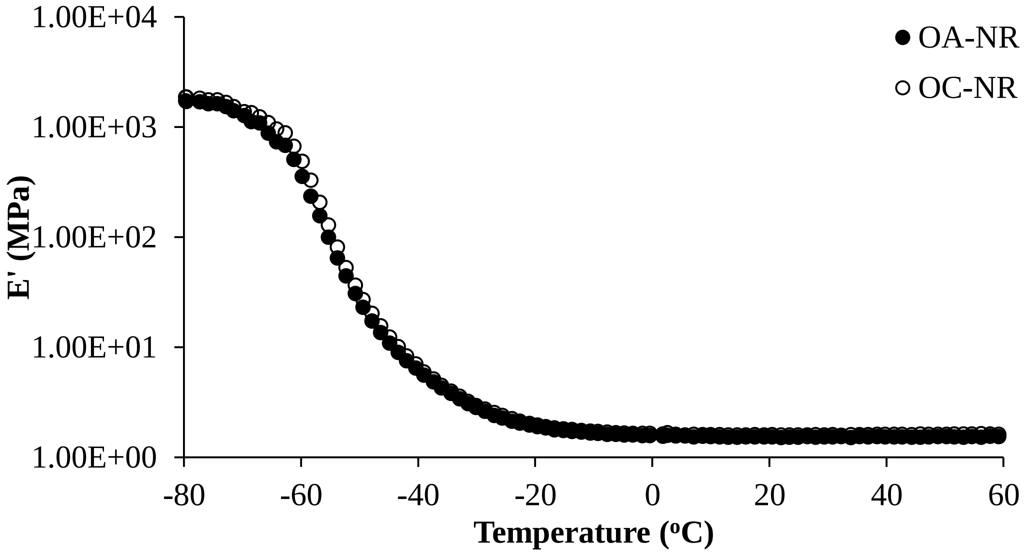


Figure 5.55 Elastic modulus as a function of temperature in NR vulcanizates incorporated with different sulfurs

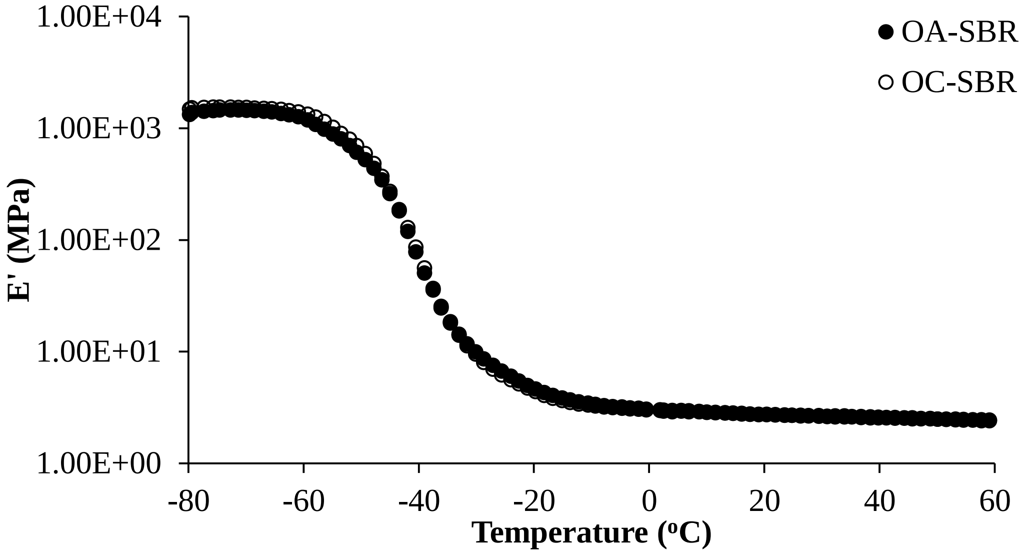


Figure 5.56 Elastic modulus as a function of temperature in SBR vulcanizates incorporated with different sulfurs

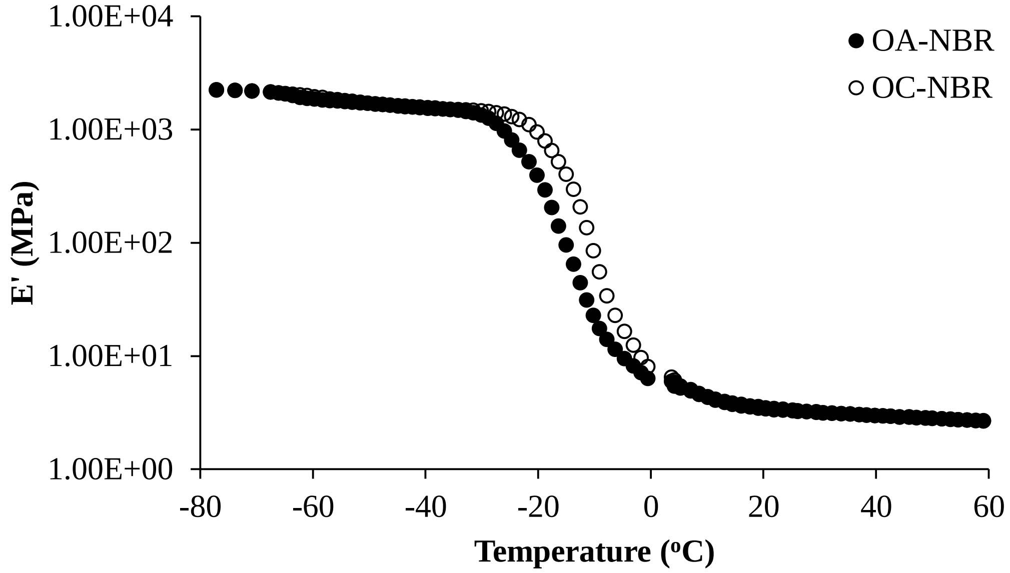


Figure 5.57 Elastic modulus as a function of temperature in NBR vulcanizates incorporated with different sulfurs

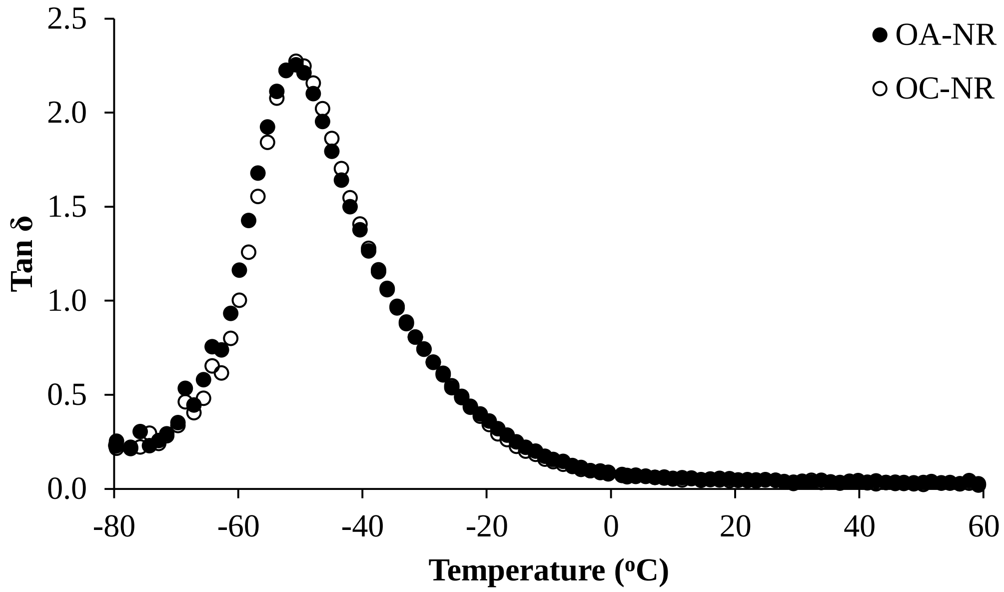


Figure 5.58 Tan δ as a function of temperature in NR vulcanizates incorporated with different sulfurs

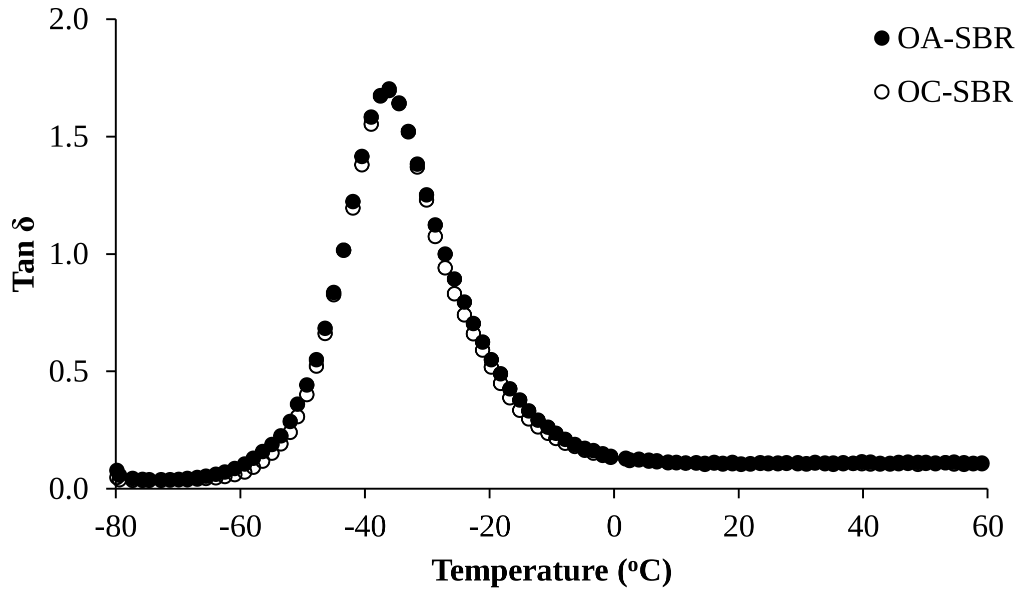


Figure 5.59 Tan δ as a function of temperature in SBR vulcanizates incorporated with different sulfurs

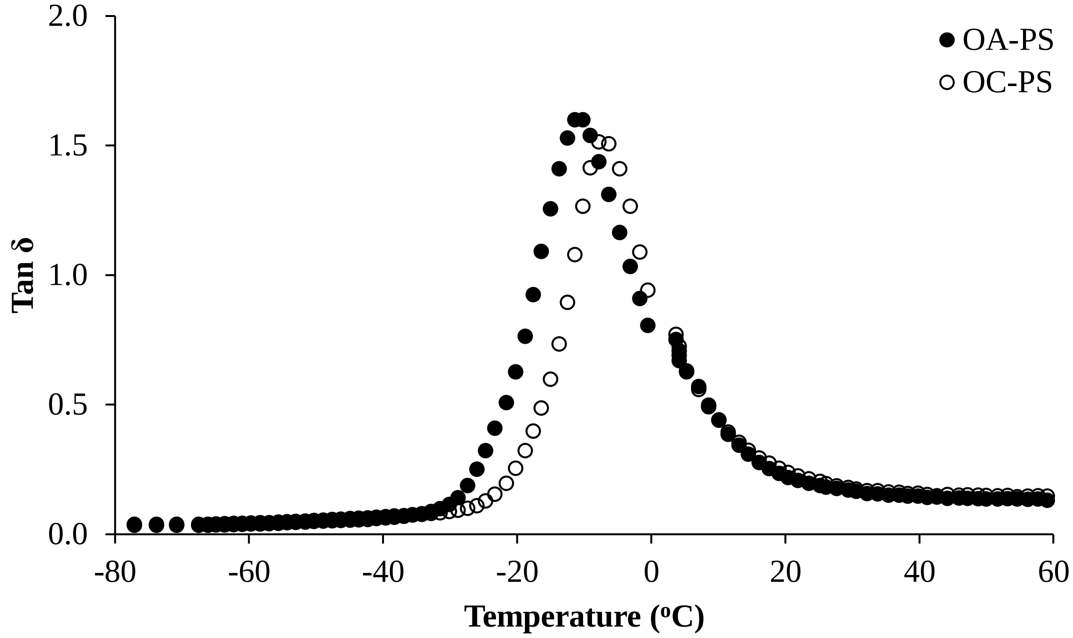


Figure 5.60 Tan δ as a function of temperature in NBR vulcanizates incorporated with different sulfurs

5.3.6 Heat build-up

Figure 5.61 displays heat build-up results of rubbers cured with different sulfurs. By considering NR and SBR vulcanizates, the temperature rise (i.e., heat build-up) of the system with OC in each rubber type shows similar trend to that with OA. Nevertheless, in the case of NBR, a significant difference is observed. Specimen cured with the OC exhibits considerably lower heat build-up than that cured with the OA. This is attributed to greater degree of sulfur dispersion in NBR matrix, and thus the higher crosslink density as the OC is used. Such enhancement in elastic contribution leads to the decreased energy dissipation under cyclic deformation, i.e., lowered heat build-up.

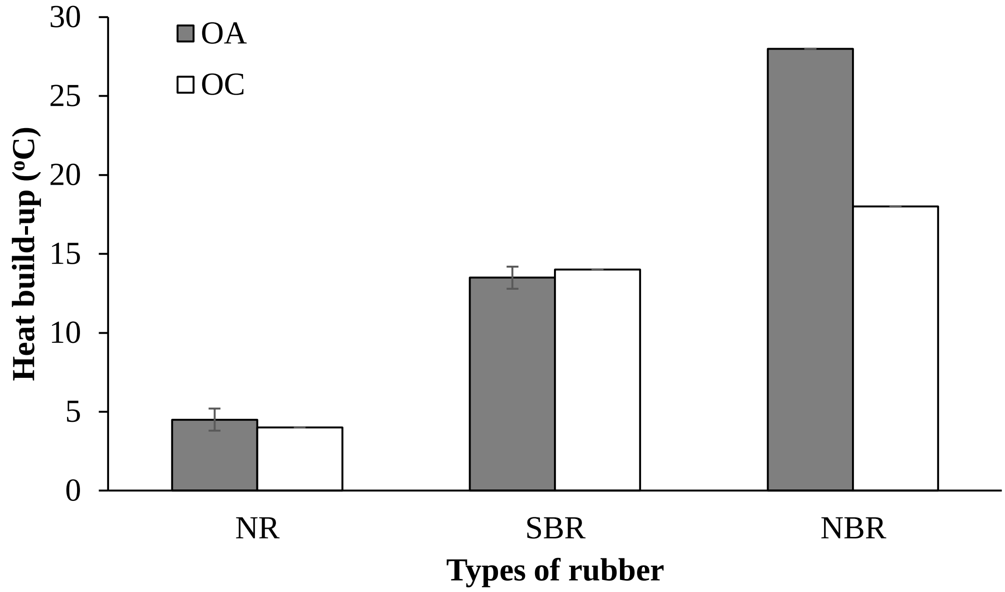


Figure 5.61 Heat build-up of vulcanizates incorporated with different sulfurs

5.3.7 Static compression set

Figures 5.62 – 5.64 show the results of static compression set of all vulcanizates. By considering NR system, the result reveals similar trend in both un-coated and oil-coated petroleum-based sulfur. However, there are disparities observed in the cases of SBR and NBR. The SBR vulcanized with OC gives lower compression set percentage compared with that vulcanized with OA. This finding is attributed to good dispersion of OC in rubber matrix and thus increased crosslink density as discussed previously. The elasticity of the rubber matrix is therefore increased leading to the lowered compression set of SBR cured with OC. Such explanation is also applied for the NBR system in which OC-vulcanized NBR possesses somewhat lower compression set compared with OA-vulcanized NBR. By this means, the OC does not only offer good dispersion of sulfur in rubber, but also give improvement in properties of rubber.

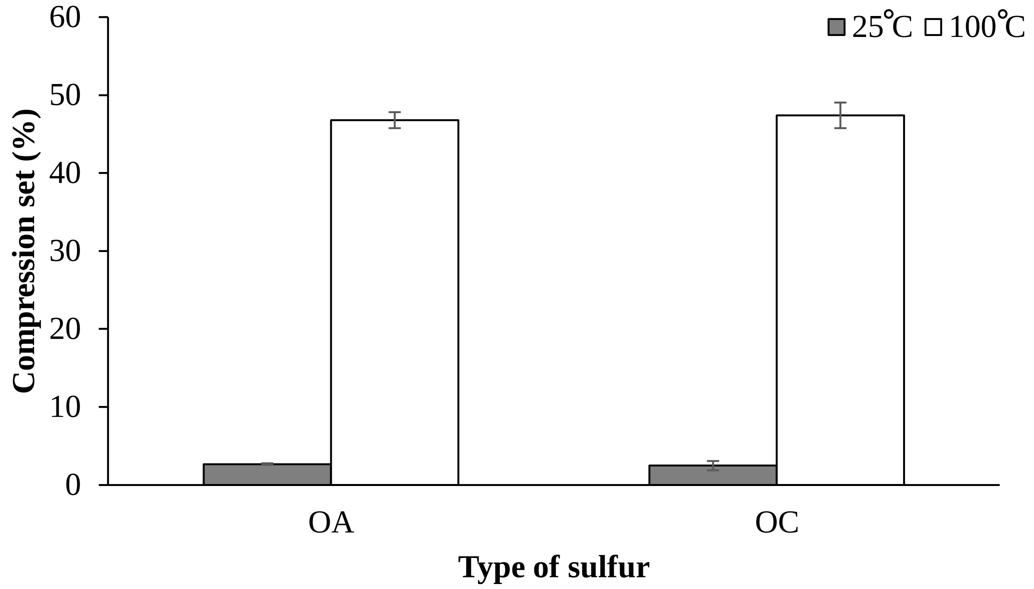


Figure 5.62 Compression set of NR vulcanizates cured with different sulfurs

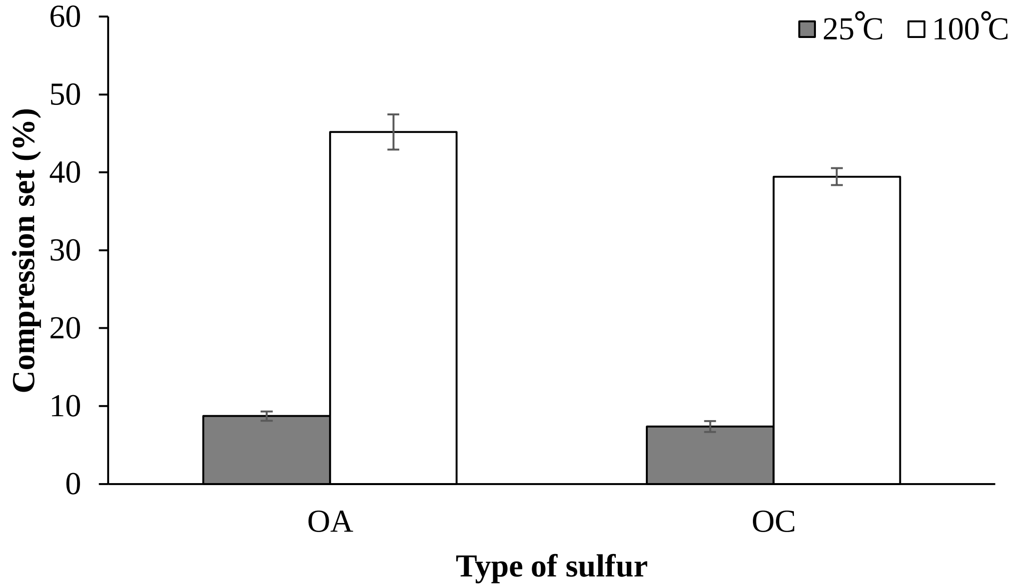


Figure 5.63 Compression set of SBR vulcanizates cured with different sulfurs

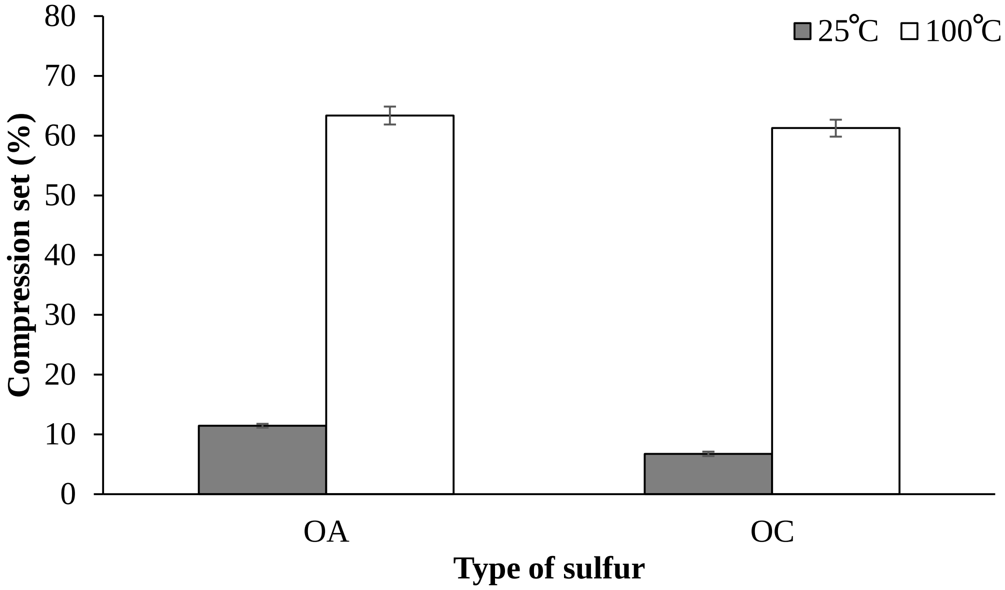


Figure 5.64 Compression set of NBR vulcanizates cured with different sulfurs

CHAPTER VI
CONCLUSIONS

The use of by-product sulfur from petroleum refinery as vulcanizing agent in rubber industry was studied. The following conclusions can be drawn.

1. Chemical structure of petroleum-based sulfur is similar to that of commercial sulfur which is rhombic structure. Sulfur content of the petroleum-based sulfur is approximate 97% comparable to that of the commercial sulfur. As a result, the utilization opportunity of petroleum-based sulfur in rubber industry is possible.

2. As vulcanizing agent in rubbers (NR, SBR, and NBR), the properties (i.e., viscoelastic, mechanical, and dynamic properties) of rubber compounds and vulcanizates incorporated with petroleum-based sulfur are similar to those cured with commercial sulfurs produced from various manufacturers. The results suggest the capability of petroleum-based sulfur in functioning as vulcanizing agent in similar manner to the conventionally used rhombic sulfur.

3. By coating the petroleum-based sulfur with TDAE oil as dispersing agent, the enhancement in properties of rubbers is received. The oil-coated petroleum-based sulfur offers superior dispersion in rubber leading to improvement in mechanical properties, while processability remains unchanged. In other words, the oil-coated petroleum-based sulfur is capable of being a functional product for rubber vulcanization which is beneficial to the collaborated company, IRPC Plc. Co., Ltd. as manufacturer of both petroleum-based sulfur and TDAE oil.

REFERENCES

1. Barlow FW. Rubber Compounding: Principles, Materials, and Techniques. 2ed. New York: Marcel Dekker, Inc.; 1993.
2. Booth EW, Beaver DJ. Vulcanization of Rubber Compounds. Industrial & Engineering Chemistry. 1940;32(7):1006-8.
3. Coran AY. The Science and Technology of Rubber. 3ed. California: Elsevier Inc.; 2005.
4. Datta RN, Ingham FAA. Rubber Technologist's Handbook. Shropshire: Rapra Technology Limited; 2001.
5. Dick JS. Rubber Technology: Compounding and Testing for Performance. 2ed. Munich: Hanser Publishers; 2009.
6. Fisher HL. Vulcanization of Rubber. Industrial & Engineering Chemistry. 1939;31(11):1381-9.
7. Goodyear C, Improvement in India-Rubber Fabrics. US1844 June 15.
8. Hofmann W. Rubber Technology Handbook. Munich: Hanser Publishers; 1989.
9. Ignatz-Hoover F, To BH. Rubber Compounding: Chemistry and Applications. New York: Marcel Dekker, Inc.; 2004.
10. Lewis WK, Squires L, Nutting RD. Mechanism of Rubber Vulcanization with Sulfur. Industrial & Engineering Chemistry. 1937;29(10):1135-44.
11. Nagdi K. Rubber as an Engineering Material: Guideline for Users. Munich: Hanser Publishers; 1993.
12. Coran AY. Chemistry of the Vulcanization and Protection of Elastomers: A review of the achievements. Journal of Applied Polymer Science. 2003;87(1):24-30.
13. Hofmann W. Vulcanization and Vulcanizing Agents. London: MacLaren and Sons; 1967.
14. Datta RN. Rubber Curing Systems. Shropshire: Rapra Technology Limited; 2002.

15. Ghosh P, Katare S, Patkar P, Caruthers JM, Venkatasubramanian V, Walker KA. Sulfur Vulcanization of Natural Rubber for Benzothiazole Accelerated Formulations: From Reaction Mechanisms to a Rational Kinetic Model. Rubber Chemistry and Technology. 2003;76(3):592-693.
16. Rostek CJ, Lin H-J, Sikora DJ, Katritzky AR, Kuzmierkiewicz W, Shobana N. Novel Sulfur Vulcanization Accelerators Based on Mercapto-Pyridine, -Pyrazine, and -Pyrimidine. Rubber Chemistry and Technology. 1996;69(2):180-202.
17. Williams I. Vulcanization of Rubber with Sulfur. Industrial & Engineering Chemistry. 1947;39(7):901-6.
18. Susamma AP, Mini VTE, Kuriakose AP. Studies on Novel Binary Accelerator System in Sulfur Vulcanization of Natural Rubber. Journal of Applied Polymer Science. 2001;79(1):1-8.
19. Aprem AS, Joseph K, Mathew T, Altstaedt V, Thomas S. Studies on Accelerated Sulphur Vulcanization of Natural Rubber Using 1-phenyl-2, 4-dithiobiuret/tertiary butyl benzothiazole sulphenamide. European Polymer Journal. 2003;39(7):1451-60.
20. Gonzalez L, Rodriguez A, Velentin JL, Marcos-Fernandez A, Posadas P. Conventional and Efficient Crosslinking of Natural Rubber: Effect of Heterogeneities on the Physical Properties. Kautsch Gummi Kunstst. 2005;12:638-43.
21. Rohana Yahya YS, Azura AR, Ahmad Z. Effect of Curing Systems on Thermal Degradation Behavior of Natural Rubber (SMR CV 60). Journal of Physical Science. 2011;22(2):1-14.
22. Enghag P. Encyclopedia of the Elements: Technical Data, History, Processing, Applications. Wiley-VCH Verlag GmbH & Co. KGaA; 2004. p. 1045-58.
23. Apodaca LE. Sulfur: U.S. Geological Survey; 2011 May 2013.
24. Büchel KH, Moretto H-H, Woditsch P. Primary Inorganic Materials. Industrial Inorganic Chemistry: Wiley-VCH Verlag GmbH; 2007. p. 1-185.
25. Meyer B. Elemental sulfur. Chemical Reviews. 1976;76(3):367-88.
26. Morais VS, Filgueiras PR, Castro EVR, Mota MFB, Malacarne MM, Morigaki MK. Investigating Petroleum Profiles and Composition of Petroleum

Fractions by means of Sulfur Analyses. Brazilian Journal of Petroleum and Gas. 2010;4(1):35-42.

27. Nehb W, Vydra K. Sulfur. Ullmann's Encyclopedia of Industrial Chemistry: Wiley-VCH Verlag GmbH & Co. KGaA; 2000.
28. Ober JA. Sulfur: US Geological Survey Minerals Yearbook; 2007.
29. Ober JA. Materials Flow of Sulfur. US: U.S. Geological Survey; 2002 02-298.
30. Steudel R, Eckert B. Solid Sulfur Allotropes Sulfur Allotropes. In: Steudel R, editor. Elemental Sulfur and Sulfur-Rich Compounds I. Topics in Current Chemistry. 230: Springer Berlin Heidelberg; 2003. p. 1-80.
31. Theilig E, United S. A Primer on Sulfur for the Planetary Geologist. Washington, D.C.: National Aeronautics and Space Administration, Scientific and Technical Information Branch; 1982. iv, p. 34.
32. Wilson LO, Jaap SSD. Geochemistry of Sulfur in Petroleum Systems. Geochemistry of Sulfur in Fossil Fuels. ACS Symposium Series. 429: American Chemical Society; 1990. p. 2-29.
33. Rodgers RP, McKenna AM. Petroleum Analysis. Analytical Chemistry. 2011;83(12):4665-87.
34. Kobe KA, McKetta JJ. Advances in Petroleum Chemistry and Refining. Vol. 1. Edited by Kenneth A. Kobe and John J. McKetta, Jr. Interscience Publishers, New York, 1958.
35. Speight JG. Handbook of Petroleum Analysis. New York: John Wiley & Sons Inc.; 2001.
36. Speight JG. Handbook of Petroleum Product Analysis. New York: John Wiley & Sons Inc.; 2002.
37. Speight JG. The Chemistry and Technology of Petroleum. 4 ed. New York: CRC Press; 2006.
38. Simanzhenkov V, Idem R. Crude Oil Chemistry. New York: Marcel Dekker Inc.; 2003.
39. George GN, Gorbaty ML. Sulfur K-edge X-ray Absorption Spectroscopy of Petroleum Asphaltenes and Model Compounds. Journal of the American Chemical Society. 1989;111(9):3182-6.

40. Eckert B, Steudel R. Molecular Spectra of Sulfur Molecules and Solid Sulfur Allotropes. Topic of Current Chemistry. 2003;231:31-98.
41. Tro NJ. Chemistry: A Molecular Approach. 2ed. New Jersey: Pearson Education Inc.; 2011.
42. Mcintyre G. Claus Sulfur Recovery Options. Bryan Research and Engineering Inc., 1997.
43. Street R, Rameshni M. Sulfur Recovery Unit: Expandsion Case Studies. Worley Parsons, 2012.
44. Akiba M, Hashim AS. Vulcanization and crosslinking in elastomers. Progress in Polymer Science. 1997;22(3):475-521.
45. Stiehler RD, Wakelin JH. Mechanism and Theory of Vulcanization. Industrial & Engineering Chemistry. 1947;39(12):1647-54.
46. Pattanasiriwisawa W, Siritapetawee J, Patarapaiboolchai O, Klysubun W. Structural Analysis of Sulfur in Natural Rubber Using X-ray Absorption Near-Edge Spectroscopy. Journal of Synchrotron Radiation. 2008;15(5):510-3.
47. Ade H, Urquhart SG. NEXAFS Spectroscopy and Microscopy of Natural and Synthetic Polymers. River Edge: World Scientific Publishing Co., Ltd.; 2002.
48. Hahner G. Near edge X-ray Absorption Fine Structure Spectroscopy as a Tool to Probe Electronic and Structural Properties of Thin Organic Films and Liquids. Chemical Society Reviews. 2006;35(12):1244-55.
49. Hemraj-Benny T, Banerjee S, Sambasivan S, Balasubramanian M, Fischer DA, Eres G. Near-Edge X-ray Absorption Fine Structure Spectroscopy as a Tool for Investigating Nanomaterials. Small. 2006;2(1):26-35.
50. Newville M. Fundamentals of XAFS. Chicago: University of Chicago; 2004.
51. Kawai J. Absorption Technique in X-ray Spectroscopy. In: Meyers RA, editor. Encyclopedia of Analytical Chemistry. Chichester: John Wiley & Sons Ltd.; 2000. p. 13288-315.
52. Willmott P. An Introduction to Synchrotron Radiation: Techniques and Applications. West Sussex: John Wiley $ Sons Ltd; 2011.

53. Prange A, Modrow H. X-ray Absorption Spectroscopy and its Application in Biological, Agricultural and Environmental Research. Reviews in Environmental Science and Biotechnology. 2002;1(4):259-76.
54. Hackett MJ, Smith SE, Paterson PG, Nichol H, Pickering IJ, George GN. X-ray Absorption Spectroscopy at the Sulfur K-Edge: A New Tool to Investigate the Biochemical Mechanisms of Neurodegeneration. ACS Chemical Neuroscience. 2012;3(3):178-85.
55. Prange A, Arzberger I, Engemann C, Modrow H, Schumann O, Trüper HG. In Situ Analysis of Sulfur in the Sulfur Globules of Phototrophic Sulfur Bacteria by X-ray Absorption Near Edge Spectroscopy. Biochimica et Biophysica Acta (BBA) - General Subjects. 1999;1428(2–3):446-54.
56. Waldo GS, Mullins OC, Penner-Hahn JE, Cramer SP. Determination of the Chemical Environment of Sulphur in Petroleum Asphaltenes by X-ray Absorption Spectroscopy. Fuel. 1992;71(1):53-7.
57. Behyan S, Hu Y, Urquhart SG. Sulfur 1s Near-Edge X-ray Absorption Fine Structure (NEXAFS) of Thiol and Thioether Compounds. The Journal of Chemical Physics. 2011;134(24):-.
58. Smith AP, Urquhart SG, Winesett DA, Mitchell G, Ade H. Use of Near Edge X-ray Absorption Fine Structure Spectromicroscopy to Characterize Multicomponent Polymeric Systems. Applied Spectroscopy. 2001;55(12):1676-81.
59. Flemmig B, Modrow H, Heinz Hallmeier K, Hormes J, Reinhold J, Szargan R. Sulfur in Different Chemical Surroundings – S K XANES Spectra of Sulfur-containing Heterocycles and their Quantum-chemically Supported Interpretation. Chemical Physics. 2001;270(3):405-13.
60. Tohsan A, Phinyocheep P, Kittipoom S, Pattanasiriwisawa W, Ikeda Y. Novel Biphasic Structured Composite Prepared by In Situ Silica Filling in Natural Rubber Latex. Polymers for Advanced Technologies. 2012;23(10):1335-42.
61. Chauvistre R, Hormes J, Bruck D, Bruck B, Sommer K, Engels HW. Structural Analysis of Sulfur in Rubber by X-ray Near Edge Absorption Spectroscopy (XANES). Kautsch Gummi Kunstst. 1992;45(10):808-13.

62. Taweepreda W, Limphirat W, Songsiriritthigul P. Oxidative Degradation Monitoring of Natural Rubber using S K-Edge X-ray Absorption Near-Edge Spectroscopy (XANES). Advanced Materials Research. 2013;620:440-5.

63. Modrow H, Hormes J, Visel F, Zimmer R. Monitoring Thermal Oxidation of Sulfur Crosslinks in SBR-Elastomers by Quantitative Analysis of Sulfur K-Edge XANES-Spectra. Rubber Chemistry and Technology. 2001;74(2):281-94.

64. Modrow H, Zimmer R, Visel F, Hormes J. Monitoring Thermal Oxidation of Sulfur Crosslinks in SBR-Elastomers using Sulfur K-edge XANES: A Feasibility Study. Kautsch Gummi Kunstst. 2000;53:328-37.

65. Ravel B, Newville M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-ray Absorption Spectroscopy Using IFEFFIT. Journal of Synchrotron Radiation. 2005;12(4):537-41.

66. Hu Y, Coulthard I, Chevrier D, Wright G, Igarashi R, Sitnikov A, Yates BW, Hallin EI, Sham TK, Reininger R. Preliminary Commissioning and Performance of the Soft X-ray Micro-characterization Beamline at the Canadian Light Source. AIP Conference Proceeding. 2010:343-6.

67. Zhan Y, Wu J, Xia H, Yan N, Fei G, Yuan G. Dispersion and Exfoliation of Graphene in Rubber by an Ultrasonically-Assisted Latex Mixing and In situ Reduction Process. Macromolecular Materials and Engineering. 2011;296(7):590-602.

68. Fuller KA, Downing HD, Querry MR. Infrared Optical Properties of Orthorhombic Sulfur. Applied Optics. 1991;30(28):4081-93.

69. Pangamol P, Sirisinha C, Hu Y, Urquhart SG. Effectiveness of By-product Sulfur from Petroleum Refining as a Rubber Vulcanizing Agent: A XANES Investigation. Industrial & Engineering Chemistry Research. 2013;52(48):17179-83.

70. Chauvistré R, Hormes J, Hartmann E, Etzenbach N, Hosch R, Hahn J. Sulfur K-Shell Photoabsorption Spectroscopy of the Sulfanes R-S_n-R, n = 2–4. Chemical Physics. 1997;223(2–3):293-302.

71. Ignatz-Hoover F, To BH. Effective Curative Dispersion for Uniform Mechanical Properties. Rubber World. 2010;243(2):21-26.
72. Tosaka M, Murakami S, Poompradub S, Kohjiya S, Ikeda Y, Toki S. Orientation and Crystallization of Natural Rubber Network As Revealed by WAXD Using Synchrotron Radiation. Macromolecules. 2004;37(9):3299-309.
73. Toki S, Hsiao BS, Kohjiya S, Tosaka M, Tsou AH, Datta S. Synchrotron X-ray Studies of Vulcanized Rubbers and Thermoplastic Elastomers. Rubber Chemistry and Technology. 2006;79(3):460-488.
74. Huneau B. Strain-induced Crystallization of Natural Rubber: A Review of X-ray Diffraction Investigations. Rubber Chemistry and Technology. 2011;84(3):425-452.

APPENDICES

APPENDIX A
PHYSICAL CHARACTERISTICS OF COMMERCIAL SULFURS

Table A1 Physical characteristics of commercial natural-based sulfurs received from various manufacturers

Type of sulfur	Inspection items				
	Purity (%)	Ash (%)	Moisture (%)	Acidity (%)	Oil content (%)
RS	99.94	0.014	0.012	0.012	-
M101	99.00	0.01	0.01	0.001	0.99
M105	95.36	0.01	0.01	0.001	4.64
SGS	99.90	0.01	0.01	0.001	-
SP400	99.90	0.02	0.1	0.01	-

Table A2 Physical characteristics of commercial petroleum-based sulfurs received from various manufacturers

Type of sulfur	Inspection items				
	Purity (%)	Ash (%)	Moisture (%)	Acidity (%)	Oil content (%)
DF325	98.5	0.005	0.3	0.01	1.0
DF5(325)	94.5	0.005	0.3	0.01	5.0
SM400	99.9	0.005	0.1	0.01	-

APPENDIX B
CHARACTERIZATIONS OF CHEMICAL STRUCTURE OF SULFUR

Table B1 Data collected from DSC experiment

Temp. (^{o}C)	Heat flow (W/g)	
	RS	PS
40.02	0.16	0.15
40.02	0.16	0.17
40.03	0.17	0.25
40.06	0.21	0.36
40.10	0.28	0.48
40.17	0.37	0.60
40.26	0.46	0.70
40.35	0.55	0.78
40.46	0.64	0.86
40.57	0.72	0.93
40.70	0.79	0.99
40.83	0.86	1.04
40.96	0.92	1.09
41.10	0.98	1.13
41.25	1.04	1.17
41.39	1.08	1.20
41.54	1.12	1.22
41.70	1.16	1.25
41.85	1.19	1.27
42.01	1.22	1.29
42.16	1.25	1.30
42.32	1.27	1.32
42.48	1.29	1.32
42.64	1.31	1.34
42.80	1.32	1.35
42.96	1.34	1.35
43.12	1.35	1.36
43.29	1.36	1.36
43.45	1.37	1.37
43.61	1.38	1.37
43.77	1.39	1.38
43.94	1.39	1.38
44.10	1.40	1.39
44.27	1.40	1.39
44.43	1.41	1.39
44.59	1.41	1.39
44.76	1.41	1.39
44.92	1.42	1.40
45.09	1.42	1.40
45.25	1.42	1.40
45.42	1.42	1.40
45.58	1.43	1.41

Temp. (^{o}C)	Heat flow (W/g)	
	RS	PS
45.75	1.43	1.41
45.92	1.43	1.41
46.08	1.43	1.41
46.25	1.43	1.41
46.41	1.44	1.42
46.58	1.44	1.42
46.74	1.44	1.42
46.91	1.44	1.42
47.07	1.45	1.42
47.24	1.45	1.43
47.41	1.45	1.43
47.57	1.45	1.43
47.74	1.45	1.43
47.90	1.46	1.43
48.07	1.46	1.44
48.24	1.46	1.44
48.40	1.46	1.44
48.57	1.46	1.44
48.73	1.46	1.44
48.90	1.47	1.44
49.07	1.47	1.45
49.23	1.47	1.45
49.40	1.47	1.45
49.57	1.47	1.45
49.73	1.47	1.45
49.90	1.48	1.45
50.07	1.48	1.46
50.23	1.48	1.46
50.40	1.48	1.46
50.56	1.48	1.46
50.73	1.48	1.46
50.90	1.48	1.46
51.06	1.48	1.46
51.23	1.49	1.46
51.40	1.49	1.46
51.56	1.49	1.47
51.73	1.49	1.47
51.90	1.49	1.47
52.06	1.49	1.47
52.23	1.49	1.47
52.40	1.49	1.47
52.56	1.49	1.47

Temp. (^{o}C)	Heat flow (W/g)	
	RS	PS
52.73	1.49	1.47
52.90	1.50	1.47
53.06	1.50	1.47
53.23	1.50	1.48
53.40	1.50	1.48
53.56	1.50	1.48
53.73	1.50	1.48
53.90	1.50	1.48
54.06	1.50	1.48
54.23	1.50	1.48
54.40	1.50	1.49
54.56	1.50	1.49
54.73	1.51	1.49
54.90	1.51	1.49
55.06	1.51	1.49
55.23	1.51	1.49
55.40	1.51	1.49
55.56	1.51	1.49
55.73	1.51	1.49
55.90	1.51	1.49
56.06	1.51	1.49
56.23	1.51	1.49
56.40	1.51	1.49
56.56	1.51	1.49
56.73	1.51	1.49
56.90	1.52	1.49
57.06	1.52	1.49
57.23	1.52	1.49
57.39	1.52	1.49
57.56	1.52	1.50
57.73	1.52	1.50
57.89	1.52	1.50
58.06	1.52	1.50
58.23	1.52	1.50
58.40	1.52	1.50
58.56	1.52	1.50
58.73	1.52	1.50
58.90	1.52	1.50
59.06	1.52	1.50
59.23	1.52	1.50
59.40	1.52	1.50
59.56	1.53	1.50

Table B1 Data collected from DSC experiment (cont.)

Temp. (°C)	Heat flow (W/g)		Temp. (°C)	Heat flow (W/g)		Temp. (°C)	Heat flow (W/g)	
	RS	PS		RS	PS		RS	PS
59.73	1.53	1.50	66.73	1.55	1.52	73.74	1.56	1.54
59.90	1.53	1.50	66.90	1.55	1.52	73.90	1.56	1.54
60.06	1.53	1.50	67.07	1.55	1.52	74.07	1.57	1.54
60.23	1.53	1.50	67.23	1.55	1.52	74.24	1.57	1.54
60.40	1.53	1.50	67.40	1.55	1.52	74.40	1.57	1.54
60.56	1.53	1.50	67.57	1.55	1.52	74.57	1.57	1.54
60.73	1.53	1.50	67.73	1.55	1.52	74.74	1.57	1.54
60.90	1.53	1.50	67.90	1.55	1.53	74.90	1.57	1.54
61.06	1.53	1.50	68.07	1.55	1.53	75.07	1.57	1.54
61.23	1.53	1.50	68.23	1.55	1.53	75.24	1.57	1.54
61.40	1.53	1.50	68.40	1.55	1.53	75.40	1.57	1.54
61.56	1.53	1.51	68.57	1.55	1.53	75.57	1.57	1.54
61.73	1.53	1.51	68.73	1.55	1.53	75.74	1.57	1.54
61.90	1.53	1.51	68.90	1.55	1.53	75.90	1.57	1.54
62.06	1.53	1.51	69.07	1.55	1.53	76.07	1.57	1.54
62.23	1.53	1.51	69.23	1.55	1.53	76.24	1.57	1.54
62.40	1.53	1.51	69.40	1.55	1.53	76.40	1.57	1.54
62.56	1.53	1.51	69.57	1.55	1.53	76.57	1.57	1.54
62.73	1.53	1.51	69.73	1.56	1.53	76.74	1.57	1.54
62.90	1.54	1.51	69.90	1.56	1.53	76.90	1.57	1.55
63.06	1.54	1.51	70.07	1.56	1.53	77.07	1.57	1.55
63.23	1.54	1.51	70.23	1.56	1.53	77.24	1.57	1.55
63.40	1.54	1.51	70.40	1.56	1.53	77.40	1.57	1.55
63.56	1.54	1.51	70.57	1.56	1.53	77.57	1.57	1.55
63.73	1.54	1.51	70.73	1.56	1.53	77.74	1.57	1.55
63.90	1.54	1.51	70.90	1.56	1.53	77.90	1.57	1.55
64.06	1.54	1.51	71.07	1.56	1.53	78.07	1.57	1.55
64.23	1.54	1.51	71.23	1.56	1.53	78.24	1.57	1.55
64.40	1.54	1.51	71.40	1.56	1.53	78.40	1.57	1.55
64.56	1.54	1.51	71.57	1.56	1.53	78.57	1.57	1.55
64.73	1.54	1.52	71.73	1.56	1.53	78.74	1.57	1.55
64.90	1.54	1.52	71.90	1.56	1.53	78.90	1.57	1.55
65.06	1.54	1.52	72.07	1.56	1.53	79.07	1.57	1.55
65.23	1.54	1.52	72.24	1.56	1.54	79.24	1.57	1.55
65.40	1.54	1.52	72.40	1.56	1.54	79.40	1.57	1.55
65.57	1.54	1.52	72.57	1.56	1.54	79.57	1.57	1.55
65.73	1.54	1.52	72.74	1.56	1.54	79.74	1.58	1.55
65.90	1.54	1.52	72.90	1.56	1.54	79.90	1.58	1.55
66.06	1.55	1.52	73.07	1.56	1.54	80.07	1.58	1.55
66.23	1.55	1.52	73.24	1.56	1.54	80.24	1.58	1.55
66.40	1.55	1.52	73.40	1.56	1.54	80.40	1.58	1.55
66.57	1.55	1.52	73.57	1.56	1.54	80.57	1.58	1.55

Table B1 Data collected from DSC experiment (cont.)

Temp. (^oC)	Heat flow (W/g)		Temp. (^oC)	Heat flow (W/g)		Temp. (^oC)	Heat flow (W/g)	
	RS	PS		RS	PS		RS	PS
80.74	1.58	1.55	87.74	1.59	1.57	94.74	1.60	1.58
80.90	1.58	1.55	87.91	1.59	1.57	94.91	1.60	1.58
81.07	1.58	1.55	88.07	1.59	1.57	95.08	1.60	1.58
81.24	1.58	1.55	88.24	1.59	1.57	95.24	1.60	1.59
81.41	1.58	1.55	88.41	1.59	1.57	95.41	1.61	1.59
81.57	1.58	1.55	88.58	1.59	1.57	95.58	1.61	1.59
81.74	1.58	1.55	88.74	1.59	1.57	95.74	1.61	1.59
81.91	1.58	1.55	88.91	1.59	1.57	95.91	1.61	1.59
82.07	1.58	1.55	89.08	1.59	1.57	96.08	1.61	1.59
82.24	1.58	1.55	89.24	1.59	1.57	96.24	1.61	1.59
82.41	1.58	1.56	89.41	1.59	1.57	96.41	1.61	1.59
82.57	1.58	1.56	89.58	1.60	1.57	96.58	1.61	1.59
82.74	1.58	1.56	89.74	1.60	1.57	96.75	1.61	1.59
82.91	1.58	1.56	89.91	1.60	1.57	96.91	1.61	1.59
83.07	1.58	1.56	90.08	1.60	1.57	97.08	1.61	1.59
83.24	1.58	1.56	90.24	1.60	1.57	97.25	1.61	1.59
83.41	1.58	1.56	90.41	1.60	1.57	97.41	1.61	1.59
83.57	1.58	1.56	90.58	1.60	1.57	97.58	1.61	1.59
83.74	1.58	1.56	90.74	1.60	1.57	97.75	1.61	1.59
83.91	1.58	1.56	90.91	1.60	1.57	97.91	1.61	1.59
84.07	1.58	1.56	91.08	1.60	1.57	98.08	1.61	1.59
84.24	1.58	1.56	91.24	1.60	1.57	98.25	1.61	1.60
84.41	1.59	1.56	91.41	1.60	1.58	98.41	1.61	1.60
84.57	1.59	1.56	91.58	1.60	1.58	98.58	1.61	1.60
84.74	1.59	1.56	91.74	1.60	1.58	98.75	1.61	1.60
84.91	1.59	1.56	91.91	1.60	1.58	98.91	1.61	1.60
85.07	1.59	1.56	92.08	1.60	1.58	99.08	1.61	1.60
85.24	1.59	1.56	92.24	1.60	1.58	99.25	1.61	1.60
85.41	1.59	1.56	92.41	1.60	1.58	99.41	1.61	1.60
85.57	1.59	1.56	92.58	1.60	1.58	99.58	1.61	1.60
85.74	1.59	1.56	92.74	1.60	1.58	99.75	1.61	1.60
85.91	1.59	1.56	92.91	1.60	1.58	99.91	1.61	1.60
86.07	1.59	1.56	93.08	1.60	1.58	100.08	1.61	1.61
86.24	1.59	1.56	93.24	1.60	1.58	100.25	1.61	1.61
86.41	1.59	1.56	93.41	1.60	1.58	100.41	1.61	1.61
86.57	1.59	1.56	93.58	1.60	1.58	100.58	1.61	1.61
86.74	1.59	1.56	93.74	1.60	1.58	100.75	1.61	1.61
86.91	1.59	1.56	93.91	1.60	1.58	100.91	1.61	1.62
87.07	1.59	1.56	94.08	1.60	1.58	101.08	1.62	1.63
87.24	1.59	1.57	94.24	1.60	1.58	101.25	1.62	1.66
87.41	1.59	1.57	94.41	1.60	1.58	101.41	1.62	1.70
87.57	1.59	1.57	94.58	1.60	1.58	101.58	1.62	1.76

Table B1 Data collected from DSC experiment (cont.)

Temp. (°C)	Heat flow (W/g)	
	RS	PS
101.75	1.62	1.85
101.91	1.62	1.96
102.08	1.62	2.13
102.25	1.62	2.39
102.41	1.62	2.76
102.58	1.62	3.29
102.75	1.62	3.99
102.91	1.62	4.83
103.08	1.62	5.79
103.25	1.62	6.84
103.41	1.62	7.80
103.58	1.62	8.54
103.75	1.62	8.99
103.91	1.63	9.04
104.08	1.64	8.68
104.25	1.67	7.99
104.41	1.73	7.13
104.58	1.80	6.21
104.74	1.91	5.38
104.90	2.06	4.69
105.06	2.28	4.15
105.22	2.60	3.72
105.37	3.03	3.38
105.52	3.55	3.09
105.66	4.17	2.86
105.79	4.87	2.67
105.93	5.65	2.52
106.06	6.47	2.39
106.18	7.23	2.28
106.31	7.86	2.19
106.44	8.28	2.12
106.59	8.42	2.06
106.74	8.23	2.01
106.91	7.88	1.97
107.09	7.52	1.94
107.27	7.10	1.91
107.45	6.57	1.89
107.65	5.90	1.87
107.84	5.21	1.85
108.04	4.56	1.84
108.24	4.00	1.83
108.44	3.57	1.82

Temp. (°C)	Heat flow (W/g)	
	RS	PS
108.63	3.24	1.82
108.82	2.96	1.81
109.00	2.74	1.81
109.18	2.55	1.81
109.36	2.40	1.81
109.54	2.27	1.81
109.71	2.17	1.80
109.88	2.08	1.80
110.06	2.01	1.80
110.23	1.95	1.80
110.40	1.90	1.80
110.57	1.86	1.80
110.74	1.83	1.80
110.90	1.81	1.80
111.07	1.79	1.80
111.24	1.77	1.80
111.41	1.76	1.80
111.58	1.75	1.80
111.74	1.74	1.80
111.91	1.73	1.80
112.08	1.73	1.80
112.25	1.73	1.81
112.41	1.73	1.81
112.58	1.72	1.81
112.75	1.72	1.82
112.91	1.72	1.82
113.08	1.72	1.84
113.25	1.72	1.85
113.41	1.73	1.87
113.58	1.73	1.89
113.75	1.75	1.92
113.91	1.79	1.94
114.08	1.92	1.98
114.24	2.14	2.01
114.40	1.98	2.05
114.57	1.92	2.08
114.74	1.92	2.11
114.90	1.92	2.14
115.07	1.90	2.18
115.24	1.85	2.23
115.41	1.83	2.29
115.57	1.82	2.36

Temp. (°C)	Heat flow (W/g)	
	RS	PS
115.74	1.81	2.42
115.91	1.80	2.51
116.08	1.79	2.59
116.24	1.79	2.69
116.41	1.79	2.80
116.58	1.79	2.91
116.75	1.79	3.03
116.91	1.79	3.16
117.08	1.79	3.29
117.24	1.79	3.43
117.41	1.79	3.57
117.58	1.80	3.73
117.74	1.81	3.91
117.91	1.83	4.11
118.08	1.86	4.34
118.24	1.89	4.61
118.41	1.93	4.92
118.57	1.97	5.28
118.74	2.04	5.68
118.90	2.11	6.14
119.06	2.22	6.66
119.23	2.37	7.23
119.39	2.60	7.86
119.54	2.93	8.56
119.69	3.43	9.37
119.83	4.19	10.40
119.97	5.27	11.92
120.08	6.67	13.65
120.19	8.24	14.96
120.28	9.80	16.06
120.37	11.18	17.13
120.47	12.40	18.30
120.57	14.07	19.51
120.65	16.23	20.17
120.72	18.23	20.50
120.79	19.63	20.59
120.87	22.10	20.36
120.91	24.67	19.70
121.01	23.32	18.21
121.17	22.57	15.48
121.34	22.31	12.18
121.52	22.13	9.89

Table B1 Data collected from DSC experiment (cont.)

Temp. (^{o}C)	Heat flow (W/g)	
	RS	PS
121.69	21.96	8.36
121.87	21.75	7.16
122.05	21.23	6.18
122.25	19.41	5.38
122.50	15.98	4.72
122.80	12.64	4.20
123.10	10.48	3.76
123.39	8.91	3.42
123.65	7.64	3.12
123.89	6.61	2.89
124.12	5.76	2.70
124.34	5.06	2.55
124.55	4.49	2.42
124.75	4.02	2.32
124.95	3.64	2.24
125.14	3.33	2.17
125.32	3.06	2.11
125.50	2.86	2.07
125.69	2.68	2.03
125.86	2.54	2.01
126.04	2.43	1.98
126.21	2.33	1.97
126.38	2.25	1.95
126.56	2.19	1.94
126.73	2.14	1.93
126.90	2.09	1.93
127.07	2.06	1.92
127.23	2.03	1.92
127.40	2.01	1.91
127.57	1.99	1.91
127.74	1.98	1.91
127.91	1.96	1.91
128.07	1.95	1.91
128.24	1.95	1.91
128.41	1.94	1.90
128.58	1.94	1.90
128.74	1.94	1.90
128.91	1.93	1.90
129.08	1.93	1.90
129.24	1.93	1.90
129.41	1.93	1.90
129.58	1.93	1.90

Temp. (^{o}C)	Heat flow (W/g)	
	RS	PS
129.74	1.93	1.90
129.91	1.92	1.90
130.08	1.92	1.90
130.25	1.92	1.90
130.41	1.92	1.90
130.58	1.92	1.89
130.75	1.92	1.89
130.91	1.92	1.89
131.08	1.92	1.89
131.25	1.92	1.89
131.41	1.92	1.89
131.58	1.92	1.89
131.75	1.92	1.89
131.91	1.92	1.89
132.08	1.91	1.90
132.25	1.91	1.90
132.41	1.91	1.90
132.58	1.91	1.90
132.75	1.91	1.90
132.91	1.91	1.90
133.08	1.91	1.90
133.25	1.91	1.90
133.41	1.91	1.90
133.58	1.91	1.90
133.75	1.91	1.90
133.91	1.91	1.90
134.08	1.91	1.90
134.25	1.91	1.90
134.41	1.91	1.90
134.58	1.91	1.90
134.75	1.91	1.90
134.91	1.91	1.90
135.08	1.91	1.90
135.25	1.91	1.90
135.41	1.91	1.90
135.58	1.91	1.90
135.75	1.91	1.91
135.91	1.91	1.91
136.08	1.91	1.91
136.25	1.92	1.91
136.41	1.92	1.91
136.58	1.92	1.91

Temp. (^{o}C)	Heat flow (W/g)	
	RS	PS
136.75	1.92	1.91
136.92	1.92	1.91
137.08	1.92	1.91
137.25	1.92	1.91
137.42	1.92	1.91
137.58	1.92	1.91
137.75	1.92	1.91
137.92	1.92	1.91
138.08	1.92	1.92
138.25	1.92	1.92
138.42	1.92	1.92
138.58	1.92	1.92
138.75	1.92	1.92
138.92	1.92	1.92
139.08	1.92	1.92
139.25	1.92	1.92
139.42	1.92	1.92
139.58	1.92	1.92
139.75	1.92	1.92
139.92	1.92	1.93
140.08	1.93	1.93
140.25	1.93	1.93
140.42	1.93	1.93
140.58	1.93	1.93
140.75	1.93	1.93
140.92	1.93	1.93
141.08	1.93	1.93
141.25	1.93	1.93
141.42	1.93	1.93
141.58	1.93	1.94
141.75	1.93	1.94
141.92	1.93	1.94
142.08	1.93	1.94
142.25	1.93	1.94
142.42	1.93	1.94
142.58	1.93	1.94
142.75	1.94	1.94
142.92	1.94	1.94
143.08	1.94	1.95
143.25	1.94	1.95
143.42	1.94	1.95
143.58	1.94	1.95

Table B1 Data collected from DSC experiment (cont.)

Temp. (°C)	Heat flow (W/g)	
	RS	PS
143.75	1.94	1.95
143.92	1.94	1.95
144.08	1.94	1.95
144.25	1.94	1.95
144.42	1.94	1.95
144.58	1.94	1.95
144.75	1.94	1.96
144.92	1.94	1.96
145.08	1.94	1.96
145.25	1.95	1.96
145.42	1.95	1.96
145.58	1.95	1.96
145.75	1.95	1.96
145.92	1.95	1.96
146.08	1.95	1.96
146.25	1.95	1.96
146.42	1.95	1.97
146.58	1.95	1.97
146.75	1.95	1.97
146.92	1.95	1.97
147.08	1.96	1.97
147.25	1.96	1.97
147.42	1.96	1.97
147.58	1.96	1.97
147.75	1.96	1.98
147.92	1.96	1.98
148.08	1.96	1.98
148.25	1.96	1.98
148.42	1.96	1.98
148.58	1.96	1.98
148.75	1.96	1.98
148.92	1.97	1.99
149.08	1.97	1.99
149.25	1.97	1.99
149.42	1.97	1.99
149.58	1.97	1.99
149.75	1.97	1.99
149.92	1.97	1.99
150.08	1.97	1.99
150.25	1.97	2.00
150.42	1.97	2.00
150.58	1.97	2.00

Temp. (°C)	Heat flow (W/g)	
	RS	PS
150.75	1.98	2.00
150.92	1.98	2.00
151.08	1.98	2.00
151.25	1.98	2.00
151.42	1.98	2.01
151.58	1.98	2.01
151.75	1.98	2.01
151.92	1.98	2.01
152.08	1.98	2.01
152.25	1.98	2.01
152.42	1.99	2.01
152.58	1.99	2.02
152.75	1.99	2.02
152.92	1.99	2.02
153.08	1.99	2.02
153.25	1.99	2.02
153.42	1.99	2.02
153.58	1.99	2.03
153.75	2.00	2.03
153.92	2.00	2.03
154.08	2.00	2.03
154.25	2.00	2.03
154.42	2.00	2.03
154.58	2.00	2.04
154.75	2.00	2.04
154.92	2.00	2.04
155.08	2.01	2.04
155.25	2.01	2.04
155.42	2.01	2.04
155.58	2.01	2.05
155.75	2.01	2.05
155.92	2.01	2.05
156.08	2.01	2.05
156.25	2.02	2.05
156.42	2.02	2.05
156.58	2.02	2.06
156.75	2.02	2.06
156.92	2.02	2.06
157.08	2.02	2.06
157.25	2.03	2.06
157.42	2.03	2.07
157.58	2.03	2.07

Temp. (°C)	Heat flow (W/g)	
	RS	PS
157.75	2.03	2.07
157.92	2.03	2.07
158.08	2.03	2.07
158.25	2.03	2.08
158.42	2.04	2.08
158.58	2.04	2.08
158.75	2.04	2.08
158.92	2.04	2.08
159.08	2.04	2.09
159.25	2.04	2.09
159.42	2.05	2.09
159.58	2.05	2.09
159.75	2.05	2.09
159.92	2.05	2.10
160.08	2.05	2.10

Table B2 Data collected from TGA experiment

Temp. (^oC)	Weight loss (%)	
	RS	PS
39.94	100.00	100.00
47.17	99.98	99.98
54.79	99.97	99.97
62.49	99.96	99.96
70.18	99.97	99.96
77.88	99.98	99.97
85.53	99.99	99.98
93.30	100.00	99.99
100.97	99.95	100.00
108.72	100.00	99.99
116.32	100.02	100.01
123.64	100.01	100.04
131.40	100.03	100.04
139.32	100.04	100.05
147.16	100.05	100.06
154.96	100.05	100.07
162.75	100.06	100.08
170.52	100.07	100.07
178.24	100.05	100.06
185.77	100.03	100.03
193.29	99.98	99.96
200.85	99.91	99.91
208.46	99.83	99.80
216.07	99.69	99.65
223.72	99.49	99.46
231.35	99.20	99.15
239.00	98.83	98.75
246.64	98.33	98.23
254.27	97.69	97.53
261.92	96.83	96.63
269.60	95.76	95.47
277.23	94.40	94.00
284.88	92.69	92.14
292.53	90.58	89.83
300.19	87.97	86.99
307.82	84.74	83.48
315.45	80.81	79.20
323.04	75.95	74.00
330.65	70.16	67.66
338.29	63.09	60.06
345.90	54.49	50.95
353.53	44.05	39.97
361.18	31.55	26.83
368.83	16.85	11.70
376.62	2.28	1.56
384.51	1.00	1.31
392.26	0.98	1.32
399.91	0.97	1.31
407.57	0.98	1.33
415.20	0.97	1.34
422.83	0.97	1.33
430.44	0.94	1.35
438.07	0.95	1.35
445.68	0.93	1.34
453.31	0.92	1.34
460.84	0.84	1.32
468.52	0.88	1.34
476.17	0.89	1.34
483.80	0.87	1.35
491.45	0.85	1.33
499.10	0.85	1.34
506.75	0.84	1.33
514.40	0.84	1.32
522.05	0.83	1.31
529.68	0.83	1.29
537.33	0.85	1.30
544.95	0.86	1.31
552.57	0.88	1.29
560.20	0.86	1.32
567.82	0.86	1.30
575.42	0.86	1.29
583.03	0.87	1.26
590.66	0.85	1.26
598.26	0.87	1.27
605.89	0.92	1.24
613.41	0.88	1.15
620.95	0.91	1.12
628.52	0.91	1.13
636.09	0.91	1.14
643.74	0.94	1.16
651.37	0.93	1.13
659.05	0.93	1.12
666.75	0.93	1.11
674.49	0.94	1.12
682.29	0.95	1.11
690.06	0.97	1.12
697.75	0.99	1.12
705.41	0.97	1.10
713.09	0.98	1.11
720.80	0.98	1.13
728.45	0.98	1.13
736.14	0.99	1.11
743.79	0.99	1.12
751.52	1.00	1.12
759.24	1.01	1.12
766.91	1.01	1.10
774.61	1.02	1.12
782.37	1.02	1.12
790.07	1.04	1.10
797.79	1.03	1.11

Table B3 Data collected from XRD experiment

2θ	Counts	
	RS	PS
5.00	3456	3328
5.08	3300	3204
5.15	3123	3068
5.23	3199	3010
5.30	3081	3006
5.38	3109	3008
5.45	2994	2944
5.53	2914	2800
5.60	3064	2818
5.68	2982	2751
5.75	2850	2812
5.83	2846	2747
5.90	2774	2623
5.98	2709	2580
6.05	2820	2729
6.13	2804	2721
6.20	2798	2718
6.28	2718	2689
6.35	2832	2700
6.43	2750	2585
6.50	2683	2594
6.58	2704	2462
6.65	2569	2439
6.73	2463	2328
6.80	2425	2313
6.88	2396	2126
6.95	2371	2155
7.03	2261	2066
7.10	2250	2095
7.18	2239	1989
7.26	2142	1982
7.33	2205	1937
7.41	2212	1950
7.48	2025	1876
7.56	2001	1924
7.63	2015	1867
7.71	1989	1839
7.78	1919	1738
7.86	1855	1697
7.93	1849	1660
8.01	1707	1626
8.08	1702	1549

2θ	Counts	
	RS	PS
8.16	1722	1434
8.23	1564	1474
8.31	1612	1392
8.38	1536	1422
8.46	1521	1310
8.53	1416	1326
8.61	1387	1173
8.68	1305	1205
8.76	1360	1174
8.83	1428	1094
8.91	1394	1043
8.98	1243	1030
9.06	1222	1056
9.13	1236	1057
9.21	1193	1001
9.28	1189	962
9.36	1215	971
9.44	1114	987
9.51	1201	884
9.59	1174	944
9.66	1149	940
9.74	1156	834
9.81	1049	913
9.89	1144	936
9.96	1105	899
10.04	1186	918
10.11	1070	888
10.19	1136	884
10.26	1110	936
10.34	1098	888
10.41	1015	885
10.49	1045	859
10.56	1040	914
10.64	1079	885
10.71	1047	905
10.79	1083	925
10.86	1019	875
10.94	1067	863
11.01	1028	840
11.09	1090	863
11.16	1082	841
11.24	1013	834

2θ	Counts	
	RS	PS
11.31	1042	836
11.39	1049	879
11.47	1032	807
11.54	1094	827
11.62	1326	846
11.69	1409	872
11.77	1065	868
11.84	1010	948
11.92	944	882
11.99	962	817
12.07	1029	851
12.14	1011	889
12.22	979	903
12.29	945	811
12.37	992	861
12.44	939	921
12.52	936	811
12.59	943	856
12.67	954	827
12.74	947	764
12.82	961	864
12.89	912	832
12.97	942	851
13.04	960	789
13.12	943	837
13.19	872	778
13.27	907	820
13.34	889	795
13.42	909	773
13.49	871	772
13.57	943	799
13.65	801	746
13.72	852	773
13.80	854	720
13.87	791	749
13.95	862	738
14.02	865	718
14.10	870	711
14.17	823	684
14.25	800	742
14.32	814	715
14.40	796	694

Table B3 Data collected from XRD experiment (cont.)

2θ	Counts		2θ	Counts		2θ	Counts	
	RS	PS		RS	PS		RS	PS
14.47	782	731	17.63	539	526	20.79	441	403
14.55	754	625	17.70	584	488	20.86	437	364
14.62	798	703	17.78	532	473	20.94	467	366
14.70	709	631	17.85	528	501	21.01	513	372
14.77	710	666	17.93	551	467	21.09	413	401
14.85	750	626	18.01	556	493	21.16	391	364
14.92	782	646	18.08	558	480	21.24	384	447
15.00	724	672	18.16	520	452	21.31	436	397
15.07	729	644	18.23	562	460	21.39	527	370
15.15	784	641	18.31	527	451	21.46	402	341
15.22	731	677	18.38	518	410	21.54	380	415
15.30	794	667	18.46	506	463	21.61	348	451
15.37	723	624	18.53	566	455	21.69	374	388
15.45	852	635	18.61	643	495	21.76	351	333
15.52	1492	643	18.68	623	432	21.84	395	341
15.60	1900	726	18.76	503	482	21.91	384	335
15.67	1186	775	18.83	483	499	21.99	615	323
15.75	1196	1108	18.91	469	443	22.06	1285	344
15.83	774	1104	18.98	503	397	22.14	813	365
15.90	699	998	19.06	496	457	22.22	426	470
15.98	699	1091	19.13	511	433	22.29	364	951
16.05	669	730	19.21	487	445	22.37	354	901
16.13	687	593	19.28	483	418	22.44	373	462
16.20	678	632	19.36	477	406	22.52	397	349
16.28	645	567	19.43	438	450	22.59	400	364
16.35	660	597	19.51	447	424	22.67	423	334
16.43	642	566	19.58	478	420	22.74	500	340
16.50	634	616	19.66	453	389	22.82	933	384
16.58	621	547	19.73	403	416	22.89	1403	382
16.65	605	557	19.81	435	413	22.97	800	422
16.73	615	570	19.88	435	417	23.04	596	519
16.80	639	599	19.96	467	391	23.12	845	796
16.88	584	574	20.04	429	426	23.19	3672	711
16.95	567	542	20.11	404	425	23.27	9614	683
17.03	601	514	20.19	422	412	23.34	3937	937
17.10	572	538	20.26	441	357	23.42	780	2779
17.18	608	540	20.34	465	366	23.49	506	8078
17.25	603	525	20.41	421	403	23.57	434	5327
17.33	537	497	20.49	431	401	23.64	415	1133
17.40	595	481	20.56	433	384	23.72	398	589
17.48	524	545	20.64	452	381	23.79	373	435
17.55	583	512	20.71	444	366	23.87	379	391

Table B3 Data collected from XRD experiment (cont.)

2θ	Counts		2θ	Counts		2θ	Counts	
	RS	PS		RS	PS		RS	PS
23.94	363	362	27.10	348	1269	30.26	226	222
24.02	334	327	27.18	344	1801	30.33	229	243
24.09	346	335	27.25	317	878	30.41	228	219
24.17	357	352	27.33	357	384	30.48	243	188
24.24	349	318	27.40	310	343	30.56	241	207
24.32	318	292	27.48	322	323	30.63	241	187
24.40	350	277	27.55	345	274	30.71	225	219
24.47	330	284	27.63	335	297	30.79	248	189
24.55	320	304	27.70	388	297	30.86	259	202
24.62	326	313	27.78	615	282	30.94	211	228
24.70	321	322	27.85	2279	281	31.01	257	228
24.77	342	309	27.93	3462	312	31.09	239	236
24.85	315	272	28.00	1768	455	31.16	267	224
24.92	308	296	28.08	590	1036	31.24	293	252
25.00	385	304	28.15	379	1981	31.31	278	201
25.07	745	307	28.23	327	1251	31.39	271	206
25.15	982	280	28.30	317	523	31.46	325	206
25.22	543	354	28.38	322	310	31.54	845	243
25.30	339	484	28.45	271	290	31.61	1023	245
25.37	328	627	28.53	342	281	31.69	560	319
25.45	334	521	28.61	294	255	31.76	293	608
25.52	321	337	28.68	409	288	31.84	255	999
25.60	365	310	28.76	597	293	31.91	255	666
25.67	304	328	28.83	1652	287	31.99	231	324
25.75	313	312	28.91	1327	309	32.06	221	266
25.82	354	288	28.98	627	503	32.14	219	216
25.90	544	304	29.06	821	1192	32.21	215	215
25.97	1983	321	29.13	1551	1440	32.29	225	202
26.05	3040	369	29.21	993	775	32.36	222	231
26.12	1297	470	29.28	447	522	32.44	236	234
26.20	472	855	29.36	376	1067	32.51	259	212
26.27	366	1773	29.43	331	1014	32.59	219	205
26.35	359	1146	29.51	304	543	32.66	230	219
26.42	408	478	29.58	302	371	32.74	232	204
26.50	510	353	29.66	280	268	32.81	223	200
26.58	456	328	29.73	277	238	32.89	233	198
26.65	378	348	29.81	226	264	32.97	191	214
26.73	406	401	29.88	246	234	33.04	227	183
26.80	666	421	29.96	254	232	33.12	227	196
26.88	1914	369	30.03	254	230	33.19	214	173
26.95	1803	401	30.11	220	238	33.27	216	203
27.03	616	522	30.18	252	218	33.34	233	167

Table B3 Data collected from XRD experiment (cont.)

2θ	Counts		2θ	Counts		2θ	Counts	
	RS	PS		RS	PS		RS	PS
33.42	257	177	36.57	198	318	39.73	205	307
33.49	373	200	36.65	202	239	39.81	169	371
33.57	305	183	36.72	199	207	39.88	172	287
33.64	309	255	36.80	214	181	39.96	147	209
33.72	269	292	36.87	184	166	40.03	160	180
33.79	232	298	36.95	226	164	40.11	177	145
33.87	219	282	37.02	225	181	40.18	181	164
33.94	207	245	37.10	282	196	40.26	186	154
34.02	237	212	37.17	743	174	40.33	168	163
34.09	217	224	37.25	994	204	40.41	191	160
34.17	247	177	37.33	584	244	40.48	165	149
34.24	408	209	37.40	258	400	40.56	186	133
34.32	792	211	37.48	288	647	40.63	220	143
34.39	782	227	37.55	329	595	40.71	204	142
34.47	461	440	37.63	304	366	40.78	248	166
34.54	308	835	37.70	236	238	40.86	232	154
34.62	221	919	37.78	224	269	40.93	223	182
34.69	215	630	37.85	244	256	41.01	206	213
34.77	198	354	37.93	306	203	41.08	189	225
34.84	232	224	38.00	531	193	41.16	151	198
34.92	255	209	38.08	498	219	41.23	159	177
34.99	341	185	38.15	551	270	41.31	153	149
35.07	507	209	38.23	432	348	41.38	149	160
35.15	453	221	38.30	251	401	41.46	155	147
35.22	298	249	38.38	191	476	41.54	143	140
35.30	192	413	38.45	177	411	41.61	154	144
35.37	224	421	38.53	196	309	41.69	186	156
35.45	230	342	38.60	174	198	41.76	180	129
35.52	191	227	38.68	180	174	41.84	170	161
35.60	210	207	38.75	193	176	41.91	181	145
35.67	212	160	38.83	171	149	41.99	171	155
35.75	196	186	38.90	199	181	42.06	172	152
35.82	190	184	38.98	185	170	42.14	226	147
35.90	224	172	39.05	210	158	42.21	372	149
35.97	335	181	39.13	158	159	42.29	379	148
36.05	774	179	39.20	208	161	42.36	393	185
36.12	711	219	39.28	200	174	42.44	248	229
36.20	471	262	39.36	215	164	42.51	225	336
36.27	460	424	39.43	282	148	42.59	186	308
36.35	375	499	39.51	610	152	42.66	199	268
36.42	255	357	39.58	504	159	42.74	201	201
36.50	225	330	39.66	368	198	42.81	353	162

Table B3 Data collected from XRD experiment (cont.)

2θ	Counts	
	RS	PS
42.89	717	162
42.96	888	183
43.04	598	298
43.11	399	619
43.19	233	813
43.26	281	651
43.34	305	442
43.41	254	242
43.49	189	239
43.56	171	277
43.64	200	229
43.72	189	212
43.79	153	170
43.87	176	139
43.94	157	154
44.02	168	142
44.09	232	166
44.17	247	146
44.24	188	168
44.32	175	188
44.39	176	232
44.47	205	208
44.54	224	178
44.62	194	143
44.69	185	184
44.77	145	234
44.84	172	192
44.92	191	172
44.99	142	154
45.07	163	190
45.14	161	156
45.22	193	149
45.29	227	135
45.37	243	167
45.44	252	172
45.52	222	209
45.59	185	244
45.67	226	229
45.74	323	199
45.82	298	162
45.90	257	187
45.97	177	290

2θ	Counts	
	RS	PS
46.05	159	313
46.12	181	241
46.20	167	199
46.27	160	158
46.35	182	163
46.42	233	149
46.50	382	155
46.57	252	149
46.65	221	190
46.72	179	239
46.80	154	279
46.87	151	224
46.95	167	152
47.02	153	142
47.10	163	173
47.17	158	141
47.25	223	148
47.32	276	139
47.40	196	164
47.47	210	195
47.55	182	405
47.62	185	270
47.70	189	251
47.77	248	186
47.85	398	171
47.92	709	210
48.00	572	213
48.08	485	406
48.15	312	560
48.23	227	527
48.30	164	479
48.38	166	343
48.45	152	243
48.53	160	174
48.60	166	169
48.68	166	175
48.75	149	142
48.83	177	133
48.90	156	133
48.98	157	149
49.05	167	139
49.13	194	151

2θ	Counts	
	RS	PS
49.20	197	152
49.28	187	146
49.35	162	154
49.43	175	181
49.50	149	182
49.58	190	149
49.65	239	138
49.73	233	128
49.80	237	179
49.88	251	149
49.95	244	203
50.03	279	195
50.11	466	216
50.18	472	215
50.26	379	209
50.33	259	279
50.41	198	360
50.48	157	309
50.56	170	258
50.63	155	172
50.71	178	160
50.78	200	140
50.86	143	132
50.93	171	175
51.01	173	134
51.08	181	152
51.16	192	133
51.23	191	163
51.31	307	161
51.38	830	183
51.46	633	217
51.53	598	318
51.61	330	619
51.68	192	976
51.76	176	578
51.83	201	498
51.91	219	210
51.98	181	184
52.06	189	169
52.13	277	171
52.21	582	185
52.29	411	195

Table B3 Data collected from XRD experiment (cont.)

2θ	Counts	
	RS	PS
52.36	385	226
52.44	209	307
52.51	180	309
52.59	165	275
52.66	196	201
52.74	159	152
52.81	164	142
52.89	166	141
52.96	191	160
53.04	199	132
53.11	423	170
53.19	667	167
53.26	653	189
53.34	599	301
53.41	418	411
53.49	264	423
53.56	214	494
53.64	159	352
53.71	182	289
53.79	172	224
53.86	168	182
53.94	200	163
54.01	221	144
54.09	447	172
54.16	450	169
54.24	345	193
54.31	264	303
54.39	186	349
54.47	162	299
54.54	169	250
54.62	175	186
54.69	164	156
54.77	161	145
54.84	167	126
54.92	173	147
54.99	156	153
55.07	174	142
55.14	172	146
55.22	210	148
55.29	238	172
55.37	232	142
55.44	252	180

2θ	Counts	
	RS	PS
55.52	253	249
55.59	312	278
55.67	238	296
55.74	265	257
55.82	233	235
55.89	317	192
55.97	355	225
56.04	365	215
56.12	298	293
56.19	244	387
56.27	170	261
56.34	183	291
56.42	191	187
56.49	170	153
56.57	166	154
56.65	164	143
56.72	199	154
56.80	366	119
56.87	488	157
56.95	364	255
57.02	344	431
57.10	223	580
57.17	222	504
57.25	225	442
57.32	222	328
57.40	298	218
57.47	485	194
57.55	415	230
57.62	346	314
57.70	464	286
57.77	310	290
57.85	270	248
57.92	300	257
58.00	263	247
58.07	202	217
58.15	194	242
58.22	176	231
58.30	146	190
58.37	151	166
58.45	150	145
58.52	157	122
58.60	134	116

2θ	Counts	
	RS	PS
58.68	143	139
58.75	148	113
58.83	155	126
58.90	143	109
58.98	144	111
59.05	158	115
59.13	138	130
59.20	213	141
59.28	240	119
59.35	203	152
59.43	192	172
59.50	191	160
59.58	137	181
59.65	160	157
59.73	147	141
59.80	171	143

Table B4 Data collected from XANES experiment

Photon energy (eV)	Normalized absorption		Photon energy (eV)	Normalized absorption	
	RS	PS		RS	PS
2460.0	2.7E-03	2.9E-02	2471.7	3.1E+00	2.8E+00
2462.0	6.3E-03	3.5E-02	2471.9	3.1E+00	2.8E+00
2464.0	1.3E-02	4.3E-02	2472.0	2.9E+00	2.7E+00
2466.0	3.0E-02	5.9E-02	2472.2	2.7E+00	2.5E+00
2466.2	3.2E-02	6.1E-02	2472.3	2.4E+00	2.2E+00
2466.3	3.4E-02	6.3E-02	2472.5	2.2E+00	2.0E+00
2466.5	3.6E-02	6.6E-02	2472.6	2.1E+00	1.8E+00
2466.6	3.8E-02	6.8E-02	2472.8	2.0E+00	1.7E+00
2466.8	4.1E-02	7.1E-02	2472.9	1.8E+00	1.6E+00
2466.9	4.4E-02	7.3E-02	2473.1	1.7E+00	1.5E+00
2467.1	4.7E-02	7.6E-02	2473.2	1.5E+00	1.4E+00
2467.2	5.1E-02	8.0E-02	2473.4	1.4E+00	1.3E+00
2467.4	5.4E-02	8.4E-02	2473.5	1.3E+00	1.3E+00
2467.5	5.8E-02	8.9E-02	2473.7	1.2E+00	1.2E+00
2467.7	6.3E-02	9.5E-02	2473.8	1.1E+00	1.2E+00
2467.8	6.8E-02	1.0E-01	2474.0	1.0E+00	1.1E+00
2468.0	7.4E-02	1.1E-01	2474.1	9.5E-01	1.1E+00
2468.1	8.1E-02	1.2E-01	2474.3	8.9E-01	1.0E+00
2468.3	8.8E-02	1.3E-01	2474.4	8.3E-01	9.6E-01
2468.4	9.6E-02	1.4E-01	2474.6	7.9E-01	9.1E-01
2468.6	1.1E-01	1.6E-01	2474.7	7.4E-01	8.7E-01
2468.7	1.2E-01	1.8E-01	2474.9	7.0E-01	8.3E-01
2468.9	1.3E-01	1.9E-01	2475.0	6.7E-01	7.9E-01
2469.0	1.4E-01	2.1E-01	2475.2	6.3E-01	7.6E-01
2469.2	1.6E-01	2.3E-01	2475.3	6.0E-01	7.3E-01
2469.3	1.8E-01	2.5E-01	2475.5	5.8E-01	7.0E-01
2469.5	2.0E-01	2.8E-01	2475.6	5.6E-01	6.8E-01
2469.6	2.3E-01	3.2E-01	2475.8	5.5E-01	6.7E-01
2469.8	2.7E-01	3.6E-01	2475.9	5.4E-01	6.7E-01
2469.9	3.2E-01	4.0E-01	2476.1	5.5E-01	6.7E-01
2470.1	3.8E-01	4.6E-01	2476.2	5.6E-01	6.9E-01
2470.2	4.7E-01	5.4E-01	2476.4	5.9E-01	7.2E-01
2470.4	6.0E-01	6.6E-01	2476.5	6.4E-01	7.7E-01
2470.5	7.9E-01	8.3E-01	2476.7	6.9E-01	8.3E-01
2470.7	1.1E+00	1.1E+00	2476.8	7.4E-01	8.8E-01
2470.8	1.4E+00	1.4E+00	2477.0	7.9E-01	9.3E-01
2471.0	1.9E+00	1.8E+00	2477.1	8.3E-01	9.7E-01
2471.1	2.4E+00	2.1E+00	2477.3	8.7E-01	1.0E+00
2471.3	2.7E+00	2.5E+00	2477.4	9.1E-01	1.0E+00
2471.4	3.0E+00	2.7E+00	2477.6	9.5E-01	1.1E+00
2471.6	3.1E+00	2.8E+00	2477.7	9.9E-01	1.1E+00

Table B4 Data collected from XANES experiment (cont.)

Photon energy (eV)	Normalized absorption	
	RS	PS
2477.9	1.0E+00	1.1E+00
2478.0	1.1E+00	1.1E+00
2478.2	1.1E+00	1.1E+00
2478.3	1.1E+00	1.1E+00
2478.5	1.1E+00	1.1E+00
2478.6	1.1E+00	1.1E+00
2478.8	1.2E+00	1.1E+00
2478.9	1.2E+00	1.1E+00
2479.1	1.2E+00	1.1E+00
2479.2	1.2E+00	1.1E+00
2479.4	1.2E+00	1.1E+00
2479.5	1.2E+00	1.1E+00
2479.7	1.1E+00	1.1E+00
2479.8	1.1E+00	1.1E+00
2480.0	1.1E+00	1.1E+00
2480.1	1.1E+00	1.1E+00
2480.3	1.1E+00	1.1E+00
2480.4	1.1E+00	1.1E+00
2480.6	1.1E+00	1.1E+00
2480.7	1.1E+00	1.1E+00
2480.9	1.0E+00	1.1E+00
2481.0	1.0E+00	1.1E+00
2481.2	1.0E+00	1.1E+00
2481.3	1.0E+00	1.1E+00
2481.5	9.9E-01	1.1E+00
2481.6	9.8E-01	1.0E+00
2481.8	9.7E-01	1.0E+00

Photon energy (eV)	Normalized absorption	
	RS	PS
2481.9	9.6E-01	1.0E+00
2482.1	9.6E-01	1.0E+00
2482.2	9.5E-01	1.0E+00
2482.4	9.5E-01	1.0E+00
2482.5	9.4E-01	9.9E-01
2482.7	9.4E-01	9.9E-01
2482.8	9.4E-01	9.9E-01
2483.0	9.4E-01	9.9E-01
2483.1	9.5E-01	9.9E-01
2483.3	9.5E-01	9.9E-01
2483.4	9.5E-01	9.9E-01
2483.6	9.6E-01	9.9E-01
2483.7	9.6E-01	1.0E+00
2483.9	9.7E-01	1.0E+00
2484.0	9.7E-01	1.0E+00
2484.2	9.8E-01	1.0E+00
2484.3	9.8E-01	1.0E+00
2484.5	9.9E-01	1.0E+00
2484.6	9.9E-01	1.0E+00
2484.8	1.0E+00	1.0E+00
2484.9	1.0E+00	1.0E+00
2485.0	1.0E+00	1.0E+00
2486.0	1.0E+00	1.0E+00
2487.0	1.0E+00	1.0E+00
2488.0	1.0E+00	1.0E+00
2489.0	1.0E+00	1.0E+00
2490.0	1.0E+00	1.0E+00

APPENDIX C
VISCOELASTIC PROPERTIES OF RUBBER COMPOUNDS INCORPORATED WITH DIFFERENT SULFURS

Table C1 Strain sweep test results at 100^{o}C and 1 rad/s as measured by RPA2000 of NR compounds incorporated with IRPC-PS compared with various commercial natural-based sulfurs: Storage modulus (G')

Strain amplitude (%)	G' (kPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
0.53	21.38	23.17	20.95	19.13	21.20	21.70
0.95	19.01	20.61	19.21	18.86	20.32	17.45
1.94	18.03	18.00	18.77	17.03	18.45	15.83
5.06	15.56	16.15	15.01	16.23	16.99	14.70
10.04	14.75	15.63	14.58	15.02	16.03	14.17
49.98	11.91	13.95	13.09	13.65	14.59	11.78
100.09	9.22	10.98	10.46	10.04	11.49	10.16
499.94	2.13	2.60	2.52	2.52	2.56	2.50
999.95	1.03	1.04	1.03	1.00	1.01	0.99
1199.95	0.78	0.82	0.78	0.77	0.77	0.76

Table C2 Strain sweep test results at 100°C and 1 rad/s as measured by RPA2000 of SBR compounds incorporated with IRPC-PS compared with various commercial natural-based sulfurs: Storage modulus (G')

Strain amplitude (%)	G' (kPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
0.53	41.74	35.32	37.74	44.28	36.07	38.53
0.95	37.40	34.32	35.63	35.58	34.60	37.56
1.94	37.01	33.41	33.26	33.38	34.50	33.94
5.06	34.60	32.39	32.52	32.10	33.39	33.61
10.04	33.64	31.29	30.41	29.58	30.88	33.06
49.98	29.76	28.43	29.65	27.13	27.34	28.71
100.09	23.32	22.42	23.01	22.71	22.45	22.38
499.94	7.65	7.38	7.73	7.56	7.66	7.65
999.95	4.30	4.07	4.38	4.35	4.38	4.26
1199.95	3.28	3.04	3.31	3.25	3.27	3.15

Table C3 Strain sweep test results at 100°C and 1 rad/s as measured by RPA2000 of NBR compounds incorporated with IRPC-PS compared with various commercial natural-based sulfurs: Storage modulus (G')

Strain amplitude (%)	G' (kPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
0.53	44.37	42.59	44.14	42.35	44.20	44.92
0.95	42.94	41.66	43.53	42.75	43.72	43.68
1.94	42.04	40.89	42.79	41.31	43.37	43.11
5.06	40.85	40.13	40.40	39.74	42.15	40.84
10.04	37.72	37.57	38.25	38.82	38.70	39.79
49.98	32.89	34.46	34.34	33.08	34.68	38.32
100.09	26.75	29.72	30.37	29.99	26.63	31.30
499.94	9.33	9.03	8.97	9.31	9.30	9.17
999.95	5.12	5.02	4.97	5.23	5.15	4.95
1199.95	3.99	3.93	3.86	4.09	4.01	3.83

Table C4 Strain sweep test results at 100^{o}C and 1 rad/s as measured by RPA2000 of NR compounds incorporated with IRPC-PS compared with various commercial petroleum-based sulfurs: Storage modulus (G')

Strain amplitude (%)	G' (kPa)			
	IRPC-PS	DF325	DF5(325)	SM400
0.52	22.35	20.74	23.01	21.02
0.95	21.02	19.18	18.89	20.15
1.94	16.17	17.40	16.61	18.27
5.01	15.35	16.78	15.16	17.41
10.04	14.27	15.91	14.86	16.02
49.94	12.75	14.08	13.49	13.29
100.05	10.65	11.27	10.97	9.78
500.01	2.61	2.62	2.64	2.59
999.89	1.02	1.04	1.03	1.04
1199.97	0.83	0.80	0.81	0.80

Table C5 Strain sweep test results at 100^{o}C and 1 rad/s as measured by RPA2000 of SBR compounds incorporated with IRPC-PS compared with various commercial petroleum-based sulfurs: Storage modulus (G')

Strain amplitude (%)	G' (kPa)			
	IRPC-PS	DF325	DF5(325)	SM400
0.52	45.07	45.25	44.63	43.08
0.95	44.59	43.87	43.66	42.38
1.94	43.99	42.15	43.42	41.52
5.01	40.80	39.83	42.38	38.82
10.04	39.99	39.29	40.50	36.13
49.94	34.26	37.14	38.70	32.63
100.05	32.51	31.75	31.26	31.03
500.01	9.09	9.16	9.08	9.36
999.89	4.81	5.04	5.08	5.23
1199.97	3.94	4.08	4.04	4.11

Table C6 Strain sweep test results at 100^{o}C and 1 rad/s as measured by RPA2000 of NBR compounds incorporated with IRPC-PS compared with various commercial petroleum-based sulfurs: Storage modulus (G')

Strain amplitude (%)	G' (kPa)			
	IRPC-PS	DF325	DF5(325)	SM400
0.52	34.97	34.29	34.28	33.75
0.95	32.55	33.60	32.84	32.71
1.94	31.89	32.47	31.27	30.98
5.01	29.90	30.38	30.78	30.74
10.04	29.15	28.49	28.48	28.41
49.94	24.85	28.13	27.62	24.13
100.05	20.56	22.28	21.60	19.94
500.01	7.02	6.74	7.01	6.77
999.89	3.87	3.68	3.81	3.64
1199.97	2.88	2.78	2.82	2.69

Table C7 Strain sweep test results at 100°C and 1 rad/s as measured by RPA2000 of rubber compounds incorporated with uncoated and TDAE oil-coated petroleum-based sulfur: Storage modulus (G')

Strain amplitude (%)	G' (kPa)					
	NR		SBR		NBR	
	OA	OC	OA	OC	OA	OC
0.56	23.61	19.90	45.89	45.19	39.66	40.28
0.98	22.32	18.44	45.11	44.18	38.34	40.15
1.95	20.10	17.97	43.35	43.58	37.70	38.90
3.07	19.01	17.62	41.99	42.58	36.98	38.68
5.02	17.96	17.55	41.07	41.78	36.58	37.58
7.53	16.92	16.93	40.31	39.75	35.78	37.47
10.04	15.31	16.19	38.92	34.61	34.58	37.10
19.95	14.66	15.86	37.13	32.80	33.93	36.76
29.99	14.56	14.87	34.25	31.41	32.03	36.20
49.94	13.53	13.89	32.15	30.21	28.66	34.28
79.93	12.25	12.47	24.82	22.28	26.64	30.18
100.02	11.09	11.01	19.14	19.87	24.80	27.08
200.04	7.45	6.76	9.87	14.44	17.65	17.53
300.06	4.97	4.19	8.74	11.96	12.48	11.94
499.97	2.72	2.80	6.33	9.61	8.35	7.97
800.03	1.53	1.64	4.91	6.70	5.86	5.72
999.94	1.07	1.16	3.39	5.19	4.84	4.70

APPENDIX D
DYNAMIC MECHANICAL PROPERTIES OF RUBBER VULCANIZATES CURED WITH DIFFERENT SULFURS

Table D1 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs: (a) Storage modulus (E')

Temp. (ºC)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-80.20	2345.72	2547.39	2534.03	2402.20	2905.26	2494.12
-76.90	2139.73	2586.33	2582.03	2251.20	2954.59	2546.06
-73.60	2118.78	2549.98	2583.30	2236.95	2931.88	2538.23
-70.70	2113.28	2484.18	2545.14	2218.09	2872.91	2479.71
-67.70	2120.17	2395.70	2488.33	2219.54	2800.06	2398.40
-64.20	2106.12	2317.93	2392.91	2197.47	2701.80	2310.89
-61.40	2045.83	2181.21	2336.89	2114.59	2531.84	2178.91
-60.10	1913.72	2121.16	2286.51	1946.66	2271.56	2107.08
-57.40	1810.08	1826.68	2228.49	1718.75	2127.31	1690.20
-56.20	1595.05	1646.72	2157.48	1479.82	1830.22	1532.81
-54.70	1334.56	1394.93	1781.30	1211.89	1543.13	1308.33
-53.60	1099.54	1176.46	1585.16	945.21	1269.43	1092.79
-52.30	892.42	963.59	1354.52	698.82	999.56	843.58
-50.90	618.05	688.49	1129.56	439.60	714.43	589.34
-49.40	388.08	421.86	879.56	245.87	447.65	351.87
-47.90	222.02	225.51	618.66	130.33	256.03	192.87
-47.00	122.75	123.57	375.46	73.93	147.27	109.97
-45.80	73.54	70.23	196.71	46.15	85.29	67.92
-44.50	46.36	42.75	108.41	30.50	52.75	44.47
-43.30	31.58	28.23	64.91	21.71	34.85	29.76
-42.10	22.60	20.25	41.43	15.65	24.79	21.46
-41.10	16.86	15.36	27.93	12.30	18.81	16.37
-39.90	13.50	12.04	20.67	9.95	14.62	12.94
-38.80	10.92	9.65	15.74	8.25	11.68	10.47
-37.50	9.05	8.00	12.43	6.98	9.55	8.71
-36.60	7.62	6.85	10.22	6.01	8.00	7.40
-35.30	6.48	5.96	8.31	5.24	6.88	6.29

Table D1 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (°C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-34.20	5.61	5.22	7.09	4.67	5.99	5.49
-33.00	4.89	4.63	6.06	4.21	5.25	4.81
-31.90	4.35	4.10	5.33	3.79	4.64	4.27
-30.80	3.88	3.72	4.76	3.45	4.18	3.82
-29.60	3.52	3.38	4.28	3.15	3.75	3.47
-28.60	3.24	3.07	3.88	2.91	3.43	3.22
-27.30	2.98	2.82	3.52	2.71	3.12	2.96
-26.10	2.76	2.63	3.25	2.52	2.93	2.75
-24.90	2.57	2.47	2.96	2.38	2.73	2.57
-23.80	2.40	2.33	2.75	2.24	2.57	2.42
-22.70	2.28	2.22	2.57	2.11	2.44	2.28
-21.50	2.16	2.13	2.43	2.02	2.32	2.20
-20.40	2.07	2.01	2.29	1.94	2.24	2.08
-19.20	2.00	1.95	2.18	1.87	2.17	1.98
-18.10	1.96	1.89	2.05	1.82	2.08	1.92
-16.90	1.88	1.84	1.98	1.78	2.05	1.86
-15.80	1.81	1.79	1.90	1.73	1.98	1.80
-14.70	1.76	1.75	1.83	1.70	1.95	1.80
-13.60	1.72	1.71	1.79	1.66	1.88	1.75
-12.20	1.70	1.68	1.74	1.66	1.84	1.71
-10.60	1.67	1.65	1.72	1.63	1.81	1.67
-9.30	1.65	1.63	1.68	1.59	1.81	1.66
-7.90	1.62	1.61	1.66	1.59	1.77	1.64
-6.30	1.61	1.59	1.65	1.57	1.77	1.61
-4.90	1.59	1.57	1.64	1.54	1.74	1.61
-3.40	1.56	1.57	1.61	1.54	1.72	1.59
-1.90	1.56	1.54	1.64	1.51	1.73	1.57
-0.50	1.56	1.52	1.61	1.52	1.71	1.56
2.90	1.55	1.53	1.58	1.49	1.69	1.55
3.20	1.55	1.52	1.60	1.49	1.70	1.55
3.80	1.54	1.52	1.59	1.49	1.68	1.54
5.50	1.55	1.50	1.57	1.48	1.66	1.53
6.70	1.53	1.51	1.57	1.47	1.67	1.52
8.70	1.52	1.50	1.55	1.47	1.67	1.53
10.20	1.50	1.49	1.55	1.47	1.69	1.56
11.80	1.51	1.50	1.55	1.46	1.67	1.53
13.10	1.51	1.48	1.57	1.48	1.66	1.51

Table D1 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
14.50	1.51	1.49	1.55	1.45	1.66	1.53
16.00	1.50	1.49	1.55	1.47	1.67	1.52
17.50	1.49	1.48	1.56	1.46	1.68	1.52
19.10	1.50	1.50	1.56	1.45	1.66	1.53
20.50	1.50	1.48	1.57	1.46	1.67	1.52
22.00	1.51	1.48	1.55	1.45	1.67	1.53
23.50	1.52	1.49	1.57	1.46	1.68	1.53
24.90	1.50	1.47	1.56	1.47	1.66	1.54
26.40	1.51	1.48	1.56	1.47	1.68	1.55
28.00	1.49	1.49	1.56	1.47	1.66	1.52
29.40	1.50	1.47	1.57	1.46	1.67	1.54
30.80	1.50	1.49	1.56	1.47	1.67	1.55
32.40	1.50	1.48	1.57	1.47	1.66	1.55
33.90	1.51	1.51	1.58	1.46	1.67	1.56
35.30	1.52	1.49	1.56	1.46	1.69	1.56
36.90	1.53	1.51	1.56	1.47	1.68	1.57
38.40	1.51	1.50	1.57	1.46	1.67	1.58
39.80	1.51	1.52	1.58	1.48	1.67	1.56
41.30	1.52	1.50	1.58	1.47	1.68	1.59
42.70	1.51	1.50	1.58	1.47	1.68	1.59
44.30	1.51	1.52	1.59	1.48	1.69	1.55
45.60	1.53	1.52	1.58	1.48	1.69	1.58
47.20	1.52	1.52	1.59	1.49	1.71	1.57
48.70	1.54	1.54	1.60	1.48	1.70	1.59
50.10	1.53	1.51	1.60	1.48	1.71	1.58
51.70	1.54	1.53	1.61	1.49	1.70	1.61
53.20	1.54	1.51	1.61	1.49	1.74	1.60
54.60	1.54	1.56	1.62	1.50	1.73	1.61
56.00	1.55	1.54	1.63	1.50	1.75	1.62
57.70	1.56	1.54	1.63	1.50	1.74	1.61
59.20	1.56	1.56	1.65	1.51	1.73	1.61
60.50	1.58	1.57	1.65	1.53	1.74	1.62
30.80	1.50	1.49	1.56	1.47	1.67	1.55
32.40	1.50	1.48	1.57	1.47	1.66	1.55
33.90	1.51	1.51	1.58	1.46	1.67	1.56
35.30	1.52	1.49	1.56	1.46	1.69	1.56
36.90	1.53	1.51	1.56	1.47	1.68	1.57

Table D1 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
38.40	1.51	1.50	1.57	1.46	1.67	1.58
39.80	1.51	1.52	1.58	1.48	1.67	1.56
41.30	1.52	1.50	1.58	1.47	1.68	1.59
42.70	1.51	1.50	1.58	1.47	1.68	1.59
44.30	1.51	1.52	1.59	1.48	1.69	1.55
45.60	1.53	1.52	1.58	1.48	1.69	1.58
47.20	1.52	1.52	1.59	1.49	1.71	1.57
48.70	1.54	1.54	1.60	1.48	1.70	1.59
50.10	1.53	1.51	1.60	1.48	1.71	1.58
51.70	1.54	1.53	1.61	1.49	1.70	1.61
53.20	1.54	1.51	1.61	1.49	1.74	1.60
54.60	1.54	1.56	1.62	1.50	1.73	1.61
56.00	1.55	1.54	1.63	1.50	1.75	1.62
57.70	1.56	1.54	1.63	1.50	1.74	1.61
59.20	1.56	1.56	1.65	1.51	1.73	1.61
60.50	1.58	1.57	1.65	1.53	1.74	1.62

Table D2 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs: (b) Tan δ

Temp. (^oC)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-80.20	0.04	0.04	0.03	0.03	0.03	0.03
-76.90	0.04	0.03	0.03	0.04	0.03	0.03
-73.60	0.04	0.03	0.03	0.04	0.03	0.03
-70.70	0.04	0.04	0.03	0.04	0.03	0.03
-67.70	0.04	0.04	0.03	0.05	0.03	0.03
-64.20	0.05	0.04	0.04	0.05	0.04	0.03
-61.40	0.06	0.06	0.04	0.06	0.05	0.05
-60.10	0.08	0.07	0.05	0.09	0.08	0.06
-57.40	0.11	0.10	0.05	0.15	0.11	0.12
-56.20	0.16	0.14	0.06	0.22	0.18	0.18
-54.70	0.24	0.20	0.11	0.30	0.25	0.25
-53.60	0.34	0.30	0.17	0.48	0.36	0.37
-52.30	0.51	0.43	0.25	0.68	0.52	0.55
-50.90	0.77	0.68	0.36	1.00	0.75	0.81
-49.40	1.10	1.03	0.52	1.38	1.08	1.17
-47.90	1.47	1.45	0.78	1.79	1.46	1.58
-47.00	1.85	1.83	1.13	2.10	1.82	1.95
-45.80	2.12	2.13	1.56	2.25	2.13	2.20
-44.50	2.28	2.29	1.93	2.28	2.31	2.34
-43.30	2.31	2.30	2.19	2.22	2.35	2.36
-42.10	2.25	2.21	2.30	2.07	2.28	2.28
-41.10	2.12	2.06	2.29	1.91	2.14	2.13
-39.90	1.96	1.90	2.19	1.74	1.97	1.97
-38.80	1.80	1.72	2.04	1.59	1.80	1.80
-37.50	1.64	1.56	1.87	1.45	1.63	1.64
-36.60	1.50	1.43	1.71	1.33	1.48	1.49
-35.30	1.36	1.31	1.54	1.22	1.36	1.36
-34.20	1.24	1.21	1.41	1.12	1.25	1.24
-33.00	1.15	1.12	1.29	1.04	1.14	1.14
-31.90	1.05	1.04	1.19	0.97	1.05	1.05
-30.80	0.97	0.94	1.11	0.89	0.96	0.96
-29.60	0.90	0.86	1.03	0.82	0.88	0.89
-28.60	0.83	0.80	0.95	0.75	0.80	0.82
-27.30	0.76	0.73	0.88	0.70	0.73	0.76
-26.10	0.69	0.67	0.81	0.64	0.67	0.70
-24.90	0.64	0.61	0.74	0.59	0.61	0.64
-23.80	0.58	0.56	0.67	0.54	0.56	0.58

Table D2 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (b) Tan δ

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-22.70	0.53	0.51	0.61	0.49	0.50	0.53
-21.50	0.49	0.46	0.56	0.43	0.46	0.49
-20.40	0.44	0.43	0.51	0.40	0.42	0.45
-19.20	0.40	0.39	0.46	0.36	0.38	0.41
-18.10	0.36	0.35	0.40	0.32	0.34	0.37
-16.90	0.32	0.31	0.35	0.29	0.30	0.33
-15.80	0.28	0.29	0.31	0.26	0.27	0.30
-14.70	0.24	0.25	0.27	0.24	0.25	0.26
-13.60	0.22	0.23	0.23	0.21	0.23	0.22
-12.20	0.19	0.21	0.21	0.19	0.20	0.19
-10.60	0.17	0.18	0.18	0.17	0.17	0.17
-9.30	0.15	0.16	0.15	0.16	0.15	0.16
-7.90	0.13	0.14	0.14	0.14	0.14	0.14
-6.30	0.12	0.12	0.12	0.12	0.11	0.12
-4.90	0.11	0.12	0.10	0.12	0.11	0.11
-3.40	0.10	0.11	0.10	0.10	0.10	0.10
-1.90	0.09	0.10	0.09	0.09	0.08	0.10
-0.50	0.09	0.08	0.07	0.09	0.08	0.08
2.90	0.08	0.08	0.08	0.08	0.07	0.08
3.20	0.08	0.08	0.07	0.07	0.07	0.07
3.80	0.08	0.07	0.07	0.07	0.06	0.07
5.50	0.07	0.07	0.07	0.06	0.07	0.06
6.70	0.07	0.07	0.06	0.06	0.06	0.06
8.70	0.07	0.06	0.06	0.06	0.06	0.06
10.20	0.06	0.06	0.06	0.06	0.05	0.06
11.80	0.06	0.06	0.06	0.05	0.05	0.06
13.10	0.06	0.06	0.06	0.05	0.05	0.05
14.50	0.06	0.05	0.05	0.05	0.05	0.06
16.00	0.06	0.05	0.05	0.05	0.04	0.05
17.50	0.06	0.05	0.06	0.06	0.05	0.04
19.10	0.05	0.05	0.05	0.04	0.04	0.04
20.50	0.04	0.04	0.04	0.04	0.04	0.05
22.00	0.05	0.05	0.04	0.04	0.04	0.05
23.50	0.04	0.04	0.05	0.04	0.04	0.05
24.90	0.05	0.05	0.05	0.04	0.04	0.03
26.40	0.05	0.05	0.04	0.04	0.05	0.04
28.00	0.04	0.03	0.05	0.04	0.04	0.04

Table D2 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (b) Tan δ

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
29.40	0.04	0.04	0.04	0.04	0.04	0.04
30.80	0.04	0.04	0.03	0.03	0.04	0.04
32.40	0.04	0.04	0.04	0.04	0.03	0.03
33.90	0.04	0.04	0.02	0.03	0.03	0.04
35.30	0.03	0.03	0.04	0.04	0.04	0.03
36.90	0.04	0.04	0.04	0.03	0.04	0.04
38.40	0.04	0.04	0.04	0.03	0.02	0.04
39.80	0.03	0.03	0.03	0.03	0.03	0.03
41.30	0.04	0.03	0.04	0.03	0.03	0.03
42.70	0.03	0.02	0.03	0.04	0.03	0.03
44.30	0.04	0.03	0.03	0.04	0.03	0.04
45.60	0.04	0.03	0.03	0.02	0.02	0.03
47.20	0.04	0.04	0.03	0.03	0.03	0.03
48.70	0.03	0.02	0.04	0.03	0.03	0.03
50.10	0.02	0.03	0.02	0.03	0.03	0.03
51.70	0.03	0.03	0.03	0.01	0.02	0.03
53.20	0.03	0.01	0.03	0.02	0.02	0.03
54.60	0.04	0.02	0.03	0.03	0.02	0.03
56.00	0.03	0.02	0.03	0.02	0.02	0.02
57.70	0.03	0.03	0.03	0.03	0.02	0.02
59.20	0.03	0.03	0.03	0.02	0.03	0.02
60.50	0.03	0.03	0.02	0.03	0.02	0.02

Table D3 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs: (a) Storage modulus (E')

Temp. (^oC)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-80.20	1481.73	1438.26	1346.63	1607.30	1630.66	1762.72
-76.90	1379.02	1398.72	1341.74	1617.31	1641.75	1638.66
-73.60	1336.03	1377.56	1293.29	1612.11	1658.75	1638.04
-70.70	1334.28	1381.66	1295.17	1605.62	1654.56	1631.75
-67.70	1330.46	1375.01	1293.43	1597.47	1650.16	1620.91
-64.20	1327.72	1368.06	1287.43	1586.84	1636.39	1597.74
-61.40	1305.31	1357.64	1281.51	1569.90	1618.63	1572.13
-60.10	1293.84	1346.96	1282.73	1552.58	1594.89	1543.55
-57.40	1280.41	1328.87	1278.86	1531.60	1571.16	1522.40
-56.20	1270.52	1312.67	1267.52	1508.96	1541.17	1484.94
-54.70	1256.62	1292.88	1260.33	1483.12	1505.47	1441.37
-53.60	1236.88	1275.56	1245.28	1452.73	1472.71	1412.14
-52.30	1229.15	1253.94	1231.12	1421.11	1441.96	1388.58
-50.90	1214.92	1239.91	1222.79	1403.80	1413.28	1376.68
-49.40	1208.09	1227.64	1216.19	1378.18	1398.64	1357.23
-47.90	1204.73	1224.83	1216.05	1362.96	1394.58	1348.60
-47.00	1207.88	1225.17	1219.93	1349.42	1396.23	1343.35
-45.80	1209.62	1227.17	1219.82	1347.16	1399.55	1332.86
-44.50	1210.74	1229.02	1222.06	1347.87	1395.88	1324.38
-43.30	1207.52	1225.12	1209.18	1340.70	1389.37	1310.48
-42.10	1197.55	1216.71	1190.42	1331.52	1368.02	1280.75
-41.10	1161.50	1194.12	1157.91	1295.92	1337.49	1232.53
-39.90	1108.42	1152.11	1104.64	1215.74	1257.68	1163.43
-38.80	984.67	1078.87	999.55	1090.28	1082.04	1034.29
-37.50	868.76	959.88	881.56	924.20	905.26	878.18
-36.60	705.03	826.34	766.26	748.75	763.57	733.23
-35.30	592.98	698.41	648.48	611.61	643.55	573.38
-34.20	461.44	579.81	522.72	495.04	529.68	446.32
-33.00	326.66	432.02	382.63	346.98	400.68	315.79
-31.90	221.38	285.22	250.30	208.33	265.21	213.89
-30.80	138.83	168.78	143.85	116.42	158.30	128.40
-29.60	80.02	91.63	78.42	63.65	96.17	71.53
-28.60	43.84	52.61	44.77	36.66	50.10	47.72
-27.30	26.36	30.27	26.91	22.52	26.54	23.31
-26.10	18.28	20.04	18.28	16.18	18.99	16.05
-24.90	12.81	14.37	13.27	12.28	13.95	12.22
-23.80	9.95	11.01	10.23	9.79	10.91	10.18

Table D3 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-22.70	8.25	8.81	8.25	8.02	8.93	8.43
-21.50	6.95	7.33	6.95	6.73	7.55	7.50
-20.40	5.99	6.31	5.97	5.85	6.42	6.34
-19.20	5.27	5.51	5.28	5.15	5.59	5.29
-18.10	4.75	4.98	4.80	4.69	5.00	4.73
-16.90	4.34	4.54	4.38	4.30	4.50	4.37
-15.80	4.01	4.21	4.05	3.99	4.06	4.28
-14.70	3.72	3.98	3.81	3.74	3.84	3.92
-13.60	3.54	3.74	3.60	3.55	3.65	3.71
-12.20	3.39	3.60	3.43	3.41	3.43	3.57
-10.60	3.26	3.46	3.29	3.28	3.28	3.44
-9.30	3.16	3.35	3.20	3.18	3.17	3.31
-7.90	3.08	3.28	3.11	3.11	3.09	3.22
-6.30	2.99	3.20	3.07	3.05	3.03	3.15
-4.90	2.91	3.16	3.00	3.00	2.97	3.08
-3.40	2.85	3.11	2.93	2.95	2.93	3.03
-1.90	2.80	3.02	2.85	2.88	2.89	2.97
-0.50	2.78	3.03	2.85	2.85	2.84	2.92
2.90	2.72	2.96	2.82	2.82	2.81	2.88
3.20	2.73	2.88	2.74	2.81	2.80	2.88
3.80	2.71	2.92	2.72	2.75	2.78	2.86
5.50	2.65	2.90	2.76	2.74	2.75	2.82
6.70	2.64	2.88	2.72	2.71	2.74	2.81
8.70	2.61	2.85	2.71	2.68	2.71	2.78
10.20	2.60	2.81	2.69	2.68	2.67	2.75
11.80	2.56	2.81	2.66	2.65	2.67	2.75
13.10	2.56	2.78	2.64	2.64	2.64	2.71
14.50	2.54	2.78	2.62	2.62	2.63	2.69
16.00	2.52	2.76	2.60	2.60	2.61	2.67
17.50	2.50	2.72	2.58	2.59	2.58	2.66
19.10	2.48	2.73	2.58	2.58	2.59	2.63
20.50	2.47	2.71	2.55	2.54	2.55	2.59
22.00	2.46	2.69	2.55	2.56	2.58	2.59
23.50	2.44	2.66	2.54	2.55	2.51	2.58
24.90	2.44	2.67	2.53	2.51	2.51	2.58
26.40	2.43	2.64	2.50	2.52	2.49	2.55
28.00	2.43	2.63	2.51	2.49	2.49	2.56

Table D3 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
29.40	2.41	2.60	2.49	2.49	2.46	2.54
30.80	2.39	2.59	2.49	2.47	2.45	2.53
32.40	2.38	2.57	2.45	2.45	2.43	2.51
33.90	2.36	2.55	2.45	2.44	2.44	2.51
35.30	2.36	2.55	2.43	2.43	2.43	2.50
36.90	2.35	2.54	2.42	2.43	2.44	2.47
38.40	2.34	2.52	2.40	2.42	2.42	2.46
39.80	2.32	2.51	2.38	2.40	2.42	2.45
41.30	2.31	2.49	2.36	2.37	2.41	2.44
42.70	2.30	2.48	2.36	2.35	2.40	2.43
44.30	2.31	2.47	2.36	2.33	2.35	2.42
45.60	2.28	2.47	2.33	2.31	2.36	2.42
47.20	2.29	2.46	2.31	2.31	2.34	2.41
48.70	2.28	2.44	2.30	2.30	2.36	2.39
50.10	2.25	2.45	2.32	2.28	2.31	2.38
51.70	2.25	2.43	2.28	2.27	2.31	2.38
53.20	2.23	2.43	2.30	2.27	2.32	2.38
54.60	2.23	2.41	2.28	2.24	2.31	2.36
56.00	2.22	2.39	2.27	2.22	2.30	2.35
57.70	2.22	2.39	2.25	2.21	2.29	2.34
59.20	2.19	2.38	2.24	2.20	2.27	2.31
60.50	2.20	2.37	2.24	2.18	2.26	2.29

Table D4 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs: (b) Tan δ

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-80.20	0.03	0.04	0.06	0.04	0.04	0.02
-76.90	0.04	0.04	0.05	0.04	0.04	0.02
-73.60	0.04	0.04	0.05	0.04	0.04	0.02
-70.70	0.04	0.04	0.05	0.04	0.03	0.02
-67.70	0.03	0.04	0.05	0.04	0.03	0.02
-64.20	0.03	0.04	0.05	0.04	0.03	0.02
-61.40	0.03	0.04	0.05	0.04	0.03	0.02
-60.10	0.03	0.04	0.05	0.04	0.04	0.02
-57.40	0.03	0.04	0.05	0.04	0.04	0.03
-56.20	0.04	0.04	0.05	0.04	0.04	0.03
-54.70	0.04	0.04	0.05	0.04	0.04	0.03
-53.60	0.04	0.04	0.05	0.05	0.04	0.03
-52.30	0.04	0.04	0.05	0.05	0.05	0.03
-50.90	0.04	0.04	0.05	0.05	0.05	0.03
-49.40	0.04	0.05	0.05	0.05	0.05	0.04
-47.90	0.04	0.05	0.05	0.05	0.05	0.04
-47.00	0.04	0.05	0.05	0.06	0.06	0.04
-45.80	0.05	0.05	0.06	0.06	0.06	0.04
-44.50	0.05	0.06	0.06	0.07	0.07	0.05
-43.30	0.05	0.06	0.07	0.07	0.07	0.05
-42.10	0.06	0.07	0.07	0.08	0.08	0.06
-41.10	0.07	0.08	0.09	0.09	0.09	0.08
-39.90	0.10	0.09	0.11	0.11	0.11	0.10
-38.80	0.15	0.12	0.15	0.15	0.17	0.15
-37.50	0.20	0.18	0.20	0.22	0.23	0.22
-36.60	0.29	0.24	0.26	0.31	0.31	0.31
-35.30	0.39	0.33	0.36	0.43	0.41	0.44
-34.20	0.53	0.44	0.48	0.56	0.53	0.59
-33.00	0.72	0.61	0.65	0.76	0.69	0.78
-31.90	0.92	0.82	0.88	1.04	0.92	0.98
-30.80	1.17	1.10	1.17	1.35	1.19	1.24
-29.60	1.44	1.40	1.47	1.64	1.44	1.51
-28.60	1.68	1.63	1.69	1.82	1.73	1.66
-27.30	1.77	1.77	1.79	1.84	1.85	1.74
-26.10	1.72	1.74	1.73	1.72	1.80	1.63
-24.90	1.56	1.59	1.57	1.53	1.64	1.46
-23.80	1.36	1.40	1.37	1.33	1.44	1.31

Table D4 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (b) Tan δ

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-22.70	1.18	1.18	1.17	1.14	1.25	1.14
-21.50	1.02	1.01	1.00	0.96	1.09	1.03
-20.40	0.88	0.86	0.86	0.82	0.92	0.88
-19.20	0.76	0.74	0.75	0.70	0.79	0.70
-18.10	0.66	0.64	0.65	0.61	0.69	0.60
-16.90	0.57	0.55	0.56	0.54	0.59	0.53
-15.80	0.50	0.49	0.49	0.47	0.50	0.48
-14.70	0.43	0.42	0.42	0.40	0.44	0.42
-13.60	0.38	0.37	0.37	0.35	0.39	0.39
-12.20	0.33	0.32	0.32	0.31	0.33	0.34
-10.60	0.29	0.28	0.28	0.27	0.28	0.30
-9.30	0.26	0.25	0.25	0.25	0.24	0.27
-7.90	0.23	0.22	0.22	0.22	0.21	0.24
-6.30	0.21	0.20	0.20	0.19	0.19	0.21
-4.90	0.18	0.18	0.18	0.18	0.18	0.19
-3.40	0.16	0.17	0.16	0.16	0.16	0.17
-1.90	0.15	0.15	0.15	0.15	0.14	0.16
-0.50	0.14	0.14	0.14	0.14	0.14	0.14
2.90	0.13	0.13	0.13	0.13	0.13	0.13
3.20	0.13	0.13	0.12	0.13	0.12	0.13
3.80	0.12	0.12	0.12	0.12	0.12	0.12
5.50	0.12	0.12	0.11	0.12	0.12	0.12
6.70	0.11	0.12	0.11	0.12	0.11	0.11
8.70	0.11	0.11	0.11	0.11	0.11	0.11
10.20	0.11	0.11	0.11	0.11	0.11	0.11
11.80	0.10	0.11	0.11	0.11	0.11	0.11
13.10	0.10	0.11	0.11	0.11	0.10	0.11
14.50	0.10	0.11	0.10	0.11	0.11	0.11
16.00	0.10	0.10	0.11	0.11	0.10	0.10
17.50	0.10	0.11	0.10	0.11	0.10	0.10
19.10	0.11	0.11	0.11	0.11	0.10	0.10
20.50	0.10	0.10	0.11	0.10	0.10	0.10
22.00	0.11	0.10	0.11	0.11	0.11	0.11
23.50	0.10	0.10	0.10	0.11	0.10	0.10
24.90	0.10	0.11	0.10	0.11	0.10	0.10
26.40	0.10	0.10	0.11	0.11	0.10	0.10
28.00	0.10	0.10	0.10	0.11	0.10	0.10

Table D4 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (b) Tan δ

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
29.40	0.10	0.11	0.11	0.11	0.10	0.10
30.80	0.10	0.10	0.10	0.10	0.10	0.11
32.40	0.10	0.10	0.10	0.11	0.10	0.10
33.90	0.10	0.11	0.10	0.11	0.10	0.10
35.30	0.10	0.10	0.10	0.11	0.10	0.10
36.90	0.09	0.10	0.11	0.11	0.10	0.10
38.40	0.10	0.10	0.10	0.11	0.10	0.11
39.80	0.10	0.10	0.10	0.11	0.10	0.10
41.30	0.10	0.10	0.10	0.11	0.10	0.10
42.70	0.10	0.11	0.10	0.10	0.10	0.10
44.30	0.10	0.11	0.10	0.10	0.10	0.09
45.60	0.10	0.10	0.10	0.10	0.10	0.09
47.20	0.09	0.10	0.10	0.10	0.10	0.10
48.70	0.09	0.10	0.10	0.10	0.10	0.10
50.10	0.10	0.10	0.10	0.10	0.10	0.09
51.70	0.09	0.10	0.09	0.10	0.10	0.10
53.20	0.09	0.10	0.09	0.10	0.09	0.10
54.60	0.10	0.09	0.09	0.10	0.09	0.10
56.00	0.09	0.09	0.09	0.09	0.09	0.09
57.70	0.09	0.10	0.10	0.10	0.09	0.09
59.20	0.09	0.09	0.09	0.09	0.09	0.10
60.50	0.09	0.10	0.10	0.09	0.09	0.09

Table D5 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs: (a) Storage modulus (E')

Temp. (°C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-80.20	1967.99	1927.67	1805.12	1703.30	1613.04	1933.50
-76.90	1997.27	1948.94	1816.81	1725.41	1644.37	1958.32
-73.60	1982.68	1958.36	1815.26	1736.76	1655.35	1925.23
-70.70	1941.60	1961.51	1813.30	1736.32	1657.31	1879.09
-67.70	1913.26	1952.38	1798.49	1728.95	1655.70	1850.66
-64.20	1853.65	1939.64	1780.57	1717.61	1649.14	1827.55
-61.40	1818.35	1926.81	1766.20	1699.20	1632.28	1803.57
-60.10	1791.83	1909.60	1747.19	1675.29	1614.53	1779.75
-57.40	1762.61	1887.90	1716.80	1651.72	1597.63	1758.35
-56.20	1734.97	1866.16	1685.36	1625.87	1573.92	1733.25
-54.70	1702.89	1841.75	1664.74	1601.13	1550.42	1701.04
-53.60	1670.74	1818.20	1639.48	1575.63	1527.97	1667.44
-52.30	1637.12	1798.01	1612.92	1550.11	1499.53	1638.92
-50.90	1600.64	1759.98	1591.15	1523.27	1474.30	1602.97
-49.40	1569.28	1729.98	1571.86	1496.75	1450.00	1565.67
-47.90	1535.57	1688.51	1541.62	1473.96	1426.03	1536.94
-47.00	1499.47	1645.18	1510.43	1447.66	1402.43	1498.43
-45.80	1463.74	1603.08	1478.51	1424.45	1369.98	1467.05
-44.50	1424.57	1563.07	1447.28	1399.30	1348.07	1437.72
-43.30	1391.69	1527.87	1419.89	1371.19	1327.24	1408.57
-42.10	1360.88	1490.50	1386.96	1351.24	1296.63	1384.89
-41.10	1334.14	1452.99	1355.86	1332.03	1271.32	1355.94
-39.90	1305.43	1413.42	1328.75	1305.87	1247.25	1328.58
-38.80	1275.69	1370.47	1297.90	1290.16	1225.96	1305.75
-37.50	1248.03	1335.46	1272.28	1270.59	1207.00	1287.82
-36.60	1228.91	1297.48	1240.38	1245.07	1184.79	1271.44
-35.30	1207.82	1272.26	1214.31	1223.73	1167.31	1254.17
-34.20	1198.50	1248.97	1190.74	1210.10	1153.24	1245.52
-33.00	1192.02	1237.30	1172.85	1197.61	1140.94	1233.36
-31.90	1192.44	1226.23	1165.49	1193.32	1145.94	1230.34
-30.80	1193.44	1227.15	1163.12	1177.38	1133.20	1227.28
-29.60	1187.21	1222.99	1165.64	1183.89	1133.24	1227.16
-28.60	1182.35	1226.41	1159.72	1172.97	1136.70	1213.65
-27.30	1175.18	1220.49	1162.20	1174.64	1125.80	1205.18
-26.10	1160.60	1222.07	1152.06	1162.41	1128.39	1195.52
-24.90	1142.72	1206.84	1144.14	1146.29	1112.40	1190.42
-23.80	1111.24	1187.92	1118.11	1122.22	1090.73	1167.66

Table D5 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-22.70	1051.37	1146.21	1082.86	1087.57	1052.70	1125.16
-21.50	962.50	1087.78	1014.42	1029.49	1007.88	1062.90
-20.40	824.46	983.65	908.44	919.59	894.69	949.76
-19.20	688.03	845.43	764.22	783.76	768.94	801.08
-18.10	559.57	703.82	629.97	643.25	645.05	662.57
-16.90	455.98	565.24	513.03	527.71	528.08	531.66
-15.80	345.59	436.33	409.26	412.77	423.23	406.73
-14.70	243.48	309.11	305.77	300.92	318.92	291.77
-13.60	165.85	208.64	202.44	197.66	217.49	190.80
-12.20	111.10	123.49	123.97	123.07	136.65	126.24
-10.60	65.71	72.25	70.68	66.69	82.73	76.99
-9.30	38.49	43.05	42.12	40.35	47.54	46.72
-7.90	23.21	25.85	25.26	24.00	27.93	27.15
-6.30	15.75	16.97	16.60	15.68	17.95	17.91
-4.90	11.89	12.23	12.28	11.33	12.44	12.83
-3.40	9.46	9.59	9.46	9.14	9.23	9.95
-1.90	7.67	7.75	7.80	7.52	7.52	7.93
-0.50	6.61	6.73	6.72	6.39	6.44	6.79
2.90	5.56	5.72	5.78	5.41	5.37	5.65
3.20	5.19	5.40	5.43	5.10	5.04	5.33
3.80	4.92	5.14	5.13	4.86	4.80	5.05
5.50	4.72	4.69	4.70	4.46	4.40	4.69
6.70	4.33	4.41	4.37	4.17	4.09	4.37
8.70	4.11	4.15	4.12	3.88	3.83	4.13
10.20	3.92	3.97	3.96	3.72	3.66	3.94
11.80	3.75	3.82	3.84	3.62	3.53	3.79
13.10	3.62	3.72	3.72	3.52	3.43	3.66
14.50	3.53	3.62	3.61	3.44	3.36	3.56
16.00	3.44	3.55	3.53	3.39	3.28	3.50
17.50	3.36	3.49	3.44	3.34	3.23	3.43
19.10	3.32	3.43	3.38	3.26	3.16	3.38
20.50	3.28	3.39	3.32	3.21	3.16	3.34
22.00	3.22	3.34	3.27	3.19	3.12	3.31
23.50	3.20	3.31	3.25	3.15	3.09	3.27
24.90	3.17	3.26	3.18	3.10	3.05	3.24
26.40	3.16	3.22	3.16	3.07	3.02	3.20
28.00	3.10	3.18	3.13	3.04	2.98	3.17

Table D5 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
29.40	3.08	3.15	3.10	3.01	2.94	3.14
30.80	3.05	3.12	3.06	2.98	2.93	3.10
32.40	3.02	3.09	3.05	2.95	2.88	3.09
33.90	3.00	3.07	3.03	2.91	2.86	3.06
35.30	2.97	3.05	2.99	2.89	2.85	3.04
36.90	2.96	3.02	2.96	2.87	2.83	3.00
38.40	2.95	2.98	2.95	2.84	2.80	2.97
39.80	2.89	2.97	2.92	2.83	2.79	2.96
41.30	2.90	2.96	2.89	2.79	2.76	2.94
42.70	2.89	2.93	2.88	2.79	2.73	2.93
44.30	2.87	2.92	2.85	2.76	2.72	2.90
45.60	2.85	2.90	2.83	2.75	2.71	2.88
47.20	2.82	2.87	2.81	2.72	2.69	2.87
48.70	2.82	2.85	2.79	2.68	2.68	2.85
50.10	2.80	2.84	2.76	2.66	2.65	2.81
51.70	2.79	2.81	2.75	2.65	2.62	2.80
53.20	2.77	2.80	2.73	2.63	2.60	2.78
54.60	2.76	2.78	2.72	2.61	2.60	2.77
56.00	2.73	2.76	2.70	2.60	2.58	2.77
57.70	2.70	2.76	2.68	2.57	2.57	2.76
59.20	2.71	2.75	2.67	2.57	2.55	2.75
60.50	2.70	2.73	2.66	2.56	2.54	2.72

Table D6 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs: (b) Tan δ

Temp. (^{o}C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-80.20	0.04	0.04	0.05	0.06	0.06	0.05
-76.90	0.04	0.04	0.05	0.06	0.05	0.05
-73.60	0.04	0.04	0.04	0.05	0.05	0.05
-70.70	0.04	0.04	0.04	0.05	0.05	0.05
-67.70	0.04	0.04	0.04	0.05	0.05	0.05
-64.20	0.04	0.04	0.04	0.05	0.05	0.05
-61.40	0.05	0.04	0.05	0.05	0.05	0.05
-60.10	0.05	0.04	0.05	0.06	0.05	0.05
-57.40	0.05	0.04	0.05	0.06	0.05	0.06
-56.20	0.05	0.04	0.05	0.06	0.05	0.06
-54.70	0.05	0.04	0.05	0.06	0.06	0.06
-53.60	0.05	0.05	0.05	0.06	0.06	0.06
-52.30	0.06	0.05	0.05	0.06	0.06	0.06
-50.90	0.06	0.05	0.05	0.06	0.06	0.06
-49.40	0.06	0.05	0.05	0.07	0.06	0.07
-47.90	0.06	0.05	0.06	0.07	0.06	0.07
-47.00	0.06	0.05	0.06	0.07	0.06	0.07
-45.80	0.07	0.06	0.06	0.07	0.06	0.07
-44.50	0.07	0.06	0.06	0.07	0.06	0.07
-43.30	0.07	0.06	0.06	0.07	0.07	0.08
-42.10	0.07	0.06	0.06	0.07	0.07	0.08
-41.10	0.07	0.06	0.06	0.08	0.07	0.08
-39.90	0.08	0.06	0.07	0.08	0.07	0.08
-38.80	0.08	0.07	0.07	0.08	0.07	0.08
-37.50	0.08	0.07	0.07	0.08	0.07	0.08
-36.60	0.08	0.07	0.07	0.08	0.08	0.09
-35.30	0.08	0.07	0.07	0.08	0.08	0.09
-34.20	0.08	0.07	0.07	0.09	0.08	0.09
-33.00	0.08	0.07	0.07	0.09	0.08	0.09
-31.90	0.08	0.07	0.07	0.09	0.08	0.09
-30.80	0.08	0.07	0.08	0.09	0.08	0.09
-29.60	0.09	0.07	0.08	0.09	0.08	0.09
-28.60	0.09	0.08	0.08	0.10	0.08	0.10
-27.30	0.10	0.08	0.08	0.10	0.09	0.10
-26.10	0.11	0.08	0.09	0.10	0.09	0.11
-24.90	0.12	0.09	0.09	0.11	0.10	0.11
-23.80	0.13	0.10	0.10	0.12	0.10	0.12

Table D6 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (b) Tan δ

Temp. (°C)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
-22.70	0.15	0.11	0.12	0.13	0.12	0.13
-21.50	0.19	0.13	0.15	0.15	0.14	0.16
-20.40	0.25	0.18	0.19	0.19	0.18	0.20
-19.20	0.32	0.24	0.26	0.26	0.25	0.27
-18.10	0.40	0.31	0.34	0.33	0.32	0.34
-16.90	0.50	0.41	0.42	0.42	0.40	0.44
-15.80	0.62	0.52	0.52	0.52	0.49	0.56
-14.70	0.77	0.67	0.65	0.66	0.61	0.70
-13.60	0.93	0.83	0.83	0.83	0.78	0.88
-12.20	1.11	1.05	1.03	1.03	0.97	1.06
-10.60	1.33	1.28	1.27	1.28	1.19	1.27
-9.30	1.52	1.47	1.46	1.46	1.41	1.46
-7.90	1.59	1.58	1.57	1.57	1.55	1.59
-6.30	1.51	1.54	1.53	1.52	1.55	1.56
-4.90	1.35	1.38	1.39	1.36	1.42	1.41
-3.40	1.18	1.19	1.19	1.20	1.22	1.22
-1.90	0.99	1.00	1.02	1.02	1.03	1.02
-0.50	0.85	0.87	0.88	0.87	0.89	0.88
2.90	0.70	0.72	0.74	0.71	0.72	0.70
3.20	0.64	0.67	0.69	0.66	0.67	0.65
3.80	0.58	0.62	0.63	0.62	0.63	0.60
5.50	0.54	0.53	0.55	0.53	0.54	0.53
6.70	0.46	0.47	0.48	0.47	0.47	0.46
8.70	0.41	0.40	0.42	0.40	0.40	0.40
10.20	0.36	0.36	0.39	0.36	0.36	0.36
11.80	0.32	0.33	0.35	0.32	0.32	0.31
13.10	0.28	0.30	0.32	0.30	0.29	0.28
14.50	0.25	0.27	0.29	0.27	0.26	0.25
16.00	0.23	0.25	0.27	0.25	0.24	0.23
17.50	0.21	0.23	0.24	0.23	0.22	0.22
19.10	0.19	0.21	0.22	0.22	0.21	0.21
20.50	0.18	0.19	0.21	0.20	0.19	0.19
22.00	0.17	0.19	0.19	0.19	0.19	0.18
23.50	0.16	0.17	0.18	0.18	0.17	0.17
24.90	0.16	0.17	0.17	0.17	0.16	0.16
26.40	0.15	0.16	0.16	0.16	0.15	0.16
28.00	0.15	0.15	0.15	0.15	0.15	0.15

Table D6 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial natural-based sulfurs (cont.): (b) Tan δ

Temp. (^oC)	E' (MPa)					
	IRPC-PS	RS	M101	M105	SGS	SP400
29.40	0.15	0.15	0.15	0.14	0.14	0.15
30.80	0.14	0.14	0.14	0.15	0.14	0.14
32.40	0.14	0.14	0.14	0.14	0.13	0.14
33.90	0.14	0.13	0.13	0.14	0.13	0.13
35.30	0.13	0.13	0.13	0.13	0.13	0.13
36.90	0.13	0.13	0.13	0.13	0.13	0.13
38.40	0.12	0.13	0.13	0.13	0.12	0.13
39.80	0.12	0.12	0.13	0.13	0.12	0.12
41.30	0.12	0.12	0.12	0.13	0.12	0.12
42.70	0.12	0.12	0.12	0.13	0.12	0.12
44.30	0.12	0.12	0.12	0.12	0.12	0.12
45.60	0.12	0.12	0.12	0.12	0.12	0.12
47.20	0.12	0.12	0.12	0.12	0.11	0.12
48.70	0.12	0.11	0.11	0.12	0.11	0.11
50.10	0.11	0.11	0.11	0.12	0.11	0.11
51.70	0.11	0.11	0.11	0.12	0.11	0.11
53.20	0.11	0.11	0.11	0.11	0.11	0.11
54.60	0.11	0.11	0.11	0.11	0.11	0.11
56.00	0.11	0.11	0.10	0.11	0.11	0.10
57.70	0.11	0.11	0.10	0.11	0.10	0.10
59.20	0.11	0.10	0.10	0.11	0.10	0.11
60.50	0.11	0.10	0.10	0.11	0.10	0.10

Table D7 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs: (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-79.90	2486.59	2409.04	2123.51	2224.65
-77.00	1984.52	2369.71	2105.91	2232.89
-74.60	1972.10	2287.76	2058.18	2217.09
-71.00	1972.73	2185.31	1932.10	2158.98
-68.30	1966.92	2104.18	1937.06	2137.00
-65.20	1940.98	2048.63	1932.16	2084.12
-62.50	1895.74	1982.27	1880.41	2000.35
-61.40	1863.11	1799.57	1843.70	1863.81
-59.90	1795.15	1698.91	1743.78	1765.62
-58.80	1690.87	1470.60	1563.58	1577.71
-57.60	1517.21	1214.43	1264.30	1344.34
-56.00	1231.37	989.97	1076.07	1142.87
-55.00	1069.15	744.07	906.22	897.52
-53.10	865.26	502.70	675.61	650.09
-51.80	669.12	297.34	443.37	399.17
-50.50	447.05	160.84	273.27	220.13
-49.30	261.68	91.03	171.47	125.17
-47.90	145.57	55.93	107.99	75.57
-46.70	86.24	36.28	65.56	46.61
-45.50	54.08	25.42	40.50	30.21
-44.30	35.41	18.70	27.18	22.00
-43.20	24.52	14.47	19.95	16.90
-42.20	18.17	11.50	15.47	13.28
-41.10	14.08	9.50	12.24	10.52
-39.60	11.01	7.99	9.94	8.55
-38.50	9.06	6.81	8.30	7.31
-37.70	7.69	5.91	7.00	6.24
-36.60	6.68	5.18	5.96	5.42
-35.30	5.76	4.58	5.07	4.74
-34.10	5.01	4.09	4.44	4.20
-33.10	4.44	3.70	3.97	3.79
-31.90	3.93	3.36	3.59	3.44
-30.70	3.56	3.10	3.26	3.13
-29.60	3.24	2.89	3.00	2.87
-28.40	2.97	2.68	2.79	2.67
-27.20	2.77	2.51	2.61	2.48
-25.70	2.57	2.36	2.45	2.33

Table D7 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-24.70	2.41	2.24	2.30	2.22
-24.10	2.30	2.13	2.20	2.13
-22.70	2.19	2.03	2.08	2.05
-21.10	2.07	1.96	1.99	1.98
-19.60	1.96	1.91	1.91	1.92
-18.20	1.90	1.86	1.87	1.86
-16.70	1.83	1.81	1.80	1.82
-15.20	1.80	1.79	1.76	1.77
-13.70	1.76	1.76	1.71	1.75
-12.20	1.73	1.71	1.68	1.71
-10.70	1.69	1.68	1.66	1.69
-9.30	1.66	1.68	1.63	1.65
-7.90	1.64	1.66	1.63	1.64
-6.40	1.63	1.64	1.59	1.62
-4.80	1.62	1.63	1.59	1.61
-3.20	1.61	1.61	1.56	1.61
-1.80	1.59	1.61	1.53	1.59
-0.50	1.56	1.60	1.55	1.58
3.00	1.58	1.59	1.54	1.56
3.20	1.55	1.56	1.53	1.56
3.70	1.55	1.56	1.53	1.53
5.50	1.57	1.59	1.52	1.56
7.20	1.54	1.56	1.51	1.56
8.70	1.56	1.58	1.50	1.54
10.10	1.54	1.53	1.48	1.50
11.60	1.54	1.54	1.51	1.53
13.10	1.52	1.54	1.49	1.54
14.50	1.53	1.54	1.51	1.52
16.00	1.54	1.54	1.52	1.55
17.40	1.54	1.54	1.51	1.55
19.00	1.54	1.54	1.51	1.55
20.50	1.52	1.55	1.50	1.50
21.90	1.54	1.54	1.50	1.54
23.50	1.53	1.54	1.51	1.53
25.00	1.54	1.54	1.48	1.52
26.30	1.54	1.53	1.49	1.55
27.90	1.54	1.54	1.50	1.53

Table D7 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^oC)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
29.30	1.55	1.55	1.50	1.53
30.70	1.54	1.53	1.50	1.53
32.30	1.53	1.55	1.50	1.55
33.80	1.52	1.55	1.51	1.54
35.40	1.54	1.55	1.51	1.52
36.70	1.53	1.56	1.50	1.53
38.40	1.55	1.55	1.50	1.53
39.70	1.54	1.56	1.49	1.52
41.40	1.57	1.56	1.50	1.55
42.70	1.54	1.56	1.49	1.56
44.20	1.58	1.56	1.51	1.56
45.70	1.58	1.58	1.51	1.56
47.20	1.57	1.58	1.50	1.56
48.70	1.59	1.59	1.51	1.57
50.10	1.58	1.59	1.52	1.58
51.60	1.59	1.60	1.52	1.59
53.20	1.60	1.61	1.54	1.57
54.70	1.61	1.62	1.55	1.59
56.10	1.58	1.61	1.56	1.59
57.50	1.60	1.61	1.55	1.58
59.00	1.58	1.62	1.53	1.60
60.50	1.61	1.62	1.54	1.59

Table D8 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs: (b) Tan δ

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-79.90	2486.59	2409.04	2123.51	2224.65
-77.00	1984.52	2369.71	2105.91	2232.89
-74.60	1972.10	2287.76	2058.18	2217.09
-71.00	1972.73	2185.31	1932.10	2158.98
-68.30	1966.92	2104.18	1937.06	2137.00
-65.20	1940.98	2048.63	1932.16	2084.12
-62.50	1895.74	1982.27	1880.41	2000.35
-61.40	1863.11	1799.57	1843.70	1863.81
-59.90	1795.15	1698.91	1743.78	1765.62
-58.80	1690.87	1470.60	1563.58	1577.71
-57.60	1517.21	1214.43	1264.30	1344.34
-56.00	1231.37	989.97	1076.07	1142.87
-55.00	1069.15	744.07	906.22	897.52
-53.10	865.26	502.70	675.61	650.09
-51.80	669.12	297.34	443.37	399.17
-50.50	447.05	160.84	273.27	220.13
-49.30	261.68	91.03	171.47	125.17
-47.90	145.57	55.93	107.99	75.57
-46.70	86.24	36.28	65.56	46.61
-45.50	54.08	25.42	40.50	30.21
-44.30	35.41	18.70	27.18	22.00
-43.20	24.52	14.47	19.95	16.90
-42.20	18.17	11.50	15.47	13.28
-41.10	14.08	9.50	12.24	10.52
-39.60	11.01	7.99	9.94	8.55
-38.50	9.06	6.81	8.30	7.31
-37.70	7.69	5.91	7.00	6.24
-36.60	6.68	5.18	5.96	5.42
-35.30	5.76	4.58	5.07	4.74
-34.10	5.01	4.09	4.44	4.20
-33.10	4.44	3.70	3.97	3.79
-31.90	3.93	3.36	3.59	3.44
-30.70	3.56	3.10	3.26	3.13
-29.60	3.24	2.89	3.00	2.87
-28.40	2.97	2.68	2.79	2.67
-27.20	2.77	2.51	2.61	2.48
-25.70	2.57	2.36	2.45	2.33

Table D8 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (b) Tan δ

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-24.70	2.41	2.24	2.30	2.22
-24.10	2.30	2.13	2.20	2.13
-22.70	2.19	2.03	2.08	2.05
-21.10	2.07	1.96	1.99	1.98
-19.60	1.96	1.91	1.91	1.92
-18.20	1.90	1.86	1.87	1.86
-16.70	1.83	1.81	1.80	1.82
-15.20	1.80	1.79	1.76	1.77
-13.70	1.76	1.76	1.71	1.75
-12.20	1.73	1.71	1.68	1.71
-10.70	1.69	1.68	1.66	1.69
-9.30	1.66	1.68	1.63	1.65
-7.90	1.64	1.66	1.63	1.64
-6.40	1.63	1.64	1.59	1.62
-4.80	1.62	1.63	1.59	1.61
-3.20	1.61	1.61	1.56	1.61
-1.80	1.59	1.61	1.53	1.59
-0.50	1.56	1.60	1.55	1.58
3.00	1.58	1.59	1.54	1.56
3.20	1.55	1.56	1.53	1.56
3.70	1.55	1.56	1.53	1.53
5.50	1.57	1.59	1.52	1.56
7.20	1.54	1.56	1.51	1.56
8.70	1.56	1.58	1.50	1.54
10.10	1.54	1.53	1.48	1.50
11.60	1.54	1.54	1.51	1.53
13.10	1.52	1.54	1.49	1.54
14.50	1.53	1.54	1.51	1.52
16.00	1.54	1.54	1.52	1.55
17.40	1.54	1.54	1.51	1.55
19.00	1.54	1.54	1.51	1.55
20.50	1.52	1.55	1.50	1.50
21.90	1.54	1.54	1.50	1.54
23.50	1.53	1.54	1.51	1.53
25.00	1.54	1.54	1.48	1.52
26.30	1.54	1.53	1.49	1.55
27.90	1.54	1.54	1.50	1.53

Table D8 Temperature sweep test results at 5 Hz as measured by DMA of NR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (b) Tan δ

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	**DF325**	**DF5(325)**	**SM400**
29.30	1.55	1.55	1.50	1.53
30.70	1.54	1.53	1.50	1.53
32.30	1.53	1.55	1.50	1.55
33.80	1.52	1.55	1.51	1.54
35.40	1.54	1.55	1.51	1.52
36.70	1.53	1.56	1.50	1.53
38.40	1.55	1.55	1.50	1.53
39.70	1.54	1.56	1.49	1.52
41.40	1.57	1.56	1.50	1.55
42.70	1.54	1.56	1.49	1.56
44.20	1.58	1.56	1.51	1.56
45.70	1.58	1.58	1.51	1.56
47.20	1.57	1.58	1.50	1.56
48.70	1.59	1.59	1.51	1.57
50.10	1.58	1.59	1.52	1.58
51.60	1.59	1.60	1.52	1.59
53.20	1.60	1.61	1.54	1.57
54.70	1.61	1.62	1.55	1.59
56.10	1.58	1.61	1.56	1.59
57.50	1.60	1.61	1.55	1.58
59.00	1.58	1.62	1.53	1.60
60.50	1.61	1.62	1.54	1.59

Table D9 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs: (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-79.90	1424.60	1549.78	1488.80	1782.26
-77.00	1437.86	1563.72	1510.72	1485.74
-74.60	1425.98	1562.39	1562.12	1408.99
-71.00	1423.07	1562.61	1577.91	1415.06
-68.30	1410.87	1557.47	1600.25	1414.83
-65.20	1395.31	1413.08	1608.47	1411.73
-62.50	1379.28	1356.18	1605.67	1406.05
-61.40	1366.46	1351.42	1575.08	1402.29
-59.90	1349.70	1346.27	1553.08	1394.70
-58.80	1340.76	1340.80	1529.74	1385.66
-57.60	1324.17	1334.68	1501.34	1380.11
-56.00	1315.52	1326.87	1471.07	1367.88
-55.00	1299.91	1323.65	1442.85	1354.05
-53.10	1284.23	1312.54	1411.14	1347.47
-51.80	1273.05	1306.76	1387.56	1326.36
-50.50	1255.49	1295.10	1363.59	1303.28
-49.30	1248.04	1286.14	1348.35	1284.26
-47.90	1240.15	1274.22	1333.69	1261.43
-46.70	1228.66	1262.89	1329.12	1241.32
-45.50	1216.14	1242.37	1323.81	1228.86
-44.30	1193.60	1216.02	1307.95	1212.20
-43.20	1158.38	1173.72	1276.86	1186.03
-42.20	1108.06	1105.48	1232.12	1126.66
-41.10	1040.76	1001.86	1148.03	1001.38
-39.60	932.01	902.19	1003.16	861.72
-38.50	846.31	819.30	826.99	751.57
-37.70	757.65	705.55	729.51	630.34
-36.60	631.85	566.74	599.72	460.12
-35.30	484.29	397.53	424.57	324.47
-34.10	313.41	247.38	278.37	235.86
-33.10	165.53	134.99	157.64	140.64
-31.90	86.04	72.95	86.39	78.96
-30.70	54.28	43.38	49.90	44.85
-29.60	26.94	26.33	30.01	26.67
-28.40	16.58	18.63	19.15	18.33
-27.20	12.71	13.29	14.67	13.59
-25.70	10.40	10.32	10.79	10.75

Table D9 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-24.70	9.10	7.90	8.65	8.37
-24.10	7.50	7.05	7.39	6.96
-22.70	6.52	6.35	6.37	6.03
-21.10	5.90	5.68	5.68	5.30
-19.60	5.44	5.17	5.18	4.83
-18.20	4.98	4.73	4.78	4.40
-16.70	4.67	4.37	4.44	4.06
-15.20	4.37	4.06	4.15	3.83
-13.70	4.12	3.83	3.90	3.65
-12.20	3.95	3.63	3.74	3.49
-10.70	3.74	3.50	3.58	3.36
-9.30	3.25	3.05	3.45	3.24
-7.90	3.10	2.94	3.27	3.16
-6.40	3.08	2.85	3.16	3.09
-4.80	2.99	2.81	3.10	3.02
-3.20	2.94	2.74	3.03	2.95
-1.80	2.90	2.70	2.99	2.89
-0.50	2.87	2.69	2.95	2.86
3.00	2.79	2.61	2.89	2.79
3.20	2.73	2.63	2.82	2.71
3.70	2.71	2.59	2.80	2.71
5.50	2.71	2.55	2.83	2.71
7.20	2.70	2.53	2.78	2.71
8.70	2.71	2.53	2.77	2.68
10.10	2.68	2.49	2.74	2.66
11.60	2.65	2.46	2.73	2.64
13.10	2.63	2.46	2.71	2.63
14.50	2.59	2.44	2.69	2.61
16.00	2.58	2.43	2.67	2.58
17.40	2.57	2.40	2.65	2.58
19.00	2.54	2.40	2.64	2.54
20.50	2.53	2.40	2.63	2.54
21.90	2.51	2.37	2.62	2.52
23.50	2.50	2.36	2.60	2.51
25.00	2.49	2.37	2.60	2.49
26.30	2.47	2.34	2.58	2.48
27.90	2.47	2.33	2.55	2.46

Table D9 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^oC)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
29.30	2.44	2.32	2.54	2.47
30.70	2.45	2.30	2.54	2.45
32.30	2.43	2.28	2.51	2.45
33.80	2.40	2.28	2.50	2.44
35.40	2.39	2.26	2.48	2.42
36.70	2.37	2.26	2.47	2.41
38.40	2.38	2.25	2.46	2.40
39.70	2.37	2.24	2.45	2.38
41.40	2.35	2.23	2.44	2.38
42.70	2.33	2.23	2.42	2.36
44.20	2.33	2.21	2.40	2.35
45.70	2.32	2.20	2.38	2.35
47.20	2.31	2.19	2.35	2.34
48.70	2.28	2.18	2.33	2.32
50.10	2.27	2.17	2.32	2.31
51.60	2.25	2.17	2.30	2.30
53.20	2.25	2.17	2.28	2.29
54.70	2.24	2.15	2.26	2.28
56.10	2.22	2.14	2.23	2.27
57.50	2.21	2.13	2.22	2.26
59.00	2.21	2.13	2.19	2.24
60.50	2.20	2.12	2.17	2.24

Table D10 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs: (b) Tan δ

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-79.90	0.04	0.02	0.02	0.01
-77.00	0.04	0.02	0.02	0.03
-74.60	0.04	0.02	0.02	0.03
-71.00	0.04	0.02	0.02	0.03
-68.30	0.04	0.02	0.02	0.03
-65.20	0.04	0.03	0.02	0.03
-62.50	0.04	0.02	0.02	0.03
-61.40	0.04	0.02	0.03	0.03
-59.90	0.04	0.02	0.03	0.03
-58.80	0.04	0.03	0.03	0.03
-57.60	0.04	0.03	0.03	0.03
-56.00	0.04	0.03	0.03	0.03
-55.00	0.04	0.03	0.03	0.03
-53.10	0.04	0.03	0.03	0.03
-51.80	0.04	0.03	0.03	0.03
-50.50	0.05	0.03	0.04	0.03
-49.30	0.05	0.03	0.04	0.04
-47.90	0.05	0.04	0.04	0.04
-46.70	0.05	0.04	0.04	0.04
-45.50	0.05	0.04	0.05	0.05
-44.30	0.06	0.05	0.05	0.05
-43.20	0.07	0.06	0.06	0.06
-42.20	0.09	0.08	0.08	0.09
-41.10	0.11	0.12	0.10	0.14
-39.60	0.16	0.17	0.16	0.21
-38.50	0.21	0.23	0.22	0.28
-37.70	0.29	0.33	0.31	0.37
-36.60	0.41	0.47	0.43	0.54
-35.30	0.58	0.66	0.61	0.73
-34.10	0.81	0.91	0.83	0.89
-33.10	1.13	1.22	1.11	1.15
-31.90	1.45	1.52	1.40	1.41
-30.70	1.64	1.72	1.63	1.62
-29.60	1.73	1.78	1.75	1.71
-28.40	1.56	1.71	1.71	1.67
-27.20	1.38	1.51	1.61	1.54
-25.70	1.21	1.30	1.38	1.38

Table D10 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (b) Tan δ

Temp. (°C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-24.70	1.10	1.04	1.16	1.17
-24.10	0.93	0.94	1.00	1.00
-22.70	0.80	0.84	0.85	0.86
-21.10	0.71	0.73	0.74	0.74
-19.60	0.64	0.64	0.65	0.66
-18.20	0.55	0.56	0.58	0.58
-16.70	0.50	0.50	0.50	0.50
-15.20	0.43	0.42	0.43	0.45
-13.70	0.38	0.37	0.38	0.40
-12.20	0.34	0.32	0.33	0.36
-10.70	0.29	0.29	0.29	0.31
-9.30	0.25	0.26	0.25	0.28
-7.90	0.24	0.23	0.23	0.25
-6.40	0.21	0.20	0.20	0.22
-4.80	0.19	0.18	0.18	0.19
-3.20	0.17	0.16	0.16	0.17
-1.80	0.15	0.15	0.15	0.15
-0.50	0.14	0.14	0.14	0.14
3.00	0.13	0.13	0.13	0.13
3.20	0.13	0.13	0.13	0.12
3.70	0.12	0.13	0.13	0.12
5.50	0.12	0.12	0.12	0.12
7.20	0.12	0.12	0.12	0.12
8.70	0.11	0.12	0.11	0.12
10.10	0.11	0.11	0.11	0.11
11.60	0.11	0.11	0.11	0.11
13.10	0.11	0.11	0.11	0.11
14.50	0.11	0.10	0.11	0.10
16.00	0.11	0.11	0.11	0.11
17.40	0.11	0.11	0.11	0.11
19.00	0.11	0.11	0.11	0.10
20.50	0.10	0.10	0.10	0.10
21.90	0.10	0.11	0.10	0.10
23.50	0.11	0.10	0.10	0.10
25.00	0.11	0.11	0.10	0.10
26.30	0.10	0.11	0.10	0.11
27.90	0.10	0.11	0.11	0.10

Table D10 Temperature sweep test results at 5 Hz as measured by DMA of SBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (b) Tan δ

Temp. (^oC)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
29.30	0.11	0.10	0.10	0.10
30.70	0.11	0.11	0.10	0.10
32.30	0.11	0.11	0.10	0.11
33.80	0.10	0.10	0.10	0.10
35.40	0.10	0.10	0.10	0.10
36.70	0.10	0.10	0.10	0.10
38.40	0.10	0.10	0.11	0.10
39.70	0.10	0.11	0.11	0.11
41.40	0.10	0.10	0.10	0.10
42.70	0.10	0.10	0.10	0.10
44.20	0.10	0.10	0.10	0.09
45.70	0.10	0.10	0.10	0.10
47.20	0.10	0.10	0.10	0.10
48.70	0.10	0.09	0.10	0.09
50.10	0.10	0.10	0.10	0.10
51.60	0.10	0.09	0.09	0.10
53.20	0.10	0.09	0.09	0.09
54.70	0.10	0.09	0.10	0.09
56.10	0.10	0.10	0.09	0.09
57.50	0.10	0.10	0.09	0.10
59.00	0.10	0.09	0.10	0.09
60.50	0.10	0.09	0.09	0.09

Table D11 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs: (a) Storage modulus (E')

Temp. (^oC)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-79.90	1927.46	1924.52	1855.37	2038.95
-77.00	1947.02	1920.51	1811.02	2050.09
-74.60	1928.87	1911.72	1795.66	2041.34
-71.00	1887.55	1892.98	1791.78	2031.81
-68.30	1834.34	1867.51	1787.27	2006.39
-65.20	1802.75	1850.51	1780.11	1977.11
-62.50	1784.02	1829.85	1769.89	1940.21
-61.40	1758.46	1809.27	1761.42	1860.47
-59.90	1733.14	1776.81	1754.31	1812.61
-58.80	1712.23	1751.06	1739.67	1776.73
-57.60	1687.03	1718.43	1722.21	1748.68
-56.00	1667.08	1685.18	1710.48	1716.92
-55.00	1635.80	1649.79	1702.23	1687.55
-53.10	1613.92	1613.36	1687.67	1659.32
-51.80	1589.25	1573.93	1674.10	1637.83
-50.50	1546.51	1543.78	1658.73	1611.51
-49.30	1510.76	1517.96	1638.05	1584.35
-47.90	1473.27	1480.56	1614.01	1556.06
-46.70	1433.11	1452.00	1593.86	1524.19
-45.50	1400.25	1431.47	1573.70	1489.47
-44.30	1375.20	1400.86	1543.45	1459.64
-43.20	1347.95	1383.92	1521.90	1426.42
-42.20	1319.53	1368.02	1499.10	1395.61
-41.10	1292.94	1349.42	1474.04	1372.01
-39.60	1268.30	1329.09	1452.31	1345.12
-38.50	1248.69	1308.99	1430.81	1318.06
-37.70	1235.27	1299.05	1409.15	1293.84
-36.60	1229.28	1290.85	1393.17	1277.36
-35.30	1224.47	1285.35	1385.08	1270.49
-34.10	1220.47	1280.95	1381.13	1266.93
-33.10	1220.27	1277.96	1377.57	1272.11
-31.90	1221.23	1281.03	1376.27	1269.69
-30.70	1218.33	1275.50	1367.54	1268.36
-29.60	1207.48	1277.04	1355.79	1259.51
-28.40	1189.41	1264.77	1334.17	1253.44
-27.20	1160.67	1251.92	1297.16	1228.99
-25.70	1118.64	1233.02	1235.96	1194.57

Table D11 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-24.70	1046.22	1196.78	1122.92	1132.81
-24.10	933.97	1136.49	979.01	1036.90
-22.70	779.96	1027.24	822.10	903.93
-21.10	640.69	889.10	675.94	787.27
-19.60	518.33	739.02	541.39	670.43
-18.20	398.78	614.77	410.46	554.53
-16.70	289.95	498.64	307.32	439.56
-15.20	202.82	357.13	220.11	309.86
-13.70	139.54	235.76	142.10	201.78
-12.20	94.17	149.07	89.53	130.22
-10.70	61.47	89.53	56.63	82.41
-9.30	39.99	52.26	38.49	51.98
-7.90	26.26	30.82	26.07	33.10
-6.40	17.33	19.49	18.48	20.16
-4.80	12.64	13.81	13.95	13.53
-3.20	9.67	10.36	11.25	10.50
-1.80	8.29	8.14	9.23	8.38
-0.50	6.90	6.86	7.86	7.12
3.00	5.74	5.54	6.31	5.72
3.20	5.40	5.22	5.98	5.41
3.70	5.15	4.95	5.72	5.15
5.50	4.80	4.64	5.37	4.82
7.20	4.44	4.30	4.98	4.45
8.70	4.17	4.07	4.67	4.22
10.10	3.98	3.88	4.34	4.02
11.60	3.82	3.74	4.10	3.85
13.10	3.71	3.60	3.88	3.68
14.50	3.59	3.50	3.75	3.59
16.00	3.49	3.43	3.64	3.50
17.40	3.45	3.36	3.56	3.43
19.00	3.38	3.30	3.50	3.37
20.50	3.32	3.24	3.44	3.31
21.90	3.31	3.22	3.38	3.27
23.50	3.27	3.19	3.34	3.24
25.00	3.26	3.17	3.32	3.20
26.30	3.22	3.14	3.29	3.16
27.90	3.20	3.10	3.26	3.14

Table D11 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
29.30	3.15	3.08	3.24	3.12
30.70	3.13	3.04	3.21	3.08
32.30	3.09	3.01	3.19	3.08
33.80	3.07	2.99	3.15	3.07
35.40	3.04	2.98	3.14	3.04
36.70	3.02	2.95	3.11	3.02
38.40	2.99	2.93	3.10	3.01
39.70	2.97	2.89	3.07	2.97
41.40	2.95	2.87	3.05	2.96
42.70	2.93	2.85	3.03	2.94
44.20	2.90	2.83	3.02	2.92
45.70	2.88	2.81	2.99	2.90
47.20	2.88	2.79	2.99	2.88
48.70	2.85	2.76	2.98	2.87
50.10	2.84	2.75	2.95	2.85
51.60	2.81	2.72	2.94	2.84
53.20	2.80	2.70	2.91	2.82
54.70	2.77	2.69	2.91	2.81
56.10	2.75	2.66	2.88	2.77
57.50	2.74	2.66	2.89	2.78
59.00	2.71	2.62	2.86	2.76
60.50	2.69	2.61	2.85	2.75

Table D12 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs: (b) Tan δ

Temp. (°C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-79.90	0.04	0.04	0.04	0.04
-77.00	0.04	0.04	0.04	0.04
-74.60	0.04	0.04	0.04	0.04
-71.00	0.04	0.04	0.04	0.04
-68.30	0.04	0.04	0.04	0.04
-65.20	0.04	0.04	0.04	0.04
-62.50	0.04	0.05	0.04	0.04
-61.40	0.04	0.05	0.04	0.04
-59.90	0.04	0.05	0.04	0.04
-58.80	0.04	0.05	0.04	0.04
-57.60	0.04	0.05	0.04	0.05
-56.00	0.05	0.05	0.04	0.05
-55.00	0.05	0.05	0.04	0.05
-53.10	0.05	0.05	0.05	0.05
-51.80	0.05	0.05	0.05	0.05
-50.50	0.05	0.06	0.05	0.05
-49.30	0.05	0.06	0.05	0.05
-47.90	0.05	0.06	0.05	0.06
-46.70	0.06	0.06	0.05	0.06
-45.50	0.06	0.06	0.05	0.06
-44.30	0.06	0.06	0.05	0.06
-43.20	0.06	0.06	0.05	0.06
-42.20	0.06	0.06	0.05	0.06
-41.10	0.06	0.06	0.05	0.06
-39.60	0.06	0.06	0.05	0.07
-38.50	0.06	0.06	0.05	0.07
-37.70	0.07	0.07	0.05	0.07
-36.60	0.07	0.07	0.05	0.07
-35.30	0.07	0.07	0.06	0.07
-34.10	0.07	0.07	0.06	0.08
-33.10	0.07	0.07	0.06	0.08
-31.90	0.07	0.07	0.06	0.08
-30.70	0.08	0.07	0.07	0.08
-29.60	0.08	0.08	0.07	0.08
-28.40	0.09	0.08	0.08	0.09
-27.20	0.10	0.08	0.10	0.09
-25.70	0.11	0.09	0.12	0.10

Table D12 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (b) Tan δ

Temp. (^{o}C)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
-24.70	0.14	0.10	0.17	0.13
-24.10	0.19	0.12	0.23	0.16
-22.70	0.26	0.16	0.30	0.22
-21.10	0.35	0.22	0.37	0.28
-19.60	0.44	0.29	0.46	0.34
-18.20	0.55	0.37	0.57	0.42
-16.70	0.68	0.46	0.69	0.52
-15.20	0.83	0.61	0.83	0.67
-13.70	0.98	0.79	1.01	0.85
-12.20	1.14	0.98	1.21	1.03
-10.70	1.31	1.20	1.39	1.23
-9.30	1.46	1.41	1.52	1.41
-7.90	1.53	1.56	1.59	1.54
-6.40	1.49	1.57	1.56	1.56
-4.80	1.35	1.45	1.46	1.43
-3.20	1.16	1.26	1.32	1.26
-1.80	1.04	1.05	1.16	1.06
-0.50	0.87	0.90	1.02	0.91
3.00	0.70	0.70	0.81	0.71
3.20	0.65	0.65	0.76	0.66
3.70	0.61	0.60	0.73	0.61
5.50	0.54	0.53	0.66	0.55
7.20	0.46	0.46	0.58	0.48
8.70	0.40	0.41	0.52	0.42
10.10	0.36	0.36	0.45	0.37
11.60	0.32	0.31	0.39	0.32
13.10	0.28	0.28	0.34	0.29
14.50	0.25	0.24	0.30	0.25
16.00	0.23	0.22	0.26	0.23
17.40	0.21	0.20	0.23	0.21
19.00	0.20	0.19	0.21	0.19
20.50	0.18	0.18	0.20	0.18
21.90	0.18	0.17	0.18	0.17
23.50	0.17	0.16	0.18	0.16
25.00	0.16	0.16	0.17	0.15
26.30	0.15	0.15	0.16	0.15
27.90	0.15	0.15	0.15	0.14

Table D12 Temperature sweep test results at 5 Hz as measured by DMA of NBR vulcanizates cured with IRPC-PS compared with various commercial petroleum-based sulfurs (cont.): (b) Tan δ

Temp. (^oC)	E' (MPa)			
	IRPC-PS	DF325	DF5(325)	SM400
29.30	0.14	0.14	0.15	0.14
30.70	0.14	0.14	0.14	0.14
32.30	0.14	0.15	0.14	0.13
33.80	0.13	0.13	0.14	0.13
35.40	0.13	0.13	0.13	0.13
36.70	0.13	0.13	0.13	0.12
38.40	0.12	0.12	0.12	0.12
39.70	0.12	0.13	0.12	0.12
41.40	0.13	0.12	0.12	0.13
42.70	0.12	0.12	0.12	0.12
44.20	0.12	0.12	0.12	0.12
45.70	0.12	0.12	0.12	0.12
47.20	0.12	0.12	0.12	0.12
48.70	0.11	0.12	0.11	0.12
50.10	0.12	0.11	0.11	0.11
51.60	0.11	0.12	0.11	0.11
53.20	0.11	0.11	0.11	0.11
54.70	0.11	0.12	0.11	0.11
56.10	0.11	0.11	0.11	0.11
57.50	0.11	0.11	0.11	0.11
59.00	0.11	0.11	0.11	0.10
60.50	0.11	0.11	0.11	0.10

Table D13 Temperature sweep test results at 5 Hz as measured by DMA of vulcanizates cured with uncoated and TDAE oil-coated petroleum-based sulfur: (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa) NR	
	OA	OC
-79.70	1729.09	1881.59
-79.60	1710.72	1875.87
-77.30	1701.65	1827.83
-75.80	1627.88	1760.92
-74.30	1632.73	1760.33
-72.80	1530.01	1668.75
-71.50	1408.11	1535.58
-69.70	1270.27	1382.80
-68.50	1119.12	1350.14
-67.10	1089.12	1235.34
-65.60	881.28	1096.93
-64.20	736.48	962.68
-62.70	681.77	887.70
-61.20	506.61	666.78
-59.80	355.62	487.04
-58.30	236.07	329.25
-56.80	155.97	207.40
-55.30	99.81	128.74
-53.80	64.78	81.07
-52.30	44.35	52.90
-50.70	30.70	36.69
-49.40	23.06	27.13
-47.90	17.32	20.36
-46.40	13.60	15.59
-44.90	10.90	12.41
-43.40	8.96	10.10
-42.00	7.53	8.31
-40.40	6.45	7.04
-39.00	5.59	5.95
-37.40	4.86	5.15
-36.00	4.28	4.50
-34.40	3.80	4.00
-32.90	3.41	3.58
-31.50	3.07	3.22
-30.10	2.83	2.96
-28.60	2.62	2.74
-27.00	2.41	2.55
-25.60	2.27	2.39
-24.00	2.13	2.24
-22.60	2.04	2.13
-21.00	1.97	2.03
-19.60	1.90	1.96
-18.20	1.85	1.90
-16.70	1.78	1.85
-15.20	1.75	1.81
-13.70	1.71	1.79
-12.10	1.69	1.75

Temp. (^{o}C)	E' (MPa) SBR	
	OA	OC
-79.80	1320.66	1485.43
-79.40	1376.70	1524.72
-77.30	1412.53	1536.84
-75.70	1438.16	1543.45
-74.60	1452.13	1543.11
-72.70	1454.42	1539.39
-71.30	1453.46	1534.75
-69.90	1442.79	1528.67
-68.50	1429.93	1516.74
-66.90	1411.86	1505.52
-65.50	1392.69	1487.85
-63.90	1354.34	1468.55
-62.50	1314.88	1432.50
-60.90	1261.68	1392.67
-59.30	1181.50	1337.72
-57.90	1082.07	1254.04
-56.40	974.77	1147.65
-54.90	883.21	1015.57
-53.50	800.02	897.80
-52.00	696.97	796.86
-50.80	605.80	695.97
-49.30	520.98	590.55
-47.80	435.42	480.71
-46.40	344.53	370.86
-45.00	258.39	271.62
-43.40	181.30	185.98
-41.90	118.75	128.54
-40.50	77.71	86.07
-39.00	50.53	55.89
-37.50	35.48	36.57
-36.10	25.31	24.59
-34.50	18.46	17.98
-33.00	14.27	13.99
-31.60	11.68	11.25
-30.10	9.91	9.48
-28.70	8.58	8.00
-27.10	7.51	6.95
-25.60	6.69	6.16
-24.00	6.00	5.57
-22.60	5.43	5.12
-21.10	4.97	4.71
-19.70	4.61	4.38
-18.20	4.29	4.05
-16.70	4.05	3.80
-15.10	3.82	3.63
-13.70	3.68	3.49
-12.20	3.54	3.38

Temp. (^{o}C)	E' (MPa) NBR	
	OA	OC
-80.30	2194.98	2222.68
-77.10	2223.45	2233.33
-73.80	2204.46	2211.31
-70.80	2171.89	2181.33
-67.50	2140.44	2137.73
-66.10	2094.02	2098.55
-64.90	2052.87	2069.24
-63.60	1983.56	2039.74
-62.30	1908.45	2014.06
-61.00	1872.55	1986.32
-59.70	1846.47	1937.43
-58.30	1819.09	1907.47
-57.00	1795.47	1850.36
-55.60	1776.52	1822.51
-54.30	1757.84	1790.26
-53.00	1739.30	1762.97
-51.60	1715.76	1731.29
-50.30	1695.35	1704.83
-48.90	1672.81	1680.62
-47.60	1653.56	1656.49
-46.30	1633.49	1632.67
-44.90	1614.80	1608.85
-43.60	1600.66	1587.58
-42.30	1586.48	1568.33
-41.00	1571.45	1552.06
-39.60	1554.48	1534.76
-38.30	1538.54	1519.47
-36.90	1516.82	1510.17
-35.60	1494.18	1497.93
-34.20	1473.87	1492.65
-32.80	1437.21	1482.30
-31.50	1396.63	1472.06
-30.10	1339.99	1454.98
-28.80	1256.37	1435.11
-27.40	1127.40	1403.20
-26.00	966.52	1361.05
-24.70	806.20	1297.69
-23.30	651.67	1219.35
-21.60	515.90	1096.83
-20.20	394.03	944.01
-18.80	291.42	787.63
-17.60	203.23	650.08
-16.40	139.86	517.60
-15.00	95.14	401.05
-13.70	64.18	296.02
-12.50	44.13	207.01
-11.40	31.13	135.19

Table D13 Temperature sweep test results at 5 Hz as measured by DMA of vulcanizates cured with uncoated and TDAE oil-coated petroleum-based sulfur (cont.): (a) Storage modulus (E')

Temp. (^{o}C)	E' (MPa)	
	NR	
	OA	OC
-10.60	1.67	1.73
-9.30	1.65	1.72
-7.70	1.62	1.69
-6.20	1.62	1.68
-4.80	1.59	1.66
-3.30	1.60	1.65
-1.70	1.57	1.65
-0.40	1.57	1.65
1.80	1.56	1.62
2.60	1.59	1.67
4.00	1.56	1.61
5.60	1.56	1.60
7.10	1.53	1.61
8.60	1.55	1.60
10.00	1.54	1.61
11.50	1.53	1.60
13.00	1.52	1.59
14.50	1.52	1.60
16.00	1.53	1.59
17.50	1.53	1.60
19.10	1.54	1.60
20.50	1.53	1.61
22.00	1.52	1.60
23.40	1.52	1.60
24.90	1.53	1.60
26.50	1.54	1.59
27.90	1.52	1.61
29.40	1.53	1.60
30.80	1.53	1.60
32.30	1.54	1.59
33.90	1.51	1.60
35.40	1.54	1.61
36.90	1.53	1.61
38.40	1.54	1.62
39.80	1.54	1.62
41.30	1.53	1.61
42.70	1.54	1.61
44.30	1.52	1.61
45.80	1.52	1.62
47.20	1.53	1.61
48.80	1.54	1.62
50.30	1.54	1.62
51.60	1.53	1.63
53.20	1.53	1.63
54.60	1.54	1.62
56.20	1.52	1.63
57.70	1.55	1.63

Temp. (^{o}C)	E' (MPa)	
	SBR	
	OA	OC
-10.60	3.44	3.31
-9.30	3.36	3.25
-7.80	3.28	3.18
-6.30	3.22	3.14
-4.70	3.18	3.10
-3.30	3.13	3.07
-1.80	3.11	3.04
-0.50	3.05	3.00
1.90	3.01	2.96
2.50	2.99	2.93
4.00	2.97	2.89
5.60	2.95	2.92
6.90	2.94	2.89
8.70	2.91	2.88
10.00	2.86	2.84
11.50	2.85	2.83
13.20	2.83	2.81
14.60	2.81	2.79
16.10	2.79	2.76
17.50	2.75	2.74
19.00	2.74	2.72
20.40	2.74	2.71
21.90	2.72	2.70
23.50	2.71	2.68
24.80	2.69	2.67
26.30	2.68	2.65
27.70	2.67	2.64
29.50	2.66	2.62
30.90	2.64	2.62
32.30	2.64	2.59
33.90	2.64	2.60
35.20	2.60	2.60
36.80	2.60	2.57
38.40	2.60	2.55
39.80	2.58	2.55
41.20	2.56	2.54
42.70	2.56	2.52
44.30	2.55	2.52
45.70	2.54	2.50
47.20	2.51	2.50
48.80	2.51	2.49
50.10	2.48	2.47
51.60	2.48	2.46
53.20	2.47	2.45
54.60	2.46	2.44
56.20	2.45	2.43
57.70	2.44	2.40

Temp. (^{o}C)	E' (MPa)	
	NBR	
	OA	OC
-10.20	22.74	84.84
-9.10	17.42	54.89
-7.80	13.90	33.90
-6.30	11.43	22.71
-4.70	9.46	16.36
-3.10	8.12	12.44
-1.70	7.11	9.64
-0.50	6.32	8.01
3.70	5.94	6.47
4.20	5.64	6.08
4.20	5.40	5.82
5.30	5.19	5.40
7.10	4.90	5.00
8.60	4.54	4.63
10.10	4.28	4.35
11.50	4.04	4.14
13.10	3.87	3.95
14.50	3.72	3.82
16.10	3.61	3.71
17.60	3.52	3.61
19.10	3.45	3.55
20.40	3.39	3.47
21.90	3.34	3.42
23.50	3.30	3.36
25.20	3.27	3.31
26.10	3.23	3.27
27.70	3.20	3.23
29.40	3.16	3.20
30.60	3.12	3.14
32.20	3.10	3.12
33.80	3.07	3.08
35.40	3.06	3.05
37.00	3.02	3.02
38.30	2.99	2.99
39.80	2.96	2.96
41.20	2.93	2.94
42.60	2.92	2.92
44.20	2.89	2.88
45.90	2.88	2.86
47.20	2.84	2.84
48.80	2.83	2.82
50.00	2.81	2.79
51.70	2.78	2.77
53.20	2.75	2.75
54.60	2.73	2.73
56.20	2.71	2.70
57.70	2.69	2.66

Table D13 Temperature sweep test results at 5 Hz as measured by DMA of vulcanizates cured with uncoated and TDAE oil-coated petroleum-based sulfur (cont.): (a) Storage modulus (E')

Temp. (^oC)	E' (MPa)	
	NR	
	OA	OC
59.20	1.54	1.62
60.60	1.55	1.63

Temp. (^oC)	E' (MPa)	
	SBR	
	OA	OC
59.10	2.43	2.39
60.50	2.42	2.39

Temp. (^oC)	E' (MPa)	
	NBR	
	OA	OC
59.10	2.66	2.64
60.50	2.65	2.61

Table D14 Temperature sweep test results at 5 Hz as measured by DMA of vulcanizates cured with uncoated and TDAE oil-coated petroleum-based sulfur: (b) Tan δ

Temp. (°C)	Tan δ NR	
	OA	OC
-79.70	0.23	0.23
-79.60	0.25	0.22
-77.30	0.22	0.21
-75.80	0.30	0.22
-74.30	0.23	0.29
-72.80	0.25	0.24
-71.50	0.29	0.28
-69.70	0.35	0.34
-68.50	0.53	0.46
-67.10	0.44	0.40
-65.60	0.58	0.48
-64.20	0.75	0.65
-62.70	0.74	0.61
-61.20	0.93	0.80
-59.80	1.16	1.00
-58.30	1.43	1.26
-56.80	1.68	1.55
-55.30	1.92	1.84
-53.80	2.11	2.08
-52.30	2.22	2.22
-50.70	2.25	2.27
-49.40	2.21	2.25
-47.90	2.10	2.16
-46.40	1.95	2.02
-44.90	1.79	1.86
-43.40	1.64	1.70
-42.00	1.50	1.55
-40.40	1.38	1.41
-39.00	1.26	1.28
-37.40	1.15	1.16
-36.00	1.06	1.07
-34.40	0.96	0.97
-32.90	0.88	0.89
-31.50	0.81	0.81
-30.10	0.74	0.74
-28.60	0.67	0.67
-27.00	0.60	0.61
-25.60	0.54	0.55
-24.00	0.48	0.49
-22.60	0.44	0.43
-21.00	0.40	0.38
-19.60	0.36	0.34
-18.20	0.32	0.29
-16.70	0.28	0.26
-15.20	0.25	0.23
-13.70	0.22	0.20
-12.10	0.20	0.18

Temp. (°C)	Tan δ SBR	
	OA	OC
-79.80	0.08	0.05
-79.40	0.06	0.04
-77.30	0.04	0.04
-75.70	0.04	0.04
-74.60	0.04	0.04
-72.70	0.04	0.04
-71.30	0.04	0.04
-69.90	0.04	0.04
-68.50	0.04	0.04
-66.90	0.05	0.04
-65.50	0.05	0.04
-63.90	0.06	0.05
-62.50	0.07	0.05
-60.90	0.08	0.06
-59.30	0.10	0.07
-57.90	0.13	0.09
-56.40	0.16	0.12
-54.90	0.19	0.15
-53.50	0.23	0.19
-52.00	0.29	0.24
-50.80	0.36	0.31
-49.30	0.44	0.40
-47.80	0.55	0.52
-46.40	0.68	0.66
-45.00	0.83	0.83
-43.40	1.02	1.02
-41.90	1.22	1.20
-40.50	1.41	1.38
-39.00	1.58	1.55
-37.50	1.67	1.67
-36.10	1.70	1.70
-34.50	1.64	1.64
-33.00	1.52	1.52
-31.60	1.38	1.37
-30.10	1.25	1.23
-28.70	1.12	1.07
-27.10	1.00	0.94
-25.60	0.89	0.83
-24.00	0.79	0.74
-22.60	0.70	0.66
-21.10	0.62	0.59
-19.70	0.55	0.52
-18.20	0.49	0.45
-16.70	0.42	0.39
-15.10	0.38	0.33
-13.70	0.33	0.30
-12.20	0.29	0.26

Temp. (°C)	Tan δ NBR	
	OA	OC
-80.30	0.04	0.04
-77.10	0.03	0.04
-73.80	0.03	0.04
-70.80	0.03	0.04
-67.50	0.03	0.04
-66.10	0.03	0.04
-64.90	0.03	0.04
-63.60	0.04	0.04
-62.30	0.04	0.04
-61.00	0.04	0.04
-59.70	0.04	0.04
-58.30	0.04	0.04
-57.00	0.04	0.04
-55.60	0.04	0.05
-54.30	0.04	0.05
-53.00	0.04	0.05
-51.60	0.05	0.05
-50.30	0.05	0.05
-48.90	0.05	0.05
-47.60	0.05	0.06
-46.30	0.05	0.06
-44.90	0.05	0.06
-43.60	0.06	0.06
-42.30	0.06	0.06
-41.00	0.06	0.06
-39.60	0.06	0.07
-38.30	0.06	0.07
-36.90	0.07	0.07
-35.60	0.07	0.07
-34.20	0.08	0.08
-32.80	0.09	0.08
-31.50	0.10	0.08
-30.10	0.11	0.09
-28.80	0.14	0.09
-27.40	0.19	0.10
-26.00	0.25	0.11
-24.70	0.32	0.13
-23.30	0.41	0.15
-21.60	0.51	0.20
-20.20	0.63	0.25
-18.80	0.76	0.32
-17.60	0.92	0.40
-16.40	1.09	0.49
-15.00	1.25	0.60
-13.70	1.41	0.73
-12.50	1.53	0.89
-11.40	1.60	1.08

Table D14 Temperature sweep test results at 5 Hz as measured by DMA of vulcanizates cured with uncoated and TDAE oil-coated petroleum-based sulfur (cont.): (b) Tan δ

Temp. (°C)	Tan δ	
	NR	
	OA	OC
-10.60	0.17	0.16
-9.30	0.16	0.14
-7.70	0.14	0.13
-6.20	0.12	0.12
-4.80	0.11	0.10
-3.30	0.10	0.09
-1.70	0.09	0.09
-0.40	0.09	0.08
1.80	0.07	0.07
2.60	0.07	0.06
4.00	0.07	0.06
5.60	0.06	0.07
7.10	0.06	0.06
8.60	0.06	0.06
10.00	0.06	0.05
11.50	0.06	0.05
13.00	0.06	0.05
14.50	0.04	0.05
16.00	0.05	0.05
17.50	0.05	0.05
19.10	0.05	0.04
20.50	0.05	0.04
22.00	0.05	0.04
23.40	0.05	0.04
24.90	0.05	0.05
26.50	0.05	0.04
27.90	0.03	0.04
29.40	0.03	0.03
30.80	0.04	0.03
32.30	0.03	0.04
33.90	0.04	0.03
35.40	0.03	0.04
36.90	0.03	0.03
38.40	0.04	0.04
39.80	0.04	0.03
41.30	0.03	0.03
42.70	0.04	0.03
44.30	0.03	0.03
45.80	0.03	0.03
47.20	0.03	0.03
48.80	0.03	0.03
50.30	0.03	0.02
51.60	0.04	0.04
53.20	0.03	0.03
54.60	0.03	0.03
56.20	0.03	0.03
57.70	0.04	0.03

Temp. (°C)	Tan δ	
	SBR	
	OA	OC
-10.60	0.26	0.24
-9.30	0.24	0.21
-7.80	0.21	0.19
-6.30	0.19	0.18
-4.70	0.17	0.16
-3.30	0.16	0.15
-1.80	0.15	0.14
-0.50	0.14	0.13
1.90	0.13	0.13
2.50	0.12	0.12
4.00	0.12	0.12
5.60	0.12	0.12
6.90	0.12	0.11
8.70	0.11	0.11
10.00	0.11	0.11
11.50	0.11	0.11
13.20	0.11	0.11
14.60	0.11	0.10
16.10	0.11	0.11
17.50	0.11	0.11
19.00	0.11	0.11
20.40	0.10	0.10
21.90	0.11	0.10
23.50	0.11	0.11
24.80	0.11	0.11
26.30	0.11	0.11
27.70	0.11	0.11
29.50	0.11	0.11
30.90	0.11	0.10
32.30	0.11	0.11
33.90	0.11	0.11
35.20	0.11	0.10
36.80	0.11	0.11
38.40	0.11	0.11
39.80	0.11	0.11
41.20	0.11	0.10
42.70	0.11	0.10
44.30	0.10	0.11
45.70	0.11	0.11
47.20	0.11	0.11
48.80	0.11	0.10
50.10	0.11	0.11
51.60	0.11	0.11
53.20	0.11	0.11
54.60	0.11	0.10
56.20	0.11	0.10
57.70	0.11	0.11

Temp. (°C)	Tan δ	
	NBR	
	OA	OC
-10.20	1.60	1.26
-9.10	1.54	1.41
-7.80	1.44	1.51
-6.30	1.31	1.51
-4.70	1.16	1.41
-3.10	1.03	1.26
-1.70	0.91	1.09
-0.50	0.81	0.94
3.70	0.75	0.77
4.20	0.71	0.72
4.20	0.67	0.69
5.30	0.63	0.63
7.10	0.57	0.56
8.60	0.50	0.49
10.10	0.44	0.44
11.50	0.38	0.39
13.10	0.34	0.35
14.50	0.31	0.32
16.10	0.28	0.29
17.60	0.25	0.27
19.10	0.23	0.25
20.40	0.22	0.24
21.90	0.21	0.22
23.50	0.20	0.21
25.20	0.19	0.20
26.10	0.18	0.19
27.70	0.18	0.19
29.40	0.17	0.18
30.60	0.16	0.17
32.20	0.16	0.17
33.80	0.16	0.17
35.40	0.15	0.16
37.00	0.15	0.16
38.30	0.15	0.16
39.80	0.15	0.16
41.20	0.14	0.15
42.60	0.14	0.15
44.20	0.14	0.15
45.90	0.14	0.15
47.20	0.14	0.15
48.80	0.14	0.15
50.00	0.14	0.15
51.70	0.14	0.15
53.20	0.14	0.15
54.60	0.13	0.14
56.20	0.13	0.15
57.70	0.13	0.15

Table D14 Temperature sweep test results at 5 Hz as measured by DMA of vulcanizates cured with uncoated and TDAE oil-coated petroleum-based sulfur (cont.): (b) Tan δ

Temp. (°C)	Tan δ	
	NR	
	OA	OC
59.20	0.02	0.02
60.60	0.04	0.03

Temp. (°C)	Tan δ	
	SBR	
	OA	OC
59.10	0.11	0.11
60.50	0.11	0.10

Temp. (°C)	Tan δ	
	NBR	
	OA	OC
59.10	0.13	0.15
60.50	0.13	0.15

APPENDIX E
CURE CHARACTERISTICS OF RUBBER VULCANIZATES CURED WITH DIFFERENT SULFURS

Table E1 Cure characteristics of NR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial natural-based sulfurs)

Time (min)	Torque (lb.in)					
	IRPC-PS	RS	M101	M105	SGS	SP400
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.01	0.36	0.46	0.33	0.38	0.47	0.21
0.26	0.35	0.37	0.38	0.40	0.39	0.41
0.52	0.23	0.24	0.25	0.26	0.25	0.27
0.78	0.21	0.22	0.22	0.22	0.22	0.24
1.04	0.21	0.22	0.21	0.22	0.22	0.24
1.30	0.20	0.22	0.22	0.22	0.22	0.23
1.56	0.21	0.22	0.21	0.21	0.21	0.24
1.82	0.20	0.22	0.21	0.22	0.21	0.23
2.08	0.20	0.21	0.21	0.21	0.21	0.23
2.34	0.20	0.21	0.21	0.21	0.21	0.23
2.60	0.19	0.21	0.21	0.21	0.21	0.22
2.86	0.19	0.21	0.21	0.21	0.20	0.22
3.12	0.19	0.21	0.20	0.21	0.21	0.23
3.38	0.19	0.21	0.21	0.21	0.21	0.22
3.64	0.19	0.21	0.21	0.21	0.21	0.23
3.90	0.19	0.21	0.21	0.21	0.20	0.23
4.16	0.19	0.21	0.21	0.21	0.21	0.23
4.42	0.19	0.21	0.21	0.21	0.20	0.22
4.68	0.20	0.21	0.21	0.21	0.21	0.23
4.94	0.19	0.21	0.21	0.21	0.21	0.23
5.20	0.20	0.21	0.21	0.21	0.21	0.23
5.46	0.19	0.21	0.21	0.21	0.21	0.23
5.72	0.20	0.22	0.21	0.21	0.21	0.23
5.98	0.20	0.21	0.21	0.22	0.21	0.23
6.24	0.20	0.22	0.22	0.21	0.22	0.23
6.50	0.20	0.22	0.22	0.21	0.22	0.23
6.76	0.20	0.22	0.22	0.22	0.22	0.23
7.02	0.21	0.22	0.22	0.22	0.22	0.24
7.28	0.21	0.22	0.22	0.22	0.22	0.24
7.54	0.21	0.23	0.22	0.22	0.23	0.24
7.80	0.21	0.23	0.22	0.23	0.23	0.24
8.06	0.22	0.23	0.23	0.23	0.23	0.25
8.32	0.22	0.24	0.23	0.23	0.24	0.25
8.58	0.23	0.24	0.25	0.23	0.25	0.26
8.84	0.23	0.25	0.25	0.24	0.25	0.27
9.10	0.24	0.26	0.26	0.24	0.26	0.28
9.36	0.25	0.28	0.27	0.25	0.27	0.29
9.62	0.26	0.29	0.28	0.26	0.29	0.31
9.88	0.28	0.31	0.30	0.27	0.32	0.32

Table E1 Cure characteristics of NR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial natural-based sulfurs) (cont.)

Time (min)	Torque (lb.in)					
	IRPC-PS	RS	M101	M105	SGS	SP400
10.14	0.30	0.36	0.33	0.28	0.36	0.38
10.40	0.35	0.45	0.40	0.30	0.47	0.46
10.66	0.42	0.64	0.54	0.34	0.64	0.63
10.92	0.53	0.91	0.80	0.40	0.90	0.88
11.18	0.70	1.26	1.14	0.54	1.20	1.21
11.44	0.91	1.61	1.47	0.73	1.55	1.55
11.70	1.18	1.93	1.82	0.99	1.86	1.88
11.96	1.45	2.23	2.11	1.27	2.16	2.17
12.22	1.74	2.44	2.36	1.56	2.41	2.42
12.48	1.97	2.67	2.59	1.86	2.60	2.63
12.74	2.23	2.83	2.74	2.12	2.83	2.81
13.00	2.40	2.96	2.92	2.37	2.95	2.94
13.26	2.60	3.08	3.05	2.55	3.10	3.04
13.52	2.72	3.13	3.13	2.74	3.18	3.16
13.78	2.84	3.24	3.23	2.84	3.27	3.19
14.04	2.94	3.26	3.26	3.00	3.37	3.31
14.30	3.04	3.33	3.34	3.05	3.40	3.32
14.56	3.09	3.35	3.37	3.18	3.46	3.39
14.82	3.11	3.37	3.41	3.21	3.45	3.40
15.08	3.17	3.43	3.43	3.30	3.55	3.43
15.34	3.16	3.39	3.43	3.30	3.56	3.43
15.60	3.24	3.45	3.47	3.39	3.58	3.45
15.86	3.22	3.43	3.47	3.35	3.57	3.48
16.12	3.27	3.48	3.49	3.40	3.58	3.46
16.38	3.26	3.44	3.51	3.41	3.58	3.50
16.64	3.28	3.50	3.49	3.45	3.61	3.46
16.90	3.30	3.47	3.51	3.44	3.58	3.50
17.16	3.29	3.48	3.49	3.47	3.61	3.49
17.42	3.32	3.49	3.54	3.47	3.60	3.47
17.68	3.27	3.50	3.50	3.46	3.61	3.52
17.94	3.32	3.52	3.49	3.49	3.57	3.49
18.20	3.29	3.48	3.55	3.45	3.62	3.52
18.46	3.29	3.50	3.51	3.50	3.59	3.48
18.72	3.34	3.47	3.54	3.45	3.61	3.48
18.98	3.28	3.52	3.52	3.49	3.56	3.51
19.24	3.33	3.49	3.53	3.47	3.61	3.48
19.50	3.31	3.52	3.53	3.46	3.56	3.52
19.76	3.31	3.49	3.49	3.49	3.61	3.48
20.02	3.33	3.49	3.53	3.45	3.57	3.51
20.28	3.28	3.50	3.48	3.50	3.61	3.48

Table E2 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial natural-based sulfurs)

Time (min)	Torque (lb.in)					
	IRPC-PS	RS	M101	M105	SGS	SP400
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.02	0.96	0.88	0.86	0.61	0.80	0.84
0.87	0.36	0.37	0.38	0.37	0.38	0.37
1.72	0.37	0.38	0.38	0.37	0.38	0.37
2.58	0.37	0.38	0.38	0.36	0.38	0.37
3.44	0.37	0.39	0.38	0.36	0.38	0.37
4.30	0.37	0.39	0.38	0.36	0.38	0.37
5.16	0.37	0.39	0.38	0.37	0.38	0.38
6.02	0.37	0.39	0.38	0.37	0.38	0.38
6.88	0.37	0.39	0.38	0.37	0.38	0.38
7.74	0.38	0.40	0.38	0.37	0.38	0.38
8.60	0.38	0.40	0.39	0.37	0.39	0.39
9.46	0.38	0.40	0.39	0.38	0.39	0.39
10.32	0.39	0.41	0.40	0.38	0.40	0.39
11.18	0.39	0.41	0.40	0.39	0.40	0.40
12.04	0.40	0.42	0.41	0.39	0.41	0.40
12.90	0.40	0.44	0.41	0.40	0.41	0.41
13.76	0.41	0.44	0.42	0.41	0.42	0.42
14.62	0.42	0.45	0.43	0.42	0.43	0.43
15.48	0.43	0.46	0.44	0.43	0.44	0.43
16.34	0.44	0.47	0.45	0.44	0.45	0.45
17.20	0.45	0.49	0.46	0.45	0.46	0.46
18.06	0.47	0.51	0.48	0.46	0.47	0.48
18.92	0.49	0.54	0.50	0.48	0.49	0.49
19.78	0.51	0.58	0.53	0.50	0.52	0.52
20.64	0.55	0.64	0.58	0.54	0.56	0.56
21.50	0.61	0.76	0.65	0.59	0.62	0.63
22.36	0.71	0.88	0.76	0.67	0.71	0.73
23.22	0.84	1.05	0.91	0.79	0.84	0.87
24.07	1.02	1.31	1.11	0.95	1.01	1.05
24.93	1.23	1.53	1.34	1.14	1.21	1.27
25.79	1.46	1.74	1.59	1.35	1.44	1.51
26.65	1.69	2.02	1.83	1.57	1.66	1.73
27.51	1.91	2.21	2.05	1.78	1.88	1.94
28.37	2.12	2.40	2.26	1.98	2.08	2.14
29.23	2.31	2.57	2.45	2.16	2.27	2.33
30.09	2.49	2.77	2.62	2.34	2.44	2.50
30.95	2.66	2.91	2.78	2.50	2.61	2.66
31.81	2.82	3.05	2.93	2.65	2.76	2.81
32.67	2.95	3.20	3.07	2.79	2.90	2.95

Table E2 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial natural-based sulfurs) (cont.)

Time (min)	Torque (lb.in)					
	IRPC-PS	RS	M101	M105	SGS	SP400
33.53	3.08	3.31	3.20	2.91	3.03	3.07
34.39	3.20	3.41	3.31	3.02	3.14	3.18
35.25	3.30	3.53	3.42	3.13	3.24	3.29
36.11	3.40	3.61	3.51	3.23	3.34	3.39
36.97	3.50	3.70	3.59	3.31	3.42	3.47
37.83	3.58	3.79	3.66	3.40	3.50	3.54
38.69	3.65	3.84	3.72	3.47	3.57	3.61
39.55	3.71	3.90	3.78	3.53	3.64	3.67
40.41	3.77	3.96	3.84	3.59	3.69	3.73
41.28	3.82	4.01	3.89	3.65	3.75	3.78
42.14	3.87	4.05	3.94	3.70	3.80	3.82
43.00	3.91	4.09	3.99	3.75	3.86	3.87
43.86	3.95	4.14	4.03	3.79	3.90	3.91
44.72	3.99	4.18	4.07	3.83	3.93	3.95
45.58	4.02	4.21	4.09	3.87	3.97	3.99
46.44	4.05	4.25	4.12	3.91	4.00	4.02
47.30	4.08	4.27	4.14	3.94	4.02	4.05
48.16	4.11	4.29	4.16	3.96	4.05	4.07
49.02	4.12	4.32	4.18	3.98	4.07	4.09
49.88	4.15	4.33	4.21	4.01	4.09	4.11
50.74	4.17	4.35	4.23	4.03	4.11	4.13
51.60	4.18	4.37	4.25	4.04	4.13	4.15
52.46	4.20	4.40	4.27	4.07	4.14	4.16
53.32	4.21	4.42	4.28	4.08	4.16	4.17
54.18	4.23	4.43	4.29	4.10	4.18	4.19
55.04	4.24	4.44	4.30	4.11	4.19	4.21
55.90	4.25	4.45	4.31	4.12	4.20	4.22
56.76	4.27	4.46	4.32	4.13	4.21	4.24
57.62	4.29	4.47	4.32	4.14	4.22	4.24
58.48	4.30	4.47	4.34	4.15	4.23	4.25
59.34	4.30	4.47	4.35	4.17	4.24	4.26
60.20	4.31	4.49	4.36	4.17	4.24	4.26

Table E3 Cure characteristics of NBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial natural-based sulfurs)

Time (min)	Torque (lb.in)					
	IRPC-PS	**RS**	**M101**	**M105**	**SGS**	**SP400**
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.01	0.51	0.87	0.61	0.74	0.75	1.46
0.27	0.33	0.30	0.32	0.30	0.31	0.32
0.52	0.29	0.27	0.29	0.23	0.26	0.27
0.78	0.28	0.25	0.28	0.26	0.25	0.25
1.04	0.28	0.26	0.27	0.26	0.25	0.26
1.30	0.27	0.25	0.27	0.26	0.25	0.25
1.56	0.27	0.25	0.27	0.26	0.25	0.26
1.82	0.27	0.25	0.27	0.26	0.25	0.25
2.08	0.27	0.25	0.27	0.26	0.25	0.25
2.34	0.27	0.25	0.27	0.26	0.25	0.25
2.60	0.27	0.25	0.27	0.26	0.25	0.25
2.86	0.27	0.24	0.27	0.26	0.25	0.25
3.12	0.27	0.25	0.27	0.25	0.25	0.25
3.38	0.27	0.25	0.27	0.26	0.25	0.25
3.65	0.28	0.25	0.26	0.26	0.25	0.25
3.91	0.27	0.25	0.27	0.26	0.25	0.25
4.17	0.28	0.25	0.26	0.26	0.25	0.25
4.43	0.27	0.25	0.27	0.26	0.25	0.25
4.69	0.27	0.24	0.27	0.26	0.25	0.25
4.95	0.27	0.25	0.26	0.26	0.25	0.25
5.21	0.27	0.25	0.26	0.26	0.25	0.24
5.47	0.27	0.25	0.26	0.26	0.25	0.25
5.73	0.27	0.25	0.27	0.26	0.25	0.24
5.99	0.28	0.25	0.27	0.26	0.25	0.25
6.25	0.28	0.25	0.26	0.27	0.25	0.24
6.51	0.28	0.25	0.27	0.26	0.25	0.25
6.77	0.28	0.25	0.26	0.26	0.25	0.25
7.03	0.29	0.25	0.26	0.26	0.25	0.25
7.29	0.29	0.25	0.26	0.26	0.25	0.25
7.55	0.30	0.25	0.26	0.27	0.25	0.25
7.81	0.31	0.25	0.26	0.27	0.25	0.25
8.07	0.33	0.25	0.27	0.27	0.25	0.25
8.33	0.37	0.25	0.27	0.27	0.25	0.25
8.59	0.43	0.25	0.27	0.27	0.25	0.25
8.85	0.54	0.25	0.27	0.28	0.26	0.25
9.11	0.70	0.25	0.27	0.29	0.25	0.25
9.37	0.96	0.25	0.27	0.32	0.26	0.25
9.63	1.30	0.25	0.27	0.37	0.26	0.26
9.89	1.65	0.26	0.27	0.48	0.26	0.26

Table E3 Cure characteristics of NBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial natural-based sulfurs) (cont.)

Time (min)	Torque (lb.in)					
	IRPC-PS	RS	M101	M105	SGS	SP400
10.15	2.02	0.26	0.27	0.70	0.26	0.26
10.41	2.34	0.26	0.27	1.03	0.26	0.26
10.67	2.59	0.26	0.27	1.39	0.26	0.26
10.93	2.86	0.26	0.27	1.78	0.26	0.26
11.19	3.02	0.26	0.27	2.11	0.27	0.26
11.45	3.21	0.26	0.27	2.43	0.27	0.27
11.71	3.32	0.27	0.27	2.63	0.28	0.27
11.97	3.46	0.27	0.28	2.86	0.29	0.28
12.23	3.60	0.28	0.28	3.04	0.31	0.29
12.49	3.65	0.29	0.28	3.18	0.36	0.31
12.75	3.79	0.30	0.29	3.31	0.45	0.37
13.01	3.82	0.33	0.30	3.39	0.62	0.48
13.27	3.92	0.38	0.31	3.54	0.90	0.68
13.53	3.95	0.51	0.34	3.59	1.23	0.98
13.79	4.01	0.68	0.40	3.71	1.60	1.35
14.05	4.08	0.96	0.53	3.74	1.91	1.69
14.31	4.08	1.24	0.77	3.84	2.25	2.04
14.57	4.16	1.57	1.08	3.87	2.48	2.32
14.83	4.15	1.84	1.42	3.94	2.74	2.58
15.09	4.23	2.14	1.76	3.99	2.90	2.78
15.35	4.26	2.35	2.06	4.00	3.09	3.00
15.61	4.24	2.60	2.34	4.10	3.18	3.11
15.87	4.33	2.75	2.56	4.05	3.37	3.28
16.13	4.28	2.94	2.78	4.14	3.43	3.37
16.39	4.36	3.06	2.95	4.11	3.57	3.50
16.65	4.35	3.22	3.07	4.21	3.61	3.58
16.91	4.37	3.31	3.25	4.20	3.75	3.67
17.17	4.41	3.42	3.31	4.24	3.76	3.73
17.43	4.38	3.52	3.46	4.26	3.88	3.83
17.69	4.47	3.61	3.54	4.27	3.91	3.87
17.95	4.40	3.68	3.63	4.29	3.99	3.93
18.21	4.49	3.76	3.72	4.27	3.99	3.97
18.47	4.42	3.84	3.74	4.34	4.07	4.05
18.73	4.50	3.87	3.84	4.32	4.08	4.05
18.99	4.50	3.95	3.88	4.36	4.14	4.12
19.25	4.50	4.00	3.94	4.31	4.18	4.13
19.51	4.53	4.01	4.00	4.40	4.20	4.21
19.77	4.48	4.09	4.02	4.34	4.24	4.19
20.03	4.57	4.14	4.10	4.39	4.26	4.28
20.29	4.52	4.15	4.13	4.37	4.30	4.25

Table E3 Cure characteristics of NBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial natural-based sulfurs) (cont.)

Time (min)	Torque (lb.in)					
	IRPC-PS	RS	M101	M105	SGS	SP400
20.55	4.59	4.20	4.17	4.44	4.30	4.34
20.81	4.57	4.21	4.18	4.39	4.35	4.28
21.07	4.56	4.30	4.24	4.47	4.34	4.37
21.33	4.59	4.29	4.25	4.43	4.40	4.31
21.59	4.53	4.37	4.26	4.47	4.36	4.40
21.85	4.63	4.35	4.34	4.44	4.45	4.37
22.11	4.58	4.42	4.31	4.46	4.39	4.43
22.37	4.60	4.40	4.38	4.44	4.48	4.39
22.63	4.63	4.45	4.36	4.47	4.41	4.47
22.90	4.60	4.46	4.39	4.50	4.49	4.42
23.16	4.66	4.48	4.41	4.49	4.45	4.47
23.42	4.59	4.48	4.40	4.52	4.52	4.48
23.68	4.67	4.50	4.48	4.46	4.46	4.46
23.94	4.62	4.55	4.44	4.54	4.54	4.50
24.20	4.65	4.56	4.49	4.46	4.49	4.49
24.46	4.67	4.56	4.45	4.55	4.56	4.54
24.72	4.58	4.58	4.49	4.47	4.52	4.48
24.98	4.70	4.59	4.53	4.55	4.57	4.55
25.24	4.61	4.60	4.48	4.52	4.52	4.50
25.50	4.69	4.60	4.54	4.55	4.61	4.54
25.76	4.61	4.62	4.51	4.51	4.56	4.53
26.02	4.69	4.62	4.53	4.52	4.59	4.59
26.28	4.65	4.67	4.55	4.56	4.57	4.55
26.54	4.67	4.66	4.52	4.56	4.63	4.58
26.80	4.69	4.68	4.59	4.57	4.59	4.54
27.06	4.63	4.69	4.55	4.52	4.61	4.60
27.32	4.71	4.70	4.60	4.57	4.61	4.56
27.58	4.61	4.69	4.57	4.53	4.63	4.62
27.84	4.69	4.72	4.59	4.58	4.59	4.54
28.10	4.66	4.72	4.61	4.52	4.62	4.63
28.36	4.68	4.73	4.59	4.60	4.62	4.57
28.62	4.70	4.75	4.64	4.52	4.62	4.64
28.88	4.66	4.70	4.56	4.61	4.64	4.60
29.14	4.71	4.78	4.65	4.52	4.64	4.64
29.40	4.65	4.71	4.62	4.60	4.66	4.58
29.66	4.71	4.78	4.63	4.56	4.64	4.62
29.92	4.69	4.72	4.63	4.61	4.66	4.61
30.18	4.71	4.76	4.62	4.57	4.64	4.64
30.44	4.73	4.73	4.68	4.60	4.67	4.62
30.70	4.64	4.80	4.64	4.58	4.67	4.62

Table E4 Cure characteristics of NR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
0.00	0.00	0.00	0.00	0.00
0.01	0.41	0.20	0.36	0.41
0.25	0.29	0.39	0.39	0.37
0.51	0.20	0.25	0.25	0.24
0.77	0.18	0.22	0.22	0.21
1.04	0.19	0.22	0.22	0.22
1.29	0.19	0.22	0.23	0.22
1.55	0.20	0.23	0.24	0.22
1.81	0.20	0.23	0.23	0.22
2.07	0.20	0.23	0.24	0.22
2.33	0.20	0.23	0.23	0.22
2.59	0.19	0.22	0.24	0.22
2.85	0.20	0.22	0.23	0.22
3.11	0.19	0.22	0.23	0.22
3.37	0.20	0.23	0.24	0.22
3.63	0.20	0.22	0.23	0.22
3.89	0.20	0.22	0.23	0.22
4.15	0.20	0.23	0.23	0.22
4.41	0.20	0.23	0.23	0.22
4.67	0.20	0.23	0.24	0.23
4.93	0.20	0.23	0.24	0.23
5.19	0.20	0.23	0.24	0.23
5.45	0.20	0.23	0.24	0.23
5.71	0.21	0.23	0.24	0.23
5.97	0.20	0.23	0.24	0.23
6.23	0.21	0.23	0.24	0.24
6.49	0.21	0.23	0.25	0.23
6.75	0.21	0.24	0.25	0.24
7.01	0.21	0.24	0.25	0.24
7.27	0.21	0.24	0.25	0.24
7.53	0.21	0.24	0.25	0.24
7.79	0.22	0.25	0.25	0.24
8.05	0.22	0.25	0.26	0.25
8.31	0.22	0.25	0.26	0.25
8.57	0.23	0.25	0.26	0.25
8.83	0.23	0.26	0.27	0.26
9.09	0.24	0.26	0.27	0.26
9.35	0.25	0.26	0.28	0.27
9.61	0.26	0.27	0.28	0.28
9.87	0.28	0.28	0.29	0.29

Table E4 Cure characteristics of NR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum -based sulfurs) (cont.)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
10.13	0.32	0.29	0.31	0.30
10.39	0.38	0.30	0.32	0.32
10.65	0.48	0.32	0.35	0.36
10.91	0.62	0.35	0.40	0.44
11.17	0.81	0.41	0.50	0.60
11.43	1.03	0.53	0.66	0.82
11.69	1.26	0.72	0.91	1.10
11.95	1.50	0.98	1.20	1.39
12.21	1.70	1.29	1.48	1.67
12.47	1.94	1.57	1.79	1.95
12.73	2.11	1.89	2.00	2.13
12.99	2.33	2.10	2.25	2.34
13.25	2.44	2.35	2.39	2.45
13.51	2.59	2.49	2.59	2.61
13.77	2.67	2.66	2.68	2.67
14.03	2.78	2.78	2.78	2.76
14.29	2.83	2.83	2.88	2.85
14.55	2.90	2.99	2.92	2.85
14.81	2.95	2.99	3.02	2.93
15.07	2.99	3.10	3.01	2.91
15.32	3.03	3.10	3.11	2.99
15.58	3.03	3.18	3.07	2.98
15.84	3.08	3.18	3.14	2.99
16.10	3.06	3.22	3.15	3.03
16.36	3.12	3.25	3.16	3.00
16.62	3.08	3.23	3.20	3.06
16.88	3.15	3.28	3.17	3.01
17.14	3.11	3.24	3.25	3.07
17.40	3.14	3.31	3.17	3.05
17.66	3.15	3.26	3.26	3.06
17.92	3.15	3.29	3.22	3.07
18.18	3.17	3.29	3.23	3.06
18.44	3.12	3.30	3.21	3.08
18.70	3.19	3.31	3.22	3.03
18.96	3.13	3.26	3.25	3.10
19.22	3.18	3.32	3.20	3.04
19.48	3.14	3.27	3.26	3.10
19.74	3.18	3.32	3.20	3.05
20.00	3.17	3.27	3.25	3.08
20.26	3.14	3.31	3.23	3.06

Table E5 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
0.00	0.00	0.00	0.00	0.00
0.01	1.67	0.69	0.79	1.50
0.26	0.66	0.61	0.62	0.63
0.53	0.57	0.53	0.54	0.55
0.78	0.57	0.54	0.54	0.53
1.05	0.57	0.53	0.54	0.54
1.30	0.56	0.53	0.53	0.53
1.56	0.55	0.53	0.52	0.53
1.82	0.56	0.52	0.52	0.52
2.08	0.55	0.52	0.52	0.52
2.34	0.55	0.52	0.53	0.52
2.60	0.56	0.53	0.53	0.53
2.86	0.55	0.53	0.52	0.53
3.12	0.55	0.52	0.53	0.53
3.38	0.56	0.52	0.52	0.53
3.64	0.56	0.52	0.52	0.53
3.90	0.55	0.53	0.52	0.53
4.16	0.55	0.52	0.52	0.53
4.42	0.56	0.53	0.53	0.53
4.68	0.55	0.53	0.53	0.53
4.94	0.55	0.53	0.52	0.53
5.20	0.55	0.53	0.52	0.53
5.46	0.55	0.53	0.53	0.53
5.72	0.56	0.53	0.52	0.53
5.98	0.55	0.53	0.53	0.53
6.24	0.56	0.53	0.53	0.53
6.50	0.55	0.53	0.53	0.54
6.76	0.55	0.53	0.53	0.53
7.02	0.55	0.53	0.53	0.54
7.28	0.56	0.54	0.53	0.54
7.53	0.56	0.54	0.53	0.54
7.79	0.56	0.54	0.53	0.54
8.05	0.56	0.54	0.53	0.53
8.31	0.56	0.54	0.54	0.54
8.57	0.56	0.54	0.54	0.54
8.83	0.57	0.54	0.54	0.55
9.09	0.56	0.55	0.54	0.54
9.35	0.57	0.55	0.54	0.55
9.62	0.57	0.55	0.55	0.55
9.88	0.57	0.55	0.55	0.56

Table E5 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs) (cont.)

Time (min)	Torque (lb.in)			
	IRPC-PS	**DF325**	**DF5(325)**	**SM400**
10.14	0.57	0.55	0.55	0.56
10.40	0.58	0.56	0.55	0.56
10.66	0.57	0.55	0.55	0.56
10.92	0.58	0.56	0.56	0.56
11.18	0.58	0.56	0.56	0.56
11.44	0.58	0.56	0.56	0.56
11.70	0.58	0.57	0.56	0.56
11.96	0.58	0.56	0.57	0.56
12.22	0.59	0.57	0.57	0.57
12.48	0.59	0.57	0.57	0.57
12.74	0.59	0.58	0.57	0.57
13.00	0.59	0.58	0.58	0.58
13.26	0.60	0.58	0.57	0.58
13.52	0.60	0.58	0.58	0.58
13.78	0.60	0.59	0.58	0.58
14.04	0.60	0.58	0.58	0.59
14.30	0.61	0.59	0.59	0.59
14.56	0.61	0.60	0.59	0.59
14.82	0.62	0.60	0.59	0.59
15.08	0.62	0.60	0.60	0.60
15.34	0.62	0.61	0.60	0.60
15.60	0.63	0.62	0.60	0.61
15.86	0.63	0.62	0.61	0.62
16.12	0.64	0.62	0.62	0.62
16.38	0.64	0.63	0.62	0.62
16.64	0.65	0.63	0.62	0.62
16.90	0.65	0.65	0.63	0.63
17.16	0.66	0.65	0.64	0.64
17.42	0.67	0.66	0.64	0.64
17.68	0.67	0.67	0.65	0.65
17.94	0.68	0.68	0.66	0.66
18.20	0.69	0.69	0.67	0.67
18.46	0.70	0.71	0.68	0.67
18.72	0.71	0.72	0.69	0.69
18.98	0.73	0.74	0.70	0.70
19.24	0.74	0.76	0.71	0.72
19.50	0.76	0.79	0.73	0.73
19.76	0.78	0.81	0.75	0.75
20.02	0.80	0.84	0.78	0.78
20.28	0.82	0.88	0.80	0.78

Table E5 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs) (cont.)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
20.54	0.85	0.92	0.82	0.83
20.80	0.88	0.97	0.86	0.86
21.06	0.91	1.01	0.89	0.89
21.32	0.95	1.06	0.93	0.92
21.58	0.99	1.12	0.97	0.97
21.84	1.03	1.18	1.02	1.01
22.10	1.08	1.24	1.07	1.06
22.36	1.14	1.32	1.12	1.11
22.62	1.19	1.39	1.18	1.18
22.88	1.26	1.47	1.24	1.25
23.14	1.32	1.55	1.31	1.31
23.40	1.39	1.64	1.38	1.39
23.66	1.46	1.73	1.46	1.48
23.92	1.53	1.82	1.53	1.56
24.18	1.61	1.91	1.61	1.65
24.44	1.70	2.00	1.70	1.73
24.70	1.77	2.09	1.78	1.83
24.96	1.86	2.18	1.87	1.92
25.22	1.95	2.27	1.96	2.01
25.48	2.03	2.36	2.04	2.11
25.74	2.12	2.44	2.13	2.21
26.00	2.20	2.53	2.22	2.30
26.27	2.28	2.62	2.31	2.39
26.53	2.36	2.70	2.39	2.48
26.79	2.45	2.78	2.47	2.57
27.05	2.53	2.86	2.56	2.66
27.31	2.62	2.95	2.64	2.75
27.57	2.70	3.03	2.73	2.86
27.83	2.78	3.11	2.81	2.93
28.09	2.86	3.19	2.89	3.02
28.35	2.94	3.26	2.97	3.10
28.61	3.02	3.34	3.06	3.20
28.87	3.10	3.42	3.13	3.28
29.13	3.18	3.50	3.22	3.35
29.39	3.25	3.57	3.29	3.42
29.65	3.32	3.65	3.37	3.49
29.91	3.39	3.72	3.43	3.57
30.17	3.45	3.78	3.50	3.64
30.43	3.52	3.85	3.56	3.71
30.69	3.59	3.92	3.63	3.79

Table E5 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs) (cont.)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
30.95	3.65	3.98	3.69	3.85
31.21	3.72	4.03	3.76	3.91
31.47	3.77	4.09	3.81	3.98
31.73	3.84	4.14	3.88	4.05
31.99	3.90	4.20	3.94	4.10
32.25	3.96	4.25	4.00	4.17
32.51	4.02	4.32	4.07	4.22
32.77	4.08	4.37	4.12	4.29
33.03	4.13	4.41	4.17	4.34
33.29	4.19	4.47	4.23	4.40
33.55	4.24	4.51	4.28	4.46
33.81	4.29	4.57	4.33	4.51
34.07	4.34	4.62	4.39	4.57
34.33	4.39	4.66	4.43	4.61
34.59	4.44	4.71	4.49	4.67
34.85	4.49	4.76	4.53	4.72
35.11	4.54	4.79	4.59	4.78
35.37	4.59	4.84	4.62	4.83
35.63	4.63	4.88	4.68	4.88
35.90	4.67	4.93	4.72	4.93
36.16	4.72	4.97	4.77	4.99
36.42	4.77	5.00	4.81	5.05
36.68	4.82	5.05	4.87	5.09
36.94	4.88	5.08	4.91	5.14
37.20	4.92	5.11	4.97	5.20
37.46	4.97	5.16	5.02	5.25
37.72	5.01	5.21	5.07	5.30
37.98	5.06	5.25	5.11	5.33
38.24	5.09	5.30	5.15	5.36
38.50	5.12	5.34	5.19	5.40
38.76	5.16	5.39	5.23	5.42
39.02	5.18	5.43	5.25	5.46
39.28	5.21	5.46	5.27	5.48
39.54	5.24	5.50	5.32	5.51
39.80	5.27	5.52	5.32	5.54
40.06	5.29	5.55	5.36	5.57
40.32	5.32	5.56	5.38	5.59
40.58	5.35	5.60	5.41	5.63
40.84	5.38	5.61	5.44	5.64
41.10	5.40	5.63	5.46	5.67

Table E5 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs) (cont.)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
41.36	5.42	5.65	5.48	5.69
41.62	5.45	5.68	5.51	5.72
41.88	5.47	5.69	5.54	5.75
42.14	5.50	5.71	5.56	5.76
42.40	5.52	5.73	5.57	5.78
42.66	5.54	5.75	5.61	5.82
42.92	5.57	5.77	5.62	5.84
43.18	5.60	5.79	5.65	5.86
43.44	5.62	5.81	5.67	5.88
43.70	5.64	5.83	5.68	5.91
43.96	5.66	5.84	5.71	5.92
44.22	5.68	5.86	5.73	5.96
44.48	5.70	5.87	5.75	5.97
44.74	5.72	5.90	5.76	6.00
45.00	5.75	5.90	5.80	6.03
45.26	5.78	5.93	5.82	6.06
45.52	5.81	5.94	5.86	6.09
45.78	5.84	5.97	5.88	6.12
46.04	5.87	5.98	5.90	6.13
46.30	5.90	6.00	5.94	6.17
46.56	5.92	6.02	5.95	6.18
46.82	5.94	6.05	5.97	6.20
47.08	5.97	6.08	6.00	6.21
47.34	5.98	6.09	6.02	6.22
47.60	5.99	6.12	6.04	6.24
47.86	6.00	6.14	6.04	6.25
48.12	6.02	6.17	6.06	6.26
48.38	6.03	6.18	6.07	6.28
48.64	6.03	6.20	6.07	6.27
48.90	6.05	6.20	6.09	6.29
49.16	6.06	6.22	6.10	6.30
49.42	6.06	6.22	6.10	6.30
49.68	6.07	6.23	6.12	6.32
49.94	6.08	6.24	6.12	6.32
50.20	6.09	6.24	6.14	6.34
50.46	6.10	6.26	6.14	6.35
50.72	6.11	6.26	6.15	6.36
50.98	6.12	6.28	6.15	6.35
51.24	6.12	6.28	6.17	6.37
51.50	6.14	6.28	6.17	6.38

Table E5 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs) (cont.)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
51.76	6.15	6.30	6.18	6.39
52.02	6.15	6.29	6.18	6.40
52.28	6.16	6.31	6.20	6.40
52.54	6.17	6.30	6.19	6.41
52.80	6.18	6.31	6.21	6.42
53.06	6.19	6.32	6.23	6.42
53.32	6.20	6.32	6.22	6.44
53.58	6.20	6.33	6.24	6.45
53.84	6.21	6.33	6.24	6.48
54.10	6.23	6.34	6.26	6.48
54.36	6.25	6.34	6.28	6.49
54.62	6.27	6.35	6.30	6.53
54.89	6.29	6.34	6.32	6.54
55.15	6.31	6.35	6.32	6.55
55.41	6.32	6.37	6.36	6.57
55.67	6.34	6.38	6.36	6.58
55.93	6.36	6.40	6.38	6.58
56.19	6.37	6.42	6.38	6.59
56.45	6.37	6.43	6.38	6.59
56.71	6.38	6.46	6.39	6.59
56.97	6.39	6.48	6.39	6.61
57.23	6.39	6.48	6.40	6.61
57.49	6.40	6.50	6.40	6.61
57.75	6.40	6.50	6.42	6.62
58.01	6.40	6.49	6.40	6.62
58.27	6.41	6.50	6.41	6.63
58.53	6.41	6.51	6.43	6.63
58.79	6.41	6.51	6.42	6.63
59.05	6.42	6.52	6.43	6.64
59.31	6.42	6.51	6.43	6.63
59.57	6.42	6.52	6.43	6.63
59.83	6.42	6.52	6.44	6.64
60.09	6.43	6.53	6.44	6.65

Table E6 Cure characteristics of NBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
0.00	0.00	0.00	0.00	0.00
0.00	0.39	0.57	0.73	0.86
0.25	0.26	0.24	0.25	0.25
0.51	0.22	0.21	0.21	0.21
0.77	0.20	0.22	0.21	0.21
1.04	0.21	0.22	0.20	0.21
1.29	0.20	0.22	0.20	0.21
1.55	0.21	0.22	0.20	0.21
1.81	0.21	0.22	0.20	0.21
2.07	0.20	0.22	0.20	0.21
2.33	0.21	0.22	0.20	0.20
2.59	0.20	0.22	0.20	0.20
2.85	0.21	0.22	0.20	0.20
3.11	0.21	0.22	0.20	0.20
3.37	0.20	0.22	0.20	0.20
3.63	0.21	0.22	0.20	0.20
3.89	0.21	0.23	0.20	0.20
4.15	0.21	0.22	0.20	0.20
4.41	0.21	0.23	0.20	0.20
4.67	0.21	0.23	0.20	0.20
4.93	0.21	0.23	0.20	0.20
5.19	0.21	0.23	0.20	0.21
5.45	0.22	0.23	0.20	0.20
5.71	0.21	0.24	0.20	0.20
5.97	0.22	0.25	0.20	0.21
6.23	0.23	0.27	0.20	0.21
6.49	0.24	0.32	0.20	0.21
6.75	0.26	0.45	0.21	0.21
7.01	0.29	0.71	0.20	0.21
7.27	0.35	1.05	0.21	0.21
7.53	0.44	1.39	0.21	0.21
7.79	0.61	1.69	0.21	0.22
8.05	0.87	1.99	0.22	0.22
8.31	1.16	2.15	0.22	0.22
8.57	1.49	2.40	0.23	0.24
8.83	1.78	2.50	0.24	0.26
9.09	2.03	2.67	0.28	0.32
9.35	2.28	2.74	0.33	0.47
9.61	2.40	2.85	0.45	0.72
9.87	2.61	2.93	0.65	1.07

Table E6 Cure characteristics of NBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs) (cont.)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
10.13	2.67	2.98	0.93	1.39
10.39	2.81	3.07	1.26	1.70
10.65	2.89	3.07	1.54	1.97
10.91	2.93	3.18	1.84	2.17
11.17	3.07	3.15	2.03	2.41
11.43	3.04	3.26	2.27	2.49
11.69	3.16	3.20	2.36	2.69
11.95	3.18	3.32	2.55	2.76
12.21	3.20	3.27	2.63	2.87
12.47	3.29	3.37	2.72	2.96
12.73	3.26	3.33	2.85	3.00
12.99	3.36	3.39	2.86	3.14
13.25	3.33	3.38	3.01	3.10
13.51	3.38	3.39	2.97	3.24
13.77	3.42	3.45	3.10	3.24
14.03	3.36	3.39	3.11	3.29
14.29	3.48	3.50	3.17	3.36
14.55	3.44	3.42	3.21	3.31
14.81	3.47	3.52	3.20	3.44
15.07	3.51	3.46	3.30	3.40
15.33	3.45	3.53	3.24	3.45
15.59	3.56	3.49	3.34	3.51
15.85	3.47	3.51	3.32	3.45
16.11	3.56	3.56	3.35	3.56
16.37	3.54	3.49	3.41	3.50
16.63	3.55	3.60	3.36	3.57
16.89	3.60	3.52	3.46	3.57
17.15	3.53	3.61	3.38	3.55
17.41	3.62	3.55	3.49	3.63
17.67	3.56	3.59	3.43	3.56
17.93	3.58	3.57	3.48	3.66
18.19	3.64	3.58	3.49	3.60
18.45	3.56	3.60	3.47	3.62
18.71	3.67	3.58	3.54	3.66
18.97	3.60	3.63	3.47	3.58
19.23	3.62	3.56	3.55	3.71
19.49	3.65	3.65	3.49	3.62
19.75	3.59	3.56	3.56	3.70
20.01	3.69	3.66	3.55	3.68
20.27	3.60	3.57	3.52	3.66

Table E6 Cure characteristics of NBR vulcanizates cured with different sulfurs (comparison between IRPC-PS and commercial petroleum-based sulfurs) (cont.)

Time (min)	Torque (lb.in)			
	IRPC-PS	DF325	DF5(325)	SM400
20.53	3.70	3.66	3.59	3.73
20.79	3.63	3.60	3.50	3.65
21.05	3.65	3.64	3.62	3.75
21.31	3.69	3.63	3.55	3.68
21.57	3.61	3.62	3.60	3.74
21.83	3.71	3.66	3.59	3.72
22.09	3.66	3.62	3.58	3.70
22.35	3.68	3.69	3.63	3.75
22.61	3.72	3.59	3.57	3.67
22.87	3.63	3.70	3.64	3.78
23.13	3.74	3.60	3.56	3.72
23.39	3.66	3.70	3.66	3.72
23.65	3.70	3.62	3.61	3.78
23.91	3.72	3.69	3.62	3.69
24.17	3.65	3.64	3.62	3.79
24.43	3.75	3.68	3.61	3.74
24.69	3.67	3.66	3.66	3.75
24.95	3.74	3.66	3.59	3.80
25.21	3.71	3.69	3.67	3.70
25.47	3.68	3.62	3.63	3.81
25.73	3.76	3.71	3.65	3.74
25.99	3.66	3.63	3.67	3.78
26.25	3.77	3.72	3.61	3.80
26.51	3.67	3.62	3.70	3.71
26.77	3.75	3.71	3.62	3.82
27.03	3.71	3.64	3.68	3.75
27.29	3.70	3.70	3.65	3.79
27.55	3.75	3.67	3.66	3.80
27.81	3.68	3.69	3.70	3.73
28.07	3.76	3.71	3.61	3.83
28.33	3.72	3.66	3.72	3.74
28.59	3.72	3.73	3.62	3.82
28.85	3.77	3.64	3.72	3.76
29.11	3.68	3.75	3.63	3.79
29.37	3.77	3.65	3.70	3.83
29.63	3.70	3.75	3.68	3.74
29.89	3.75	3.66	3.65	3.84
30.15	3.74	3.73	3.71	3.78
30.41	3.72	3.69	3.62	3.79
30.67	3.77	3.73	3.73	3.82

Table E7 Cure characteristics of NR vulcanizates cured with different sulfurs (comparison between OA and OC)

Time (min)	Torque (lb.in)	
	OA	OC
0.00	0.00	0.00
0.01	0.57	0.69
0.26	0.45	0.46
0.52	0.33	0.32
0.78	0.32	0.30
1.04	0.31	0.30
1.30	0.31	0.29
1.56	0.31	0.29
1.82	0.30	0.29
2.08	0.30	0.28
2.34	0.29	0.28
2.60	0.29	0.28
2.86	0.30	0.28
3.12	0.29	0.28
3.39	0.29	0.28
3.65	0.29	0.28
3.91	0.30	0.28
4.17	0.29	0.28
4.43	0.29	0.29
4.69	0.29	0.29
4.95	0.30	0.29
5.21	0.30	0.29
5.47	0.30	0.29
5.73	0.30	0.30
5.99	0.31	0.30
6.25	0.31	0.30
6.51	0.32	0.31
6.77	0.33	0.32
7.03	0.34	0.32
7.29	0.35	0.33
7.55	0.38	0.35
7.81	0.41	0.36
8.07	0.45	0.38
8.33	0.50	0.40
8.59	0.58	0.44

Time (min)	Torque (lb.in)	
	OA	OC
8.85	0.69	0.50
9.11	0.85	0.63
9.37	1.06	0.86
9.63	1.34	1.19
9.89	1.67	1.61
10.15	2.02	2.04
10.41	2.38	2.45
10.67	2.69	2.82
10.93	2.99	3.13
11.19	3.24	3.38
11.45	3.46	3.62
11.71	3.63	3.80
11.97	3.77	3.95
12.23	3.89	4.07
12.49	3.99	4.18
12.75	4.06	4.25
13.01	4.13	4.31
13.27	4.18	4.36
13.53	4.22	4.42
13.79	4.25	4.45
14.05	4.26	4.48
14.31	4.28	4.49
14.57	4.30	4.49
14.83	4.31	4.49
15.09	4.31	4.50
15.35	4.32	4.51
15.62	4.32	4.51
15.88	4.33	4.51
16.14	4.33	4.52
16.40	4.34	4.51
16.66	4.34	4.51
16.92	4.34	4.50
17.18	4.34	4.50
17.44	4.34	4.50
17.70	4.34	4.49

Table E8 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between OA and OC)

Time (min)	Torque (lb.in)	
	OA	OC
0.00	0.00	0.00
0.01	1.17	0.67
0.26	0.55	0.54
0.52	0.48	0.48
0.79	0.48	0.48
1.04	0.49	0.49
1.30	0.49	0.50
1.56	0.49	0.50
1.82	0.49	0.50
2.08	0.49	0.50
2.34	0.49	0.50
2.60	0.49	0.49
2.86	0.49	0.49
3.12	0.49	0.49
3.38	0.49	0.49
3.64	0.48	0.50
3.90	0.49	0.50
4.16	0.49	0.50
4.42	0.49	0.50
4.68	0.49	0.50
4.94	0.49	0.50
5.20	0.49	0.50
5.46	0.49	0.50
5.72	0.49	0.50
5.98	0.49	0.50
6.24	0.49	0.50
6.50	0.49	0.50
6.76	0.49	0.51
7.02	0.49	0.51
7.28	0.49	0.51
7.54	0.49	0.51
7.80	0.49	0.51
8.06	0.49	0.51
8.32	0.50	0.51
8.58	0.50	0.51
8.84	0.49	0.52
9.10	0.49	0.51
9.36	0.50	0.52
9.62	0.50	0.52
9.88	0.50	0.52

Time (min)	Torque (lb.in)	
	OA	OC
10.14	0.50	0.51
10.40	0.50	0.52
10.66	0.50	0.52
10.92	0.51	0.52
11.18	0.50	0.52
11.44	0.51	0.52
11.70	0.51	0.52
11.96	0.51	0.52
12.22	0.51	0.53
12.48	0.51	0.53
12.74	0.51	0.53
13.00	0.51	0.53
13.26	0.51	0.53
13.52	0.52	0.53
13.78	0.52	0.53
14.04	0.52	0.54
14.30	0.52	0.54
14.56	0.52	0.54
14.82	0.52	0.54
15.08	0.53	0.54
15.34	0.53	0.54
15.60	0.53	0.54
15.86	0.53	0.54
16.12	0.53	0.55
16.38	0.54	0.56
16.64	0.54	0.56
16.90	0.54	0.56
17.16	0.54	0.56
17.42	0.54	0.56
17.68	0.55	0.57
17.94	0.55	0.57
18.20	0.55	0.57
18.46	0.55	0.58
18.72	0.56	0.58
18.98	0.56	0.59
19.24	0.57	0.59
19.50	0.57	0.60
19.76	0.58	0.61
20.02	0.58	0.62
20.28	0.59	0.62

Table E8 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between OA and OC) (cont.)

Time (min)	Torque (lb.in)	
	OA	OC
20.54	0.59	0.63
20.80	0.60	0.65
21.06	0.61	0.66
21.32	0.62	0.67
21.58	0.63	0.69
21.84	0.64	0.71
22.10	0.65	0.73
22.36	0.66	0.75
22.62	0.68	0.77
22.88	0.69	0.79
23.14	0.71	0.81
23.40	0.73	0.84
23.66	0.75	0.87
23.92	0.77	0.89
24.18	0.79	0.93
24.44	0.82	0.95
24.70	0.84	0.99
24.96	0.87	1.02
25.22	0.90	1.06
25.48	0.93	1.10
25.74	0.96	1.14
26.00	0.99	1.18
26.26	1.03	1.23
26.52	1.06	1.27
26.78	1.10	1.32
27.04	1.14	1.37
27.30	1.18	1.42
27.56	1.22	1.46
27.82	1.26	1.51
28.08	1.31	1.57
28.34	1.35	1.62
28.60	1.40	1.67
28.86	1.44	1.72
29.12	1.49	1.78
29.38	1.54	1.83
29.64	1.58	1.88
29.90	1.63	1.93
30.16	1.68	1.98
30.42	1.74	2.03
30.68	1.79	2.08

Time (min)	Torque (lb.in)	
	OA	OC
30.94	1.84	2.14
31.20	1.89	2.19
31.46	1.94	2.24
31.72	1.99	2.29
31.98	2.04	2.34
32.24	2.08	2.39
32.50	2.13	2.44
32.76	2.18	2.49
33.02	2.23	2.53
33.28	2.27	2.58
33.54	2.32	2.63
33.80	2.37	2.68
34.06	2.41	2.72
34.32	2.46	2.77
34.58	2.50	2.81
34.84	2.55	2.86
35.10	2.60	2.90
35.36	2.64	2.95
35.62	2.69	2.98
35.88	2.73	3.03
36.14	2.77	3.07
36.40	2.81	3.11
36.66	2.85	3.15
36.92	2.89	3.19
37.18	2.93	3.23
37.44	2.97	3.26
37.70	3.01	3.30
37.96	3.04	3.33
38.22	3.08	3.36
38.48	3.12	3.40
38.74	3.16	3.44
39.00	3.19	3.47
39.26	3.23	3.50
39.52	3.26	3.53
39.78	3.29	3.56
40.04	3.33	3.59
40.30	3.36	3.62
40.56	3.40	3.65
40.82	3.42	3.68
41.08	3.46	3.71

Table E8 Cure characteristics of SBR vulcanizates cured with different sulfurs (comparison between OA and OC)

Time (min)	Torque (lb.in)	
	OA	OC
41.34	3.49	3.73
41.60	3.51	3.76
41.86	3.54	3.79
42.12	3.57	3.81
42.38	3.60	3.84
42.64	3.63	3.87
42.90	3.65	3.89
43.16	3.68	3.92
43.42	3.71	3.93
43.68	3.73	3.96
43.94	3.76	3.98
44.20	3.78	4.00
44.46	3.80	4.02
44.72	3.83	4.04
44.98	3.85	4.06
45.24	3.88	4.09
45.50	3.90	4.11
45.76	3.93	4.13
46.02	3.94	4.14
46.28	3.96	4.16
46.54	3.98	4.17
46.80	4.00	4.20
47.06	4.02	4.22
47.32	4.04	4.23
47.58	4.06	4.25
47.84	4.08	4.27
48.10	4.09	4.29
48.36	4.11	4.30
48.62	4.12	4.32
48.88	4.14	4.33
49.14	4.16	4.34
49.40	4.18	4.36
49.66	4.20	4.38
49.92	4.21	4.39
50.18	4.23	4.41
50.44	4.24	4.41
50.70	4.26	4.42
50.96	4.27	4.43
51.22	4.28	4.44
51.48	4.30	4.46

Time (min)	Torque (lb.in)	
	OA	OC
51.74	4.31	4.48
52.00	4.33	4.49
52.26	4.34	4.50
52.52	4.35	4.51
52.78	4.36	4.52
53.04	4.37	4.53
53.30	4.38	4.54
53.56	4.39	4.55
53.82	4.40	4.56
54.08	4.42	4.58
54.34	4.43	4.59
54.60	4.44	4.60
54.86	4.46	4.61
55.12	4.47	4.61
55.38	4.48	4.62
55.64	4.49	4.63
55.90	4.50	4.64
56.16	4.50	4.65
56.42	4.51	4.66
56.68	4.52	4.67
56.94	4.53	4.68
57.20	4.55	4.68
57.46	4.56	4.69
57.72	4.56	4.69
57.98	4.57	4.71
58.24	4.58	4.71
58.50	4.59	4.72
58.76	4.60	4.73
59.02	4.60	4.74
59.28	4.60	4.75
59.54	4.62	4.75
59.80	4.62	4.76
60.06	4.63	4.77

Table E9 Cure characteristics of NBR vulcanizates cured with different sulfurs (comparison between OA and OC)

Time	Torque (lb.in)	
(min)	OA	OC
0.00	0.00	0.00
0.01	0.88	0.59
0.26	0.48	0.43
0.52	0.39	0.36
0.78	0.37	0.35
1.04	0.38	0.35
1.30	0.38	0.35
1.56	0.38	0.35
1.82	0.39	0.36
2.08	0.41	0.36
2.34	0.46	0.37
2.60	0.61	0.41
2.86	0.92	0.51
3.12	1.34	0.80
3.38	1.78	1.35
3.64	2.19	1.99
3.90	2.54	2.59
4.16	2.82	3.11
4.42	3.05	3.54
4.68	3.23	3.89
4.94	3.38	4.16
5.20	3.50	4.37
5.46	3.60	4.53
5.72	3.69	4.65
5.98	3.76	4.76
6.24	3.82	4.84
6.50	3.87	4.92
6.76	3.91	4.98
7.02	3.96	5.03
7.28	4.00	5.07
7.54	4.03	5.11
7.80	4.07	5.15
8.06	4.09	5.18
8.32	4.12	5.21
8.58	4.14	5.24
8.84	4.17	5.27
9.10	4.18	5.29
9.36	4.20	5.31
9.62	4.22	5.33
9.88	4.24	5.35
10.16	4.26	5.36
10.40	4.28	5.38
10.67	4.29	5.40
10.92	4.30	5.40
11.18	4.32	5.43
11.44	4.33	5.45
11.70	4.35	5.45
11.96	4.36	5.47
12.22	4.37	5.48
12.48	4.38	5.49
12.74	4.39	5.50
13.00	4.40	5.51
13.26	4.42	5.52
13.51	4.43	5.53
13.77	4.45	5.54
14.03	4.45	5.54
14.29	4.47	5.56
14.55	4.47	5.58
14.81	4.48	5.59
15.07	4.49	5.59
15.33	4.50	5.60
15.59	4.51	5.61
15.85	4.51	5.61
16.11	4.53	5.62
16.37	4.53	5.63
16.63	4.54	5.64
16.89	4.54	5.65
17.15	4.55	5.66
17.41	4.56	5.67
17.67	4.57	5.67
17.93	4.58	5.67
18.19	4.59	5.68
18.45	4.59	5.68
18.71	4.60	5.69
18.97	4.60	5.70
19.23	4.61	5.71
19.49	4.61	5.72
19.75	4.62	5.73
20.01	4.62	5.73
20.27	4.63	5.73
20.53	4.64	5.73
20.79	4.64	5.74
21.05	4.65	5.74
21.31	4.66	5.75
21.57	4.66	5.76
21.83	4.66	5.76
22.09	4.67	5.77
22.35	4.67	5.77
22.61	4.68	5.77
22.87	4.68	5.78
23.13	4.69	5.78
23.39	4.69	5.79
23.65	4.70	5.80
23.91	4.71	5.80
24.17	4.71	5.81
24.43	4.71	5.81
24.69	4.71	5.81
24.95	4.71	5.82
25.21	4.72	5.81
25.47	4.72	5.81
25.73	4.73	5.82
25.99	4.73	5.83
26.25	4.74	5.84
26.51	4.74	5.84
26.77	4.74	5.84
27.03	4.75	5.84
27.29	4.75	5.84
27.55	4.75	5.84
27.81	4.75	5.85
28.07	4.76	5.85
28.33	4.77	5.86
28.59	4.77	5.86
28.85	4.77	5.87
29.11	4.78	5.87
29.37	4.78	5.87
29.63	4.78	5.87
29.89	4.79	5.87

APPENDIX F
XANES INVESTIGATION OF RUBBER VULCANIZATES CURED WITH DIFFERENT SULFURS

Table F1 Data collected from XANES experiment of NR vulcanizates

Photon energy (eV)	Normalized absorption	
	RS	PS
2460.01	2.00E-02	2.03E-02
2460.76	2.32E-02	2.12E-02
2461.51	2.23E-02	2.52E-02
2462.26	2.38E-02	2.57E-02
2463.01	2.48E-02	2.81E-02
2463.76	3.09E-02	3.29E-02
2464.51	3.40E-02	3.53E-02
2465.01	3.51E-02	3.51E-02
2465.11	3.67E-02	3.70E-02
2465.21	3.82E-02	3.87E-02
2465.31	3.60E-02	3.96E-02
2465.41	3.81E-02	4.01E-02
2465.51	3.99E-02	3.98E-02
2465.61	3.98E-02	4.46E-02
2465.71	4.28E-02	4.33E-02
2465.81	4.21E-02	4.49E-02
2465.91	4.24E-02	4.59E-02
2466.01	4.29E-02	4.44E-02
2466.11	4.46E-02	4.77E-02
2466.21	4.39E-02	4.34E-02
2466.31	4.24E-02	4.72E-02
2466.41	4.73E-02	4.85E-02
2466.51	4.83E-02	4.79E-02
2466.61	4.92E-02	4.96E-02
2466.71	4.70E-02	5.25E-02
2466.81	5.32E-02	5.42E-02
2466.91	5.27E-02	5.30E-02
2467.01	5.32E-02	5.45E-02
2467.11	5.41E-02	5.76E-02
2467.21	5.25E-02	5.64E-02
2467.31	5.87E-02	5.94E-02
2467.41	5.71E-02	6.08E-02
2467.51	6.06E-02	6.46E-02
2467.61	6.29E-02	6.35E-02
2467.71	6.63E-02	6.93E-02
2467.81	6.43E-02	6.86E-02
2467.91	6.70E-02	7.47E-02
2468.01	7.32E-02	7.32E-02
2468.11	7.24E-02	7.36E-02
2468.21	7.65E-02	7.68E-02
2468.31	7.94E-02	8.47E-02

Photon energy (eV)	Normalized absorption	
	RS	PS
2468.41	8.16E-02	8.19E-02
2468.51	8.45E-02	8.86E-02
2468.61	9.19E-02	9.10E-02
2468.71	9.40E-02	9.64E-02
2468.81	9.64E-02	0.100501
2468.91	9.88E-02	0.103769
2469.01	0.102779	0.109395
2469.11	0.114208	0.115904
2469.21	0.11592	0.117745
2469.31	0.123917	0.139624
2469.41	0.135592	0.142952
2469.51	0.149149	0.14793
2469.61	0.158131	0.162484
2469.71	0.17719	0.173062
2469.81	0.194185	0.188862
2469.91	0.203528	0.209675
2470.01	0.229214	0.220373
2470.11	0.260302	0.262055
2470.21	0.294038	0.294656
2470.31	0.335712	0.333753
2470.41	0.391405	0.396345
2470.51	0.463903	0.43225
2470.61	0.544774	0.548567
2470.71	0.658833	0.663851
2470.81	0.799608	0.817259
2470.91	0.961215	0.96182
2471.01	1.127489	1.146613
2471.11	1.306299	1.343263
2471.21	1.499386	1.503209
2471.31	1.653046	1.681232
2471.41	1.797826	1.83667
2471.51	1.938233	1.936433
2471.61	1.999735	2.019437
2471.71	2.045	2.087389
2471.81	2.07744	2.12094
2471.91	2.102809	2.125937
2472.01	2.094756	2.135289
2472.11	2.087259	2.130497
2472.21	2.104921	2.111079
2472.31	2.097355	2.116562
2472.41	2.060019	2.092257

Table F1 Data collected from XANES experiment of NR vulcanizates (cont.)

Photon energy (eV)	Normalized absorption		Photon energy (eV)	Normalized absorption	
	RS	PS		RS	PS
2472.51	2.057272	2.084467	2476.61	1.099916	1.103675
2472.61	2.028542	2.046434	2476.71	1.087786	1.104437
2472.71	1.984298	2.016825	2476.81	1.095472	1.10759
2472.81	1.930486	1.953589	2476.91	1.118677	1.110744
2472.91	1.87474	1.863669	2477.01	1.110832	1.123949
2473.01	1.816241	1.811426	2477.11	1.105301	1.116142
2473.11	1.718498	1.736189	2477.21	1.122235	1.124968
2473.21	1.64859	1.649768	2477.31	1.121171	1.130782
2473.31	1.547461	1.542353	2477.41	1.123532	1.123503
2473.41	1.449433	1.445742	2477.51	1.122004	1.139768
2473.51	1.371205	1.341025	2477.61	1.126015	1.120044
2473.61	1.27061	1.276749	2477.71	1.145732	1.129321
2473.71	1.212169	1.190723	2477.81	1.13565	1.132572
2473.81	1.143566	1.12425	2477.91	1.149403	1.139899
2473.91	1.076102	1.097243	2478.01	1.134618	1.147856
2474.01	1.070344	1.052951	2478.11	1.145178	1.129472
2474.11	1.037466	1.025987	2478.21	1.132325	1.13738
2474.21	1.017121	1.018371	2478.31	1.120712	1.13539
2474.31	1.018837	0.999504	2478.41	1.137168	1.132782
2474.41	1.014359	1.021869	2478.51	1.117918	1.132268
2474.51	1.012262	0.988581	2478.61	1.118871	1.133266
2474.61	1.022546	1.005163	2478.71	1.120211	1.132165
2474.71	1.01584	1.016845	2478.81	1.123716	1.121119
2474.81	1.021433	1.029261	2478.91	1.121755	1.130607
2474.91	1.036176	1.004901	2479.01	1.114471	1.118725
2475.01	1.040846	1.01688	2479.11	1.107517	1.10297
2475.11	1.046943	1.02899	2479.21	1.106054	1.109615
2475.21	1.040582	1.037271	2479.31	1.098519	1.102981
2475.31	1.036459	1.043155	2479.41	1.103909	1.105585
2475.41	1.035501	1.037124	2479.51	1.102197	1.101011
2475.51	1.056093	1.058571	2479.61	1.098969	1.105544
2475.61	1.030226	1.045969	2479.71	1.097886	1.089739
2475.71	1.058622	1.049822	2479.81	1.088706	1.109245
2475.81	1.061811	1.042316	2479.91	1.085309	1.08278
2475.91	1.054091	1.055729	2480.01	1.088691	1.088881
2476.01	1.065832	1.060303	2480.11	1.083115	1.077016
2476.11	1.059807	1.063528	2480.21	1.088888	1.076494
2476.21	1.065685	1.081245	2480.31	1.077026	1.069893
2476.31	1.067013	1.082533	2480.41	1.066435	1.089892
2476.41	1.077005	1.090009	2480.51	1.068893	1.076446
2476.51	1.076414	1.087387	2480.61	1.071529	1.075665

Table F1 Data collected from XANES experiment of NR vulcanizates (cont.)

Photon energy (eV)	Normalized absorption	
	RS	PS
2480.71	1.063446	1.064126
2480.81	1.058269	1.056886
2480.91	1.067655	1.067916
2481.01	1.063617	1.056616
2481.11	1.055984	1.060154
2481.21	1.064067	1.07327
2481.31	1.049937	1.05337
2481.41	1.0602	1.056955
2481.51	1.055837	1.059811
2481.61	1.055202	1.054423
2481.71	1.042725	1.045103
2481.81	1.041317	1.043572
2481.91	1.040199	1.039192
2482.01	1.025812	1.044095
2482.11	1.028147	1.031395
2482.21	1.033622	1.029803
2482.31	1.028724	1.02822
2482.41	1.016818	1.030639
2482.51	1.019126	1.028611
2482.61	1.008502	1.023997
2482.71	1.022543	1.033125
2482.81	1.015277	1.01369
2482.91	1.012081	1.013733
2483.01	1.011673	1.006995
2483.11	1.011796	1.017429
2483.21	0.997367	1.007472
2483.31	1.010604	1.017806

Photon energy (eV)	Normalized absorption	
	RS	PS
2483.41	1.014217	1.008472
2483.51	1.017065	1.007796
2483.61	1.023384	1.016698
2483.71	1.006777	1.012399
2483.81	1.017642	1.016554
2483.91	1.003753	1.019505
2484.01	1.019208	1.021546
2484.11	1.018893	1.032645
2484.21	1.019531	1.017125
2484.31	1.020563	1.02946
2484.41	1.030292	1.025042
2484.51	1.010972	1.017144
2484.61	1.018706	1.020637
2484.71	1.01082	1.021532
2484.81	1.020951	1.020755
2484.91	1.018301	1.025253
2485.01	1.026359	1.033872
2485.51	1.036394	1.033046
2486.01	1.038527	1.039153
2486.51	1.02641	1.019922
2487.01	1.028776	1.03301
2487.51	1.040659	1.035161
2488.01	1.030587	1.024279
2488.51	1.022542	1.025911
2489.01	1.027562	1.022536
2489.51	1.022799	1.026007
2490.01	1.017189	1.012862

Table F2 Data collected from XANES experiment of SBR vulcanizates

Photon energy (eV)	Normalized absorption		Photon energy (eV)	Normalized absorption	
	RS	PS		RS	PS
2460.01	1.33E-02	1.60E-02	2468.41	6.94E-02	7.15E-02
2460.76	1.49E-02	1.67E-02	2468.51	6.98E-02	7.66E-02
2461.51	2.04E-02	1.74E-02	2468.61	7.28E-02	7.53E-02
2462.26	1.61E-02	2.01E-02	2468.71	7.45E-02	7.65E-02
2463.01	2.05E-02	2.31E-02	2468.81	7.46E-02	8.40E-02
2463.76	1.94E-02	2.53E-02	2468.91	8.31E-02	8.98E-02
2464.51	2.43E-02	2.80E-02	2469.01	8.58E-02	9.31E-02
2465.01	2.72E-02	3.00E-02	2469.11	8.61E-02	9.27E-02
2465.11	2.85E-02	3.19E-02	2469.21	9.67E-02	9.73E-02
2465.21	3.15E-02	3.20E-02	2469.31	0.106192	0.105539
2465.31	2.78E-02	3.18E-02	2469.41	0.103592	0.112864
2465.41	3.04E-02	3.18E-02	2469.51	0.116669	0.113864
2465.51	2.96E-02	3.43E-02	2469.61	0.128293	0.129295
2465.61	3.29E-02	3.21E-02	2469.71	0.129432	0.13936
2465.71	3.24E-02	3.45E-02	2469.81	0.144897	0.149051
2465.81	3.14E-02	3.64E-02	2469.91	0.159741	0.161789
2465.91	2.90E-02	3.42E-02	2470.01	0.176246	0.175393
2466.01	3.55E-02	3.59E-02	2470.11	0.187977	0.199888
2466.11	3.36E-02	3.69E-02	2470.21	0.209055	0.223423
2466.21	3.11E-02	3.64E-02	2470.31	0.238127	0.243935
2466.31	3.12E-02	3.58E-02	2470.41	0.269174	0.280516
2466.41	3.56E-02	3.94E-02	2470.51	0.314037	0.320078
2466.51	3.44E-02	4.01E-02	2470.61	0.365126	0.363076
2466.61	4.13E-02	4.04E-02	2470.71	0.424117	0.431831
2466.71	4.33E-02	4.38E-02	2470.81	0.489647	0.50497
2466.81	4.27E-02	4.26E-02	2470.91	0.579591	0.608784
2466.91	4.31E-02	4.40E-02	2471.01	0.692911	0.716031
2467.01	4.37E-02	4.51E-02	2471.11	0.831464	0.84751
2467.11	4.14E-02	4.89E-02	2471.21	0.96462	0.992978
2467.21	4.76E-02	4.82E-02	2471.31	1.103509	1.137378
2467.31	4.53E-02	4.79E-02	2471.41	1.274879	1.291532
2467.41	4.68E-02	5.11E-02	2471.51	1.437362	1.451451
2467.51	4.53E-02	4.93E-02	2471.61	1.583325	1.517882
2467.61	5.11E-02	5.38E-02	2471.71	1.721088	1.738256
2467.71	4.95E-02	5.75E-02	2471.81	1.845034	1.88539
2467.81	5.35E-02	5.77E-02	2471.91	1.980526	2.014421
2467.91	5.89E-02	5.91E-02	2472.01	2.105013	2.115363
2468.01	5.67E-02	6.24E-02	2472.11	2.147645	2.162454
2468.11	5.84E-02	6.34E-02	2472.21	2.186101	2.203796
2468.21	5.76E-02	6.65E-02	2472.31	2.189675	2.171121
2468.31	6.86E-02	7.31E-02	2472.41	2.146799	2.152235

Table F2 Data collected from XANES experiment of SBR vulcanizates (cont.)

Photon energy (eV)	Normalized absorption	
	RS	PS
2472.51	2.138839	2.12129
2472.61	2.045259	2.074817
2472.71	2.030242	2.013574
2472.81	1.943719	1.961355
2472.91	1.885247	1.880519
2473.01	1.832393	1.799977
2473.11	1.74774	1.742476
2473.21	1.664329	1.667914
2473.31	1.572897	1.578556
2473.41	1.482197	1.476916
2473.51	1.399398	1.410241
2473.61	1.324804	1.316319
2473.71	1.288132	1.267289
2473.81	1.224548	1.223651
2473.91	1.203778	1.178182
2474.01	1.173435	1.151865
2474.11	1.15152	1.146598
2474.21	1.137509	1.133977
2474.31	1.144169	1.140245
2474.41	1.131398	1.134924
2474.51	1.135258	1.126172
2474.61	1.124034	1.146045
2474.71	1.132149	1.132197
2474.81	1.147241	1.126128
2474.91	1.129796	1.121804
2475.01	1.124191	1.128332
2475.11	1.13896	1.118766
2475.21	1.140007	1.119569
2475.31	1.106009	1.126884
2475.41	1.109151	1.119104
2475.51	1.114253	1.104944
2475.61	1.123715	1.116156
2475.71	1.112291	1.110765
2475.81	1.131544	1.107579
2475.91	1.127808	1.110763
2476.01	1.108262	1.109589
2476.11	1.100575	1.118816
2476.21	1.114733	1.125512
2476.31	1.141563	1.139752
2476.41	1.14012	1.11851
2476.51	1.132651	1.144632

Photon energy (eV)	Normalized absorption	
	RS	PS
2476.61	1.147939	1.137645
2476.71	1.127465	1.148535
2476.81	1.151495	1.139315
2476.91	1.1383	1.145484
2477.01	1.141104	1.146874
2477.11	1.159716	1.146001
2477.21	1.160741	1.148476
2477.31	1.177544	1.168454
2477.41	1.15946	1.153805
2477.51	1.155109	1.160493
2477.61	1.158133	1.157231
2477.71	1.172598	1.158077
2477.81	1.173652	1.151644
2477.91	1.165031	1.165545
2478.01	1.151405	1.164975
2478.11	1.155786	1.155037
2478.21	1.153406	1.164084
2478.31	1.170682	1.168557
2478.41	1.15498	1.153995
2478.51	1.161546	1.154388
2478.61	1.167905	1.15724
2478.71	1.150854	1.148224
2478.81	1.133792	1.151171
2478.91	1.155949	1.139448
2479.01	1.145463	1.134557
2479.11	1.146515	1.13814
2479.21	1.133827	1.143932
2479.31	1.131658	1.147604
2479.41	1.132705	1.14263
2479.51	1.127304	1.137332
2479.61	1.128351	1.137402
2479.71	1.121082	1.137717
2479.81	1.136276	1.134131
2479.91	1.149083	1.141855
2480.01	1.143786	1.132422
2480.11	1.146399	1.128966
2480.21	1.139744	1.138077
2480.31	1.110924	1.136758
2480.41	1.1279	1.124081
2480.51	1.124268	1.137707
2480.61	1.124897	1.124781

Table F2 Data collected from XANES experiment of SBR vulcanizates (cont.)

Photon energy (eV)	Normalized absorption	
	RS	PS
2480.71	1.111376	1.132676
2480.81	1.125959	1.126621
2480.91	1.131689	1.122723
2481.01	1.137507	1.138442
2481.11	1.147095	1.135627
2481.21	1.148152	1.134023
2481.31	1.135966	1.148802
2481.41	1.147751	1.162239
2481.51	1.156299	1.160416
2481.61	1.15734	1.153989
2481.71	1.182124	1.157347
2481.81	1.185565	1.166822
2481.91	1.153201	1.157513
2482.01	1.143836	1.149654
2482.11	1.163936	1.142686
2482.21	1.140935	1.147794
2482.31	1.109186	1.119684
2482.41	1.114287	1.127953
2482.51	1.100129	1.10516
2482.61	1.091068	1.099411
2482.71	1.097132	1.096698
2482.81	1.044961	1.086276
2482.91	1.07277	1.073358
2483.01	1.056427	1.065329
2483.11	1.057466	1.058773
2483.21	1.054879	1.047632
2483.31	1.037493	1.049748

Photon energy (eV)	Normalized absorption	
	RS	PS
2483.41	1.038849	1.056269
2483.51	1.054172	1.051759
2483.61	1.049378	1.048939
2483.71	1.048655	1.046596
2483.81	1.040121	1.052486
2483.91	1.044711	1.039453
2484.01	1.048155	1.047114
2484.11	1.044298	1.053603
2484.21	1.043158	1.057597
2484.31	1.055036	1.063876
2484.41	1.054835	1.042711
2484.51	1.043277	1.046215
2484.61	1.058381	1.05409
2484.71	1.030783	1.065611
2484.81	1.044963	1.058905
2484.91	1.052883	1.050622
2485.01	1.037255	1.060956
2485.51	1.042393	1.056111
2486.01	1.063904	1.067925
2486.51	1.053516	1.065173
2487.01	1.059057	1.056532
2487.51	1.063243	1.054559
2488.01	1.040427	1.052705
2488.51	1.035677	1.053249
2489.01	1.035091	1.038835
2489.51	1.04025	1.019724
2490.01	1.018919	1.023215

Table F3 Data collected from XANES experiment of NBR vulcanizates

Photon energy (eV)	Normalized absorption	
	RS	PS
2460.01	1.73E-02	1.51E-02
2460.76	2.03E-02	1.56E-02
2461.51	2.26E-02	1.99E-02
2462.26	2.48E-02	2.25E-02
2463.01	2.77E-02	2.44E-02
2463.76	2.75E-02	2.60E-02
2464.51	3.34E-02	2.74E-02
2465.01	3.40E-02	2.83E-02
2465.11	3.57E-02	3.03E-02
2465.21	3.37E-02	3.46E-02
2465.31	3.41E-02	3.30E-02
2465.41	3.61E-02	3.48E-02
2465.51	3.54E-02	3.24E-02
2465.61	3.53E-02	3.57E-02
2465.71	4.00E-02	3.50E-02
2465.81	3.94E-02	3.37E-02
2465.91	4.20E-02	3.71E-02
2466.01	4.20E-02	3.54E-02
2466.11	4.15E-02	3.79E-02
2466.21	4.15E-02	4.04E-02
2466.31	4.20E-02	4.06E-02
2466.41	4.32E-02	4.48E-02
2466.51	4.48E-02	4.17E-02
2466.61	4.70E-02	4.57E-02
2466.71	4.62E-02	4.46E-02
2466.81	4.99E-02	4.30E-02
2466.91	5.04E-02	4.43E-02
2467.01	5.13E-02	4.46E-02
2467.11	5.14E-02	4.85E-02
2467.21	5.11E-02	4.92E-02
2467.31	5.37E-02	5.05E-02
2467.41	5.51E-02	5.61E-02
2467.51	5.85E-02	5.61E-02
2467.61	5.85E-02	5.62E-02
2467.71	5.80E-02	5.70E-02
2467.81	6.33E-02	6.03E-02
2467.91	6.46E-02	6.00E-02
2468.01	6.40E-02	6.37E-02
2468.11	6.72E-02	7.15E-02
2468.21	6.94E-02	6.69E-02
2468.31	7.65E-02	7.30E-02
2468.41	8.07E-02	7.22E-02
2468.51	8.16E-02	7.80E-02
2468.61	8.34E-02	8.37E-02
2468.71	8.88E-02	8.02E-02
2468.81	9.24E-02	8.93E-02
2468.91	9.52E-02	8.71E-02
2469.01	0.103456	9.45E-02
2469.11	0.109076	0.103068
2469.21	0.112627	0.107594
2469.31	0.122515	0.115099
2469.41	0.12326	0.126728
2469.51	0.137307	0.134367
2469.61	0.141263	0.144639
2469.71	0.16191	0.151129
2469.81	0.17627	0.165664
2469.91	0.190273	0.18669
2470.01	0.210442	0.209497
2470.11	0.241849	0.232744
2470.21	0.264112	0.262195
2470.31	0.295738	0.300127
2470.41	0.350725	0.338534
2470.51	0.407074	0.394749
2470.61	0.486398	0.433129
2470.71	0.569819	0.559066
2470.81	0.689966	0.657991
2470.91	0.811769	0.790626
2471.01	0.981557	0.941404
2471.11	1.13341	1.117366
2471.21	1.307191	1.191111
2471.31	1.4846	1.447547
2471.41	1.634975	1.621993
2471.51	1.780126	1.731542
2471.61	1.87731	1.849664
2471.71	1.971715	1.944213
2471.81	2.018367	2.017866
2471.91	2.056202	2.049474
2472.01	2.074722	2.072145
2472.11	2.092612	2.104084
2472.21	2.121355	2.094052
2472.31	2.09	2.091077
2472.41	2.071451	2.063031

Table F3 Data collected from XANES experiment of NBR vulcanizates (cont.)

Photon energy (eV)	Normalized absorption		Photon energy (eV)	Normalized absorption	
	RS	PS		RS	PS
2472.51	2.048002	2.034488	2476.61	1.041041	1.044559
2472.61	1.989614	2.014681	2476.71	1.041864	1.049292
2472.71	1.948291	1.961888	2476.81	1.052532	1.059481
2472.81	1.897424	1.91616	2476.91	1.04955	1.054471
2472.91	1.842107	1.857865	2477.01	1.054312	1.069293
2473.01	1.805388	1.785433	2477.11	1.061243	1.078189
2473.11	1.706654	1.72765	2477.21	1.073905	1.082509
2473.21	1.637378	1.635526	2477.31	1.073282	1.080619
2473.31	1.52636	1.55221	2477.41	1.087936	1.091944
2473.41	1.448313	1.467264	2477.51	1.085754	1.0952
2473.51	1.36288	1.383203	2477.61	1.108479	1.104314
2473.61	1.327744	1.300636	2477.71	1.103453	1.114691
2473.71	1.194467	1.1967	2477.81	1.107766	1.111806
2473.81	1.128711	1.128134	2477.91	1.1072	1.098475
2473.91	1.071153	1.078397	2478.01	1.11827	1.120864
2474.01	1.017197	1.040836	2478.11	1.131717	1.111005
2474.11	1.005295	1.015288	2478.21	1.12659	1.141313
2474.21	0.977054	0.998233	2478.31	1.12938	1.136123
2474.31	0.981276	0.989596	2478.41	1.126442	1.115696
2474.41	0.970531	0.979764	2478.51	1.116483	1.145684
2474.51	0.969148	0.975057	2478.61	1.131773	1.124416
2474.61	0.974495	0.990897	2478.71	1.125638	1.134542
2474.71	0.960568	0.99347	2478.81	1.141039	1.14092
2474.81	0.99517	0.995054	2478.91	1.133299	1.152141
2474.91	0.987117	1.006267	2479.01	1.14683	1.149303
2475.01	0.989307	1.002129	2479.11	1.139202	1.136398
2475.11	0.986919	1.011833	2479.21	1.140715	1.16207
2475.21	0.996261	1.016893	2479.31	1.14623	1.157689
2475.31	1.010266	1.013929	2479.41	1.145022	1.162191
2475.41	0.996093	1.015648	2479.51	1.163349	1.172135
2475.51	1.008757	1.012868	2479.61	1.176044	1.189442
2475.61	1.012846	1.005276	2479.71	1.18161	1.202395
2475.71	1.007388	1.012095	2479.81	1.217907	1.212709
2475.81	1.012247	1.024989	2479.91	1.21055	1.229742
2475.91	1.016073	1.013819	2480.01	1.216575	1.239379
2476.01	1.017776	1.022118	2480.11	1.225524	1.240993
2476.11	1.020448	1.036568	2480.21	1.241724	1.245343
2476.21	1.015192	1.017931	2480.31	1.228676	1.249206
2476.31	1.015251	1.021156	2480.41	1.22758	1.256323
2476.41	1.015153	1.029688	2480.51	1.225698	1.252805
2476.51	1.033921	1.037667	2480.61	1.23619	1.223784

Table F3 Data collected from XANES experiment of NBR vulcanizates (cont.)

Photon energy (eV)	Normalized absorption		Photon energy (eV)	Normalized absorption	
	RS	PS		RS	PS
2480.71	1.21655	1.229477	2483.41	1.025615	1.046459
2480.81	1.210347	1.240366	2483.51	1.027761	1.030346
2480.91	1.201939	1.211398	2483.61	1.032985	1.037157
2481.01	1.208614	1.212727	2483.71	1.030567	1.017093
2481.11	1.180931	1.204535	2483.81	1.009486	1.032419
2481.21	1.165833	1.171378	2483.91	1.030507	1.027169
2481.31	1.131252	1.160986	2484.01	1.027504	1.035066
2481.41	1.141967	1.143665	2484.11	1.019055	1.025694
2481.51	1.130758	1.151989	2484.21	1.023167	1.043384
2481.61	1.126883	1.136046	2484.31	1.032468	1.044772
2481.71	1.117564	1.120422	2484.41	1.025684	1.040618
2481.81	1.11428	1.12773	2484.51	1.032742	1.027222
2481.91	1.103043	1.109314	2484.61	1.026618	1.033465
2482.01	1.093196	1.105364	2484.71	1.023778	1.028048
2482.11	1.097794	1.105311	2484.81	1.028995	1.03143
2482.21	1.084618	1.090858	2484.91	1.030897	1.02869
2482.31	1.067183	1.08851	2485.01	1.034978	1.040175
2482.41	1.065165	1.081614	2485.51	1.037562	1.032285
2482.51	1.054764	1.079309	2486.01	1.03096	1.02947
2482.61	1.048116	1.059339	2486.51	1.035229	1.043274
2482.71	1.054315	1.065155	2487.01	1.047173	1.040638
2482.81	1.047686	1.042698	2487.51	1.030464	1.040498
2482.91	1.042585	1.047153	2488.01	1.038412	1.045019
2483.01	1.02878	1.050676	2488.51	1.023377	1.040933
2483.11	1.023912	1.045618	2489.01	1.025606	1.028171
2483.21	1.035807	1.02801	2489.51	1.016366	1.016292
2483.31	1.028463	1.036758	2490.01	1.016596	1.016878

APPENDIX G
MANUSCRIPTS PUBLISHED ON CONFERENCE PROCEEDINGS

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CERTIFICATE

15 December 2012

This is to acknowledge that **Pathompong Pangamol** from Mahidol University, Thailand has presented the work entitled "**Utilization of Petroleum-based Sulfur as by-product from Refinery Process in Rubber Vulcanization**" as an Oral presenter in The 28th International Conference of The Polymer Processing Society (PPS-28) which was held during December 11 - 15, 2012 at Royal Cliff Beach Hotel, Pattaya, Thailand.

Asst. Prof. Dr. Krisda Suchiva
Chairman of PPS-28

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O-13-118

UTILIZATION OF PETROLEUM-BASED SULFUR AS BY-PRODUCT FROM REFINERY PROCESS IN RUBBER VULCANIZATION

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Abstract - Petroleum-based sulfur treated as by-product from refinery process is shown for its potential utilization as vulcanizing agent in rubber industry by substituting the elemental sulfur (rhombic sulfur) usually used in rubber vulcanization. According to XRD, FT-IR, and TGA results, the chemical structures of the petroleum-based and rhombic sulfurs are similar. As vulcanizing agent in natural rubber (NR), the petroleum-based ground sulfur and rhombic sulfur from 3 manufacturers are compared in the aspects of cure efficiency and its influences on mechanical properties of NR vulcanizates. Results revealed that cure characteristics (scorch time and cure time) and crosslink density of the NR vulcanized by petroleum-based sulfur were similar to those vulcanized by rhombic sulfur. Moreover, viscoelastic properties as well as mechanical properties of NR vulcanizates are comparable with the commercial sulfur. Therefore, it could be summarized that the petroleum-based sulfur was capable of functioning as vulcanizing agent in rubber products in similar manner to the conventionally used rhombic sulfur.

Keywords: Sulfur; Vulcanization; Cure characteristics; Mechanical properties

Introduction

Generally, raw rubber cannot be used as-received because of its unstable shape, low elasticity, and poor mechanical properties. Thus, the raw rubber needs to be transformed into vulcanized rubber through the vulcanization process [1-4], resulting in crosslink between rubber molecules. Enhancement in elasticity and mechanical properties of cured specimens are resulted. Generally, there are 3 major curing agents used, i.e., sulfur, peroxide, and metal oxide [1-4]. However, sulfur is the most widely used for curing diene rubbers because of its superiority in mechanical properties and ease of curing behavior adjustment [5-9].

Actually, there are 2 main sources of sulfur which are natural source (sulfur flow) and petroleum-based refinery [10]. The sulfur originated from the former is a major source of sulfur widely used in rubber industry while that from the latter is generally treated as by-product from refinery process, and sold in low cost for preparing sulfuric acid as reagent [11-14].

Therefore, this work aims to add the value of petroleum-based sulfur by investigating the potential utilization of such sulfur as vulcanizing agent in rubber industry to substitute the elemental sulfur (rhombic sulfur) usually used in rubber vulcanization.

Experimental

Materials

Natural rubber (STR 5L) was purchased from Union Rubber Product Co., Ltd. Conventional rhombic sulfurs used in this research consisting of RS, SGS, and SP400 were supplied by Chemmin Corporation Ltd., Cosan (Thailand) Co.,Ltd., and Miwon Commercial Co., Ltd., respectively while a petroleum-based sulfur (PS) was supported by IRPC Plc. Co., Ltd. Other chemical ingredients, namely, stearic acid and zinc oxide (ZnO) were supplied by Chemmin Corporation Ltd., and N-tret-butyl-2-benzothiazole sulfonamide (Santocure-TBBS) was by Reliance Technochem Co., Ltd. Except for the PS, all ingredients were used as-received. In the case of PS, the as-received PS was ground with ball-milling process to achieve desirable particle size.

Compounds preparation and testing

Compounding recipes were shown in **Table 1**. Two-roll mill (LabTech, model LRM 150 electric mill, Thailand) was used as a mixer with the mixing time of 10 min at 50°C. Viscoelastic properties were investigated using Rubber Process Analyzer (RPA) (Alpha Technologies model RPA 2000). Storage modulus (G') of the rubber compounds was measured as a function of strain (from 0.56 to 1200%) at test frequency and temperature of 1.0 Hz and 100°C, respectively. Cure characteristics were examined by Moving Die Rheometer (MDR) (TechPro MD+) at 150°C.

Characterization of sulfur characteristics

The chemical structure of PS was characterized, and compared with RS by the uses of x-ray diffractometer (XRD) (Bruker AXS Model D8 Discover) at 25°C, Fourier transform infrared spectrometer (FT-IR) under a diffuse reflectance infrared Fourier Transform (DRIFT) mode (Bruker Equinox 55) at 25°C, and Thermogravimeter (TGA) (Mettler Toledo model TGA/SDTA851[e]) at heating rate of 20°C/min. Temperatures were scanned from ambient temperature to 600°C under nitrogen atmosphere. After 600°C, the atmosphere was switched to oxygen and the test was carried out until 800°C.

Testing of rubber vulcanizates

Hardness was measured using Shore A Durometer (Wallace model COGENIX) as per ASTM D2240. Tensile properties of cured specimens were determined using Universal Testing Machine (Instron model 5566) according to ASTM D412 Die C at crosshead speed and load cell of 500 mm/min and 1 kN, respectively. Dynamic mechanical properties of the vulcanizates were examined using dynamic mechanical analyzer (GABO EPLEXOR 25N) under strain sweep test mode at 30°C and frequency of 5 Hz. Heat build-up test was conducted using BF Goodrich Flexometer (Model II) as per ASTM D623-07.

Table 1 Formula of rubber compounds

Chemicals	Loading (phr*)			
	RS	PS	SGS	SP400
NR	100	100	100	100
ZnO	3	3	3	3
SA	1	1	1	1
TBBS	1	1	1	1
Sulfur (RS)	1.75	-	-	-
Sulfur (PS)	-	1.75	-	-
Sulfur (SGS)	-	-	1.75	-
Sulfur (SP400)	-	-	-	1.75

*phr = part per hundred of rubber

Determination of crosslink density

Cured specimens (aka. vulcanizates) were cut into rectangles with dimensions of 10x10x2 mm^3, and weighed before and after soaked in toluene for 7 days. Volume fraction of rubber in the swollen network (υ_r) was calculated according to **Eq. 1** [15]. The crosslink density was calculated using the Flory-Rehner equation as shown in **Eq. 2** [15].

$$v_r = \frac{\left(\frac{w_1}{\rho_d}\right)}{\left(\frac{w_1}{\rho_d} + \frac{(w_2 - w_1)}{\rho_s}\right)} \quad (1)$$

where w_1 is the mass of rubber before swelling, w_2 is the mass of the swollen rubber, ρ_d is the rubber density before swelling, and ρ_s is the toluene density.

$$v_e = \frac{-\left[\ln(1-v_r) + v_r + \chi_1 v_r^2\right]}{\left[v_1\left(v_r^{1/3} - \frac{v_r}{2}\right)\right]} \quad (2)$$

where υ_e is the network chain density, υ_1 is molar volume of toluene, and χ_1 is the Flory–Huggins interaction parameter between rubber and toluene.

The swelling ratio (S) could be calculated following **Eq. 3** [15].

$$S = \frac{(w_2 - w_1)}{w_1} \quad (3)$$

Results and Discussion

Chemical structure of PS

Fig. 1 shows the XRD pattern comparison of RS and PS. Evidently, both RS and PS give similar XRD pattern, implying similar in chemical structure.

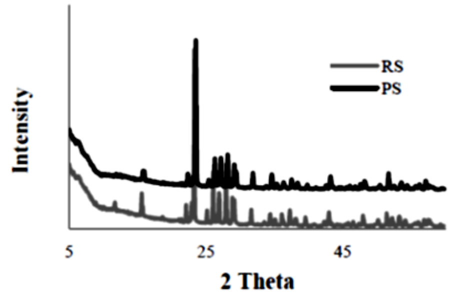

Figure 1 XRD patterns of RS and PS

Fig. 2 exhibits the FT-IR spectra of RS and PS. The spectrum of the RS show characteristic peak of sulfur at 1101, 845, and 468 cm^{-1}, which are also observed in that of PS. The results suggest similarity in functional groups on RS and PS.

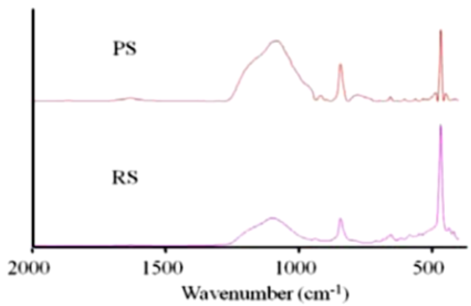

Figure 2 FT-IR spectra of RS and PS

Fig. 3 displays similarity in TGA thermograms of RS and PS, supporting FTIR and XRD results that the chemical structure of both RS and PS are in common with the decomposition temperature of approximately 370°C.

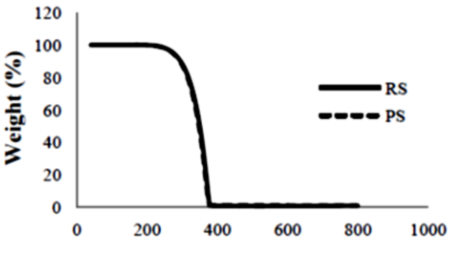

Figure 3 TGA curves of RS and PS

Properties of compounds and vulcanizates

Table 2 illustrates a comparison of cure characteristics of rubber compounds incorporated with different types of sulfurs. Obviously, there are no significant differences between scorch time and cure time in all compounds. Similarly, there is no disparity of crosslink density observed, indicating the comparable cure reactivity of all sulfurs.

Table 2 Cure characteristics, swelling ratio (S), and calculated crosslink density (υ_e) of vulcanizates

Formula	**Cure characteristics**		**S**	**υ_e (10^{-4} mol.cm^{-3})**
	Scorch time (min)	Cure time (min)		
RS	11.59	17.26	3.80	1.28
PS	12.43	17.10	3.94	1.23
SGS	12.01	17.10	3.64	1.33
SP400	12.01	16.39	3.75	1.11

Fig. 4 shows viscoelastic properties as a function of shear strain of rubber compounds incorporated with different sulfurs. It is evident that, regardless of sulfur types used, the storage modulus (G') of all compounds is superimposable suggesting no profound effect of sulfur on rheological behavior of rubber compounds. In other words, the processability of rubber compounds incorporated with all sulfurs is similar.

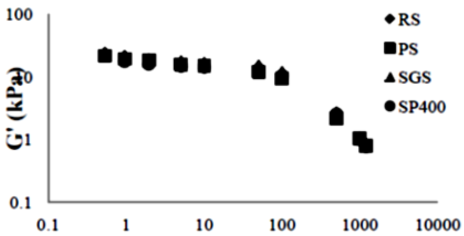

Figure 4 Storage modulus as a function of strain in rubber compounds incorporated with different types of sulfurs

Fig. 5 exhibits dynamic mechanical properties as a function of shear strain of vulcanizates incorporated with different sulfurs. Obviously, the storage modulus (E') of vulcanizates shows similar trend which has no change while increasing strain. The results imply that the PS can be used as vulcanizing agent by replacing the commercial rhombic sulfurs while still offers similar dynamic mechanical properties to conventional rhombic sulfurs.

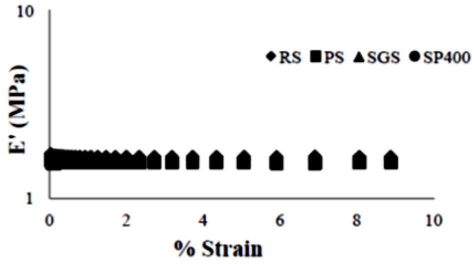

Figure 5 Storage modulus as a function of strain in vulcanizates incorporated with different types of sulfurs

Fig. 6 shows hardness of vulcanizates prepared with different sulfurs. Compared with the other rhombic sulfurs, the PS gives the vulcanizates with similar hardness range which is in good agreement with the results of crosslink density as discussed previously in **Table 2**. Moreover, tensile strength, elongation at break and tear strength of vulcanizates with PS and RS are comparable as depicted in **Figs. 7-9**.

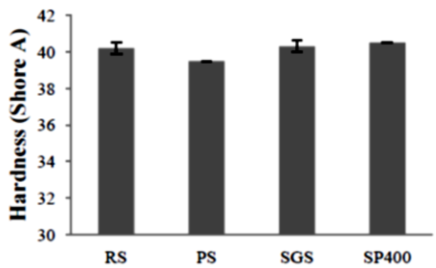

Figure 6 Hardness values of vulcanizates

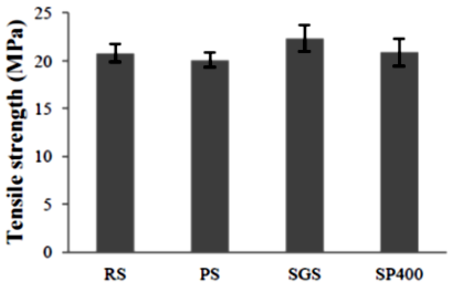

Figure 7 Tensile strength of vulcanizates

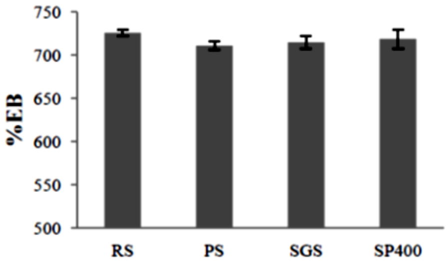

Figure 8 Elongation at break of vulcanizates

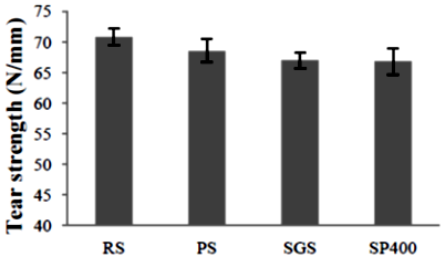

Figure 9 Tear strength of vulcanizates

Fig. 10 exhibits heat build-up (HBU) test results demonstrating similar in PS gives similar trend of HBU performance which is in agreement with the results of viscoelastic and mechanical properties.

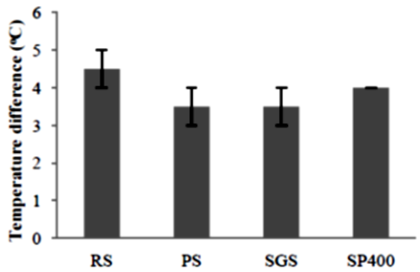

Figure 10 Heat build-up (HBU) of vulcanizates

Conclusions

Petroleum-based sulfur (PS) as a by-product from refinery process was used as vulcanizing agent in rubber vulcanization process. According to XRD, FTIR-DRIFT and TGA results, the chemical structure of PS and RS are similar. Thus, both offer comparable cure behavior, viscoelastic and mechanical properties. Thus, it can be summarized that the PS possesses the potential utilization to replace rhombic sulfur in rubber industry.

Acknowledgements

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References

1. W. Hofmann, *Rubber Technology Handbook*, Hanser Publishers, Munich, 1980.
2. K. Nagdi, *Rubber as an Engineering Material: Guildline for Users*, Hanser Publishers, Munich, 1993.
3. A. Y. Coran, in *The Science and Technology of Rubber 3rd*, J. E. Mark, B. Erman, F. R. Eirich Ed.; Elsevier Academic Press, London, 2005; 321 - 366.
4. W. Hofmann, *Vulcanization and Vulcanizing Agents*, Palmerton Publisher Co., Inc., New York, 1967.
5. A. P. Susamma; V. T. Elizabeth Mini.; A. P. Kuriakose, *J. Appl. Polym. Sci.* 2001, 79, 1.
6. S. C. Debnath; S. K. Mandal; D. K. Basu, *J. Appl. Polym. Sci.* 1995, 57, 555.
7. A. S. Aprem; K. Joseph; T. Mathew; V. Altstaedt; S. Thomas, *Eur. Polym. J.* 2003, 39, 1451.
8. J. M. Vergnaud; L. D. Rosca, *Rubber Curing and Properties*, CRC Press, New York, 2009.
9. A. Y. Coran, *J. Appl. Polym. Sci.* 2003, 87, 24.
10. W. N. Karel, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag, 2006.
11. V. Simanzhenkov; R. Idem, *Crude Oil Chemistry*, Marcel Dekker Inc., New York, 2003.
12. J. G. Speight, *Handbook of Petroleum Analysis*, John Wiley & Sons Inc., New York, 2001.
13. J. G. Speight, *Handbook of Petroleum Product Analysis*, John Wiley & Sons Inc., New York, 2002.
14. J. G. Speight, *The Chemistry and Technology of Petroleum*, CRC Press, New York, 2006.
15. Y. Zhan; J. Wu; H. Xia; N. Yan; G. Fei; G. Yuan, *Macromol. Mater. Eng.* 2011, 296, 590.

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Potential use of petroleum-based sulfur in rubber industry

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Abstract— *Potential use of petroleum-based sulfur generally classified as a by-product from refinery process is investigated as vulcanizing agent in rubber, and compared with commercial rhombic sulfur. Styrene-butadiene rubber (SBR) and nitrile rubber (NBR) are used as rubber matrices. Results obtained show that, between 2 types of sulfurs, the SBR system reveals similarity in cure behaviors whereas the NBR system demonstrates faster cure behavior when vulcanized by petroleum-based sulfur. However, rheological properties, mechanical properties, and dynamic mechanical properties of both rubbers show comparable results regardless of sulfur type. The results suggest the strong potential utilization of petroleum-based sulfur as vulcanizing agent as an alternative to the commercial rhombic sulfur usually used in rubber vulcanization.*

Keywords— **Sulfur, Vulcanization, Mechanical Properties, Dynamic Properties.**

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1. INTRODUCTION

In general, as-received raw rubber possesses unstable shape, low elasticity, and poor mechanical properties. To overcome such problem, a vulcanization is therefore required [1]-[4]. By this means, a 3-dimensional elastic network of rubber molecules is resulted, and the vulcanized product is usually known as vulcanizates. Typically, there are 3 major curing agents used in rubber industry, i.e., sulfur, peroxide, and metal oxide [1]-[4]. Because of superiority in mechanical properties and ease of curing behavior adjustment, the sulfur vulcanization is, therefore, widely used for curing the diene rubbers [5]-[9].

Generally speaking, the sulfur originates from 2 main sources: i.e., natural source (or sulfur flow) and petroleum-based refinery [10]. The sulfur coming from the former is a major source of sulfur widely used in rubber industry while that from the latter is generally classified as a by-product from refinery process, and typically sold in low cost for preparing sulfuric acid [11]-[14].

In Thailand, there are a number of refinery companies including IRPC (Plc.) Co.,Ltd., and their major products are various types of gases and oils. During the refinery process, sulfur mixed up in crude oil must be eliminated to avoid corrosion in machines. In order to add value of a by-product sulfur, the extension of sulfur utilization must be carried out. This research is initialed by the IRPC (Plc.) Co.,Ltd. as a one of large refinery in Thailand for maximizing the use of petroleum-based sulfur in rubber industry. Our previous work suggests that the petroleum-based sulfur possesses similarity in chemical structure and the potential use as vulcanizing agent in natural rubber (NR) by replacing commercial rhombic sulfur [15]. However, such capability in synthetic rubbers is still required. Thus, the objective of this work is to study of the potential utilization of petroleum-based sulfur as vulcanizing agent in rubber industry comparing with commercial rhombic sulfur usually used in vulcanization process of synthetic rubber, namely, styrene-butadiene rubber (SBR) and nitrile rubber (NBR). The former is important especially in tire application while the latter is widely used in oil-resistant seal and hose applications.

2. EXPERIMENTAL

Materials

Styrene-butadiene rubber (SBR 1502) and nitrile rubber (NBR) were purchased from BST Elastomers Co., Ltd. and JSR 230SL JSR Co., respectively. Commercial rhombic sulfur (RS) was supplied by Chemmin Co. Ltd., while petroleum-based sulfur (PS) was supported by IRPC Plc. Co., Ltd. Other chemical ingredients, namely, stearic acid and zinc oxide (ZnO) were purchased from Chemmin Co. Ltd., and N-tret-butyl-2-benzothiazole sulfonamide (Santocure-TBBS) from Reliance Technochem Co., Ltd. Except for the PS, all ingredients were used as-received. In the case of PS, the as-received PS was ball-milled to achieve desirable particle size [15].

Compound preparation and testing

Compounding recipes were illustrated in Table 1. All rubber formula were prepared using a single step mixing technique on two-roll mill (LabTech, model LRM 150, Thailand) with mixing time of 10 min at 50°C. Viscoelastic properties were determined using Rubber Process Analyzer (RPA) (Alpha Technologies model RPA 2000, USA). Storage modulus (G') of the rubber compounds was measured as a function of strain (from 0.56 to 1200%) at test frequency and temperature of 1.0 Hz and 100°C, respectively. Cure characteristics were monitored by Moving Die Rheometer (MDR) (TechPro MD+, USA) at 150°C. Designation of PS and RS vulcanized SBR were PS-SBR and RS-SBR, respectively. Likewise, the NBR vulcanized with PS and RS were denoted as PS-NBR and RS-NBR, respectively.

Table 1. Compounding recipes used in this work

Chemical ingredients	Amount (phr*)	
	RS	PS
Rubber	100	100
ZnO	3	3
Stearic acid	1	1
TBBS	1	1
RS	1.75	-
PS	-	1.75

*phr = part per hundred of rubber

Determination of vulcanizate properties

Hardness was measured using Shore A Durometer (Wallace model COGENIX, UK) as per ASTM D2240. Tensile properties of cured specimens were determined using Universal Testing Machine (Instron model 5566, USA) according to ASTM D412 Die C at crosshead speed and load cell of 500 mm/min and 1 kN, respectively. Dynamic mechanical properties of vulcanizates were measured using dynamic mechanical analyzer (GABO EPLEXOR 25N) under temperature sweep test mode (from -80°C to 60°C) at strain of 1% and frequency of 5 Hz. Heat build-up test was conducted using BF Goodrich Flexometer (Model II), USA as per ASTM D623-07.

Investigation of crosslink density

Vulcanizates were cut into rectangles with dimensions of approximately 10 mm x 10 mm x 2 mm, and weighed before and after soaked in solvent for 7 days. Volume fraction of rubber in the swollen network (υ_r) was calculated according to Eq. (1) [16]. The crosslink density was calculated using the Flory-Rehner equation as shown in Eq. (2) [16].

$$v_r = \frac{\left(\frac{w_1}{\rho_d}\right)}{\left(\frac{w_1}{\rho_d} + \left(\frac{(w_2 - w_1)}{\rho_s}\right)\right)} \quad (1)$$

Where w_1 is the mass of rubber before swelling; w_2 is the mass of the swollen rubber; ρ_d is the rubber density before swelling, and ρ_s is the solvent density.

$$v_e = \frac{-\left[\ln(1-v_r)+v_r+\chi_1 v_r^2\right]}{\left[v_1\left(v_r^{1/3}-\frac{v_r}{2}\right)\right]} \quad (2)$$

Where υ_e is the network chain density; υ_1 is molar volume of solvent, and χ_1 is the Flory–Huggins interaction parameter between rubber and solvent. In this case, toluene and acetone were used as good solvents for SBR and NBR, respectively.

The swelling ratio (S) could be calculated following Eq. (3) [16].

$$S = \frac{(w_2 - w_1)}{w_1} \quad (3)$$

3. RESULTS AND DISCUSSION

Properties of compounds and vulcanizates

Comparison of cure behaviors of rubber vulcanizates is tabulated in Table 2. Obviously, there are no discrepancies observed in the case of SBR whereas there are slight differences of cure behaviors in the case of NBR system. Both scorch time and cure time of PS-vulcanized NBR are faster than those of RS-vulcanized NBR. However, such phenomena do not play a significant effect on swelling ratio and crosslink density of NBR as tabulated in Table 3. Similarly, there is no disparity of crosslink density observed, indicating the comparable cure reactivity of all sulfurs.

Table 2. Cure characteristics of vulcanizates

Specimens	Cure characteristics	
	Scorch time (min)	Cure time (min)
PS-SBR	29.30	43.06
RS-SBR	28.13	42.36
PS-NBR	10.21	16.18
RS-NBR	15.14	22.33

Table 3. Swelling ratio (S) and calculated crosslink density (υ_e) of vulcanizates

Specimens	S	υ_e ($\times 10^{-4}$ mol.cm^3)
PS-SBR	4.54	0.94
RS-SBR	4.47	0.99
PS-NBR	2.88	2.41
RS-NBR	2.71	2.71

Figures 1 and 2 display viscoelastic properties as a function of shear strain of SBR and NBR compounds incorporated with different types of sulfurs, respectively. It is evident that the storage modulus (G') of all compounds is superimposable suggesting no profound effect of sulfur on rheological behavior of rubber compounds regardless of sulfur types used. In other words, the processability of rubber compounds remains similar.

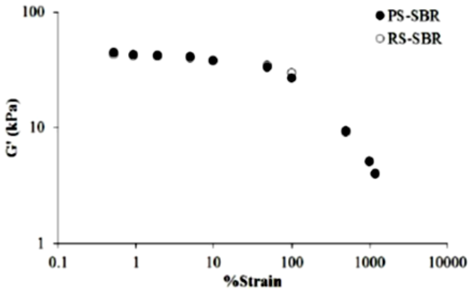

Fig.1. Viscoelastic properties of SBR compounds incorporated with different sulfurs

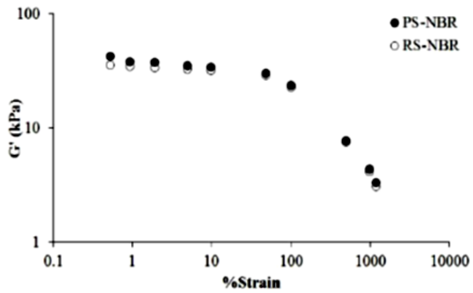

Fig.2. Viscoelastic properties of NBR compounds incorporated with different sulfurs

Figures 3 and 4 show dynamic mechanical properties as a function of temperature of SBR vulcanizates cured with different sulfurs. Evidently, there is similarity in storage modulus (E') and damping factor (tan δ) of all vulcanizates. This means types of sulfur have no significant effect on dynamic mechanical properties of SBR vulcanizates. These similar results are also found in the case of NBR vulcanizates as exhibited in Figures 5 and 6.

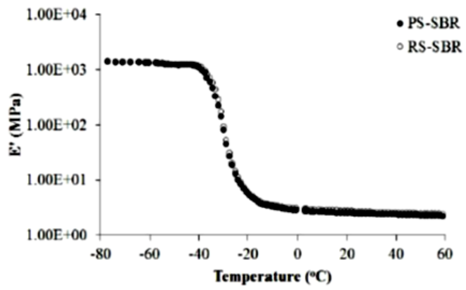

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Fig.3. Storage modulus of SBR vulcanizates incorporated with different sulfurs

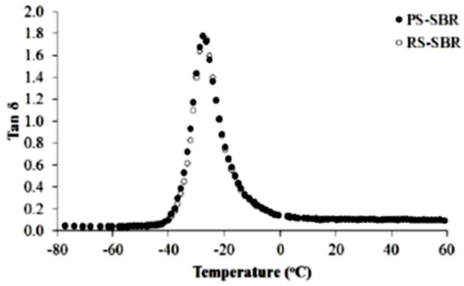

Fig.4. Tan δ of SBR vulcanizates incorporated with different sulfurs

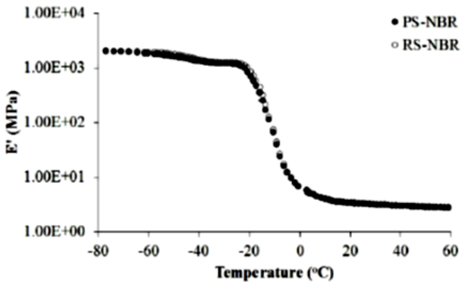

Fig.5. Storage modulus of NBR vulcanizates incorporated with different sulfurs

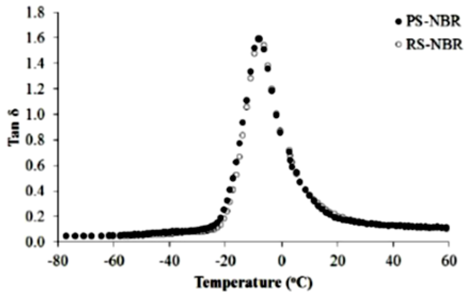

Fig.6. Tan δ of NBR vulcanizates incorporated with different sulfurs

Figures 7 illustrates hardness of vulcanizates prepared with different sulfurs. The PS as vulcanizing agent offers similar hardness range. This result agrees well with the results of crosslink density as discussed previously. Moreover, tensile strength and elongation at break are not significantly affected by types of sulfur as illustrated in Figures 8 – 9, respectively.

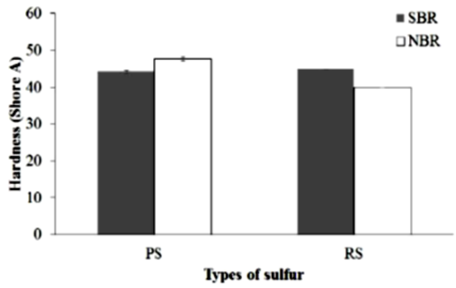

Fig.7. Hardness of vulcanizates

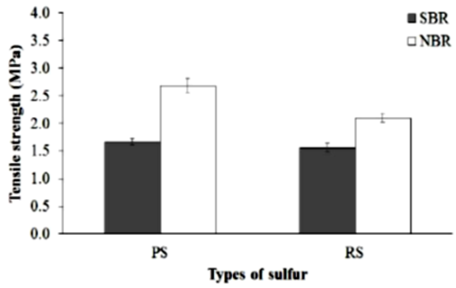

Fig.8. Tensile strength of vulcanizates

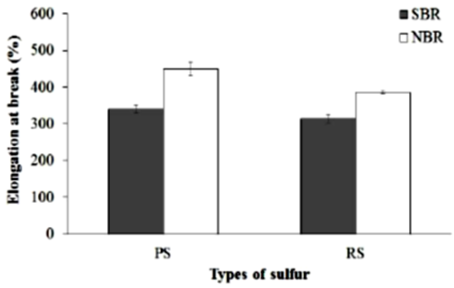

Fig.9. Elongation at break of vulcanizates

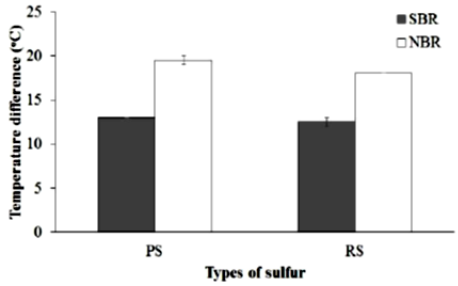

Fig.10. Heat build-up (HBU) of vulcanizates

Figure 10 reveals heat build-up (HBU) test results, demonstrating insignificant difference in HBU of the vulcanizates prepared with different type of sulfur. This finding is the case for both SBR and NBR systems.

4. CONCLUSION

Petroleum-based sulfur (PS) classified as a by-product from refinery process demonstrates good potential utilization as vulcanizing agent in rubber. In the case of NBR, although the PS gives faster curability than RS, there is no profound effect on properties of vulcanizates. Consequently, it is suggested that, as a curing agent purpose, the PS is capable of replacing the RS. By this means, the value adding of PS is possible which is beneficial to the refinery companies and rubber industries.

ACKNOWLEDGMENT

The authors would like to express our profound gratitude toward IRPC Plc. Co., Ltd. for supporting petroleum-based sulfur. Financial support from Thailand Research Fund through the Royal Golden Jubilee PhD Program (Grant No PHD/0116/2553) is also acknowledged.

REFERENCES

[1] Hofmann W. Rubber technology handbook. New York: Hanser; 1989.
[2] Nagdi K. Rubber as an engineering material: guideline for users. New York: Hanser; 1993.
[3] Coran AY. Vulcanization. In: Mark JE, Erman B, Eirich FR, editors. The science and technology of rubber. 3rd ed. New York: Elsevier Inc.; 2005, p. 321-366.
[4] Hofmann W. Vulcanization and vulcanizing agents. London: Maclaren and Sons Ltd.; 1967.
[5] Susamma AP, Elizabeth Mini VT, Kuriakose AP. Studies on novel binary accelerator system in sulfur vulcanization of natural rubber. J Appl Polym Sci 2001; 79(1): 1-8.
[6] Debnath SC, Mandal SK, Basu DK. A new synergistic combination of safe accelerators for the improvement of physical properties in gum and filled vulcanizates. J Appl Polym Sci 1995; 57(5): 555-562.
[7] Aprem AS, Joseph K, Mathew T, Altstaedt V, Thomas S. Studies on accelerated sulphur vulcanization of natural rubber using 1-phenyl-2,4-dithiobiuret/tertiary butyl benzothiazole sulphenamide. Eur Polym J 2003; 39(7): 1451-1460.
[8] Vergnaud JM, Rosca LD. Rubber curing and properties. New York: CRC Press; 2009.
[9] Coran AY. Chemistry of the vulcanization and protection of elastomers: a review of the acheivements. J Appl Polym Sci 2003; 87(1): 24-30.
[10] Karel WN. Ullmann's encyclopedia of industrial chemistry. Wiley-VCH Verlag; 2006.
[11] Simanzhenkov V, Idem R. Crude oil chemistry. New York: Marcel Dekker Inc.; 2003.
[12] Speight JG. Handbook of petroleum analysis. New York: John Wiley & Sons Inc.; 2001.
[13] Speight JG. Handbook of petroleum product analysis. New York: John Wiley & Sons Inc.; 2002.
[14] Speight JG. The chemistry and technology of petroleum. New York: CRC Press; 2006.
[15] Pangamol P, Sirisinha C. Utilization of petroleum-based sulfur as by-product from refinery process in rubber vulcanization. Proceedings of the Polymer Processing Society 28th Annual Meeting: Thailand; 2012.
[16] Zhan Y, Wu J, Xia H, Yan N, Fei G, Yuan G. Dispersion and exfoliation of graphene in rubber by an ultrasonically-assisted latex mixing and in situ reduction process. Macromol Mater Eng 2011; 296(7): 590-602.

APPENDIX H
MANUSCRIPTS PUBLISHED ON JOURNALS

Decision Letter (ie-2013-031456.R1)

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CC:
Subject: Decision on Manuscript ID ie-2013-031456.R1
Body: 05-Nov-2013

Journal: Industrial & Engineering Chemistry Research
Manuscript ID: ie-2013-031456.R1
Title: "Effectiveness of by-product Sulfur from Petroleum Refining as a Rubber Vulcanizing Agent: An XANES Investigation" Author(s): Sirisinha, Chakrit; Pangamol, Pathompong; Hu, Yongfeng; Urquhart, Stephen

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Effectiveness of By-product Sulfur from Petroleum Refining as a Rubber Vulcanizing Agent: A XANES Investigation

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ABSTRACT: Sulfur plays an important role in the rubber industry as a vulcanizing agent, providing an enhancement in mechanical properties relative to unvulcanized rubber. The sulfur used in industry originates from natural and petroleum sources. Petroleum-based sulfur (PS), usually a by-product from a refinery process, was used as the vulcanizing sulfur in the present work. The chemical structure of PS was characterized and compared to that of a commercial rhombic sulfur (RS) using sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy. The results reveal that sulfur K-edge XANES spectroscopy has good sensitivity to the chemical structure of sulfur, and the chemical structures of sulfur in rubbers vulcanized with PS and RS are very similar. Furthermore, different types of rubbers vulcanized with PS or RS exhibit comparable mechanical properties. This work shows that PS can be used to replace RS as a vulcanizing agent for rubber.

■ INTRODUCTION

Vulcanization is a necessary process for generating intermolecular linkages in bulk rubber, leading to increased mechanical strength and elasticity.[1,2] Vulcanizing agents used in the rubber industry include sulfur and peroxides.[3−5] Of these, sulfur is preferred, mainly because of its superiority in cure behavior adjustment and mechanical properties of the vulcanizates.[6,7] Generally, sulfur originates from natural sources and as a by-product of petroleum refining.[8] The former is the major source of sulfur used in the rubber industry, whereas the latter is generally treated as a by-product and sold at low cost for preparing sulfuric acid.[9] It is of interest to use the sulfur that originates in refineries as a vulcanizing agent, motivating this research. The aim of this work was to characterize the structure of petroleum-based sulfur at the molecular level both before and after it has been used for rubber vulcanization.

X-ray absorption spectroscopy (XAS) is a synchrotron-based techniques that is widely used to study the geometric and electronic structures of various types of materials, in the solid,[10] liquid,[11] and gas[12] phases. In this work, X-ray absorption near-edge structure (XANES) spectroscopy was used to determine the structure of sulfur from petroleum refinery by-products and from natural sources. XANES spectroscopy is known to be sensitive to the oxidation state of sulfur.[13,14] This good sensitivity was further demonstrated by recent research, in which XANES spectroscopy was applied to investigate the chemical structure of sulfur in rubber.[15−19]

The rubbers used in this work include natural rubber (NR) and synthetic rubber. Both polar and non-polar synthetic rubbers, composed of nitrile rubber (NBR) and styrene−butadiene rubber (SBR), respectively, were used. These rubbers are generally used in the rubber industry. Attention was paid to the use of XANES spectroscopy for investigating the sulfur structure in rubbers by comparison with commercial rhombic sulfur coming from natural sources that is widely used in rubber industry.

■ EXPERIMENTAL SECTION

Petroleum-based sulfur (PS) was received from IRPC Co., Ltd. (Rayong, Thailand) and was ground prior to being used. Commercial rhombic sulfur (RS) was purchased from Chemmin Co. Ltd. (Samut Prakan, Thailand) and used as-received. The quantities of chemical ingredients (measured in units of parts per hundred rubber, phr) used in this work were as follows: 3 phr of zinc oxide (ZnO), 1 phr of stearic acid, 1 phr of *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS), and 1.75 phr of sulfur (PS or RS). The ZnO and stearic acid were purchased from Chemmin Co. Ltd., whereas the TBBS was purchased from Reliance Technochem (Flexsys) Co., Ltd. (Bangkok, Thailand). All of these chemicals were used as-received.

A two-roll mill was used to mix the rubbers. First, raw rubber was masticated for 2 min, and then ZnO and stearic acid were added. After this mixture had been mixed for 8 min, TBBS and sulfur were charged. A total mixing time of 10 min was used. Subsequently, the rubber compounds were determined for their cure characteristics including optimum cure time using a moving die rheometer (MDR) at 150 °C, after which they were vulcanized using a hydraulic hot press at similar temperature. All rubbers (NR, SBR, and NBR) were prepared using similar procedures, but with different sulfurs (i.e., RS and PS). The

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vulcanizates prepared using RS are designated as NR-RS, SBR-RS, and NBR-RS, whereas those prepared using PS are designated as NR-PS, SBR-PS, and NBR-PS.

The mechanical properties of the vulcanized specimens were measured using an Instron model 5566 universal testing machine at a crosshead speed of 500 mm/min and a load cell of 1 kN in accordance with standard method ASTM D412 Die C.

The swelling ratios of the cured specimens were also determined, as an indication of the cross-linking efficiency of sulfur in the rubber. Toluene was used as the solvent for both NR and SBR, whereas NBR was tested using acetone as the solvent. The specimens were soaked in the solvent for 7 days to ensure swelling equilibrium. The swelling ratio was calculated as $S = (w_2 - w_1)/w_1$, where w_1 is the weight of the rubber specimen before being soaked in solvent and w_2 is the weight of swollen vulcanizate. In addition, the cross-link densities of the specimens were calculated according to the Flory−Rehner equation.[20]

XANES measurements were conducted at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source (CLS) in the energy range of 1.7−10 keV. A Si(111) double-crystal monochromator was used to select the photon energy, and the energy resolution ($\Delta E/E$) was approximately 1×10^{-4}. The sulfur powders were placed on carbon tape on a sample holder. In the case of rubber vulcanizates (cured specimens), the vulcanizate sheets were cut into pieces with dimensions of 10 mm × 5 mm before being placed on the sample holder. The photon beam size was 5 mm × 1 mm. Total electron yield (TEY, obtained by measuring the specimen current) was used to measure the sulfur powders, and a Si drift detector was used to record the fluorescence yield (FY) spectra of nonconducting rubbers. All XANES spectra were recorded around the sulfur K-edge in a vacuum environment and were averaged and normalized using ATHENA software version 0.8.056.[21]

■ RESULTS AND DISCUSSION

Figure 1 shows the vulcanization curves of all rubber compounds prepared with RS and PS. Evidently, there were

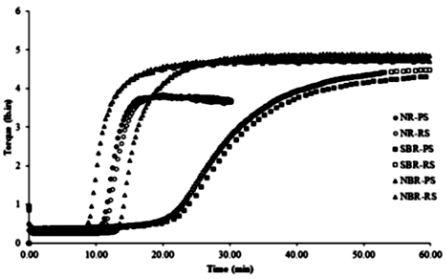

Figure 1. Vulcanization curves of rubbers prepared with rhombic sulfur (RS) and petroleum-based sulfur (PS).

no significant disparities in the cure times for the NR and SBR systems. Therefore, processing adjustments were not required. Nevertheless, a significant difference in cure time was found for the NBR system. Obviously, PS-vulcanized NBR exhibited a faster cure time than RS-vulcanized NBR. This phenomenon, however, did not have a significant effect on the mechanical properties of the vulcanizates, as demonstrated in Figures 2 and 3.

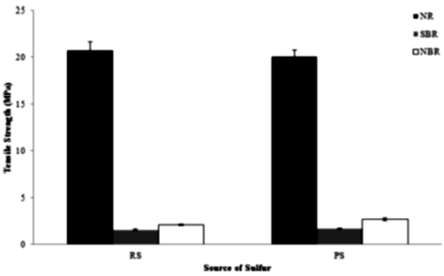

Figure 2. Tensile strength of rubber vulcanizates prepared with rhombic sulfur (RS) and petroleum-based sulfur (PS).

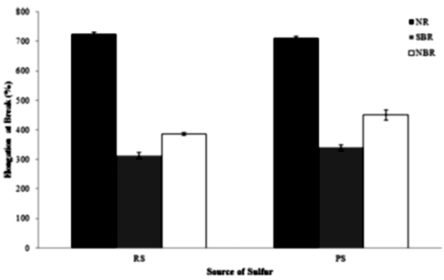

Figure 3. Elongation at break of rubber vulcanizates prepared with rhombic sulfur (RS) and petroleum-based sulfur (PS).

The mechanical properties of all of the rubbers were measured to monitor the effects of the sulfur source, and the results are shown in Figures 2 and 3. Evidently, the tensile strength and elongation at break for a given rubber type are comparable, regardless of the sulfur sources. This implies that the PS treated as a by-product from refinery processes can potentially be used as a vulcanizing agent for rubber, replacing the commercially sourced rhombohedral sulfur (RS). In contrast, the mechanical properties (tensile properties) depend strongly on the type of rubber matrix. NR exhibited considerably greater properties than SBR and NBR, mainly because of the occurrence of strain-induced crystallization in NR when it was stretched.[1,22] Compared with SBR, NBR demonstrated somewhat superior mechanical properties because of its stronger molecular interactions through the dipole−dipole interactions of acrylonitrile groups.

In addition, the reactivities of sulfur during the vulcanization process of each rubber were different, resulting in different numbers of sulfur linkages, as evidenced by the swelling tests and calculated cross-link densities illustrated in Figures 4 and 5, respectively. Basically, the swelling ratio is used to determine the cross-link efficiency of a curing agent in rubber, together with the calculated cross-link density according to the Flory−Rehner equation.[20] The lower the swelling ratio, the higher the cross-link density, leading to superior mechanical properties.[23] In other words, the swelling ratio generally exhibits a trend

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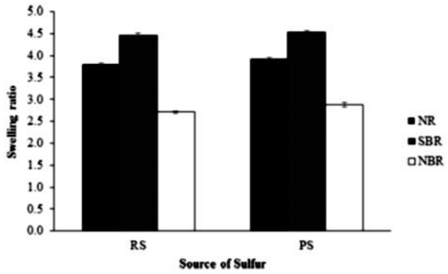

Figure 4. Swelling tests of rubber vulcanizates prepared with rhombic sulfur (RS) and petroleum-based sulfur (PS).

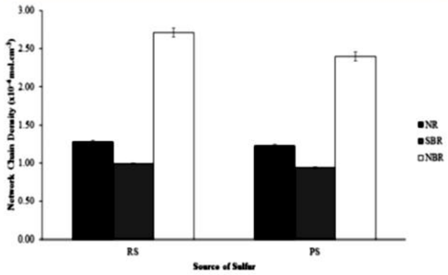

Figure 5. Calculated cross-link densities of vulcanizates prepared with rhombic sulfur (RS) and petroleum-based sulfur (PS).

opposite to that of the cross-link density. Considering the same rubber type, it can be clearly seen that the two sources of sulfur resulted in similar swelling ratios and cross-link densities, giving rise to comparable mechanical properties. In the case of SBR, the swelling ratio exhibited the highest value, whereas the cross-link density had the lowest value regardless of sulfur sources. These results imply a low reactivity of sulfur, causing low mechanical properties, as explained earlier. Furthermore, the NR specimens offered better mechanical properties than the NBR samples, even though the NR vulcanizates of both sulfur types had higher swelling ratios and lower cross-link densities than the NBR vulcanizates. This is attributed to the good compatibility between NR and sulfur, as well as strain-induced crystallization of NR, leading to the good mechanical properties shown in Figures 2 and 3, as mentioned previously.[1,22,23]

The XANES results for the S K-edge of sulfur powders as presented in Figure 6 reveal similar spectra of PS and RS. The main absorption peak of PS appears at 2471.7 eV, whereas that of RS occurs at 2471.6 eV. This feature is assigned as a sulfur 1s → σ* (S−S) resonance, suggesting a similarity in the rhombic structures of PS and RS. However, the peak of RS is slightly broader than that of PS. This is probably due to the difference in sulfur chain length owing to the chemical nature of natural occurring RS.[24] Although the rhombic structure (S_8) is more stable, other structures such as S_n (n = 2, 3, 4, ...) can occur in nature.[24] On the other hand, the PS originates from a chemical reaction during the refinery process (Claus process), resulting in a stable form of sulfur.[25] Thus, the chemical structure of PS, which is S_8, is more uniform, leading to narrowness in the peak

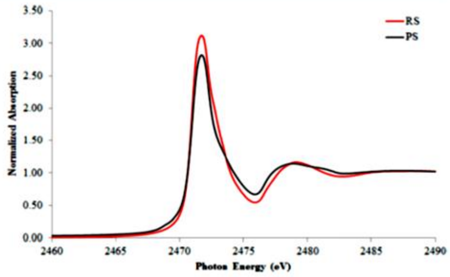

Figure 6. Sulfur K-edge XANES spectra of rhombic sulfur (RS) and petroleum-based sulfur (PS) powders, recorded in terms of total electron yield (TEY).

measured by XANES spectroscopy, as exhibited in Figure 6. Nevertheless, this slight difference in sulfur structure does not appear to influence the mechanical properties of rubber vulcanizates strongly, as demonstrated previously in Figures 2 and 3.

Figure 7 shows a comparison of the XANES spectra of NR samples vulcanized by RS and PS. The XANES spectra of the

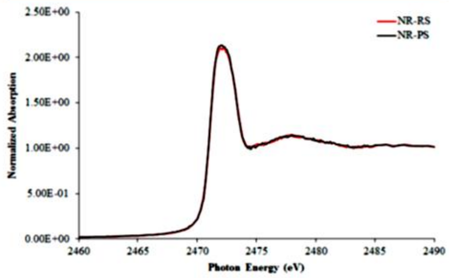

Figure 7. Sulfur K-edge XANES spectra of NR vulcanizates prepared with rhombic sulfur (RS) and petroleum-based sulfur (PS), recorded in terms of fluorescent yield (FY).

two samples are similar. The highest peak for each PS- and RS-vulcanized NR can be observed at 2472.2 eV, corresponding to the sulfur 1s → σ* (S−C) resonance, assigned to a polysulfidic cross-link.[15−18] Figures 8 and 9 present the XANES spectra of NBR and SBR samples, respectively. The results reveal that PS as the vulcanizing agent in both NBR and SBR shows similar spectral patterns to RS. These results agree well with the NR samples described previously in terms of the peak position. The maxima of the peaks can be observed at 2472.2 eV, corresponding to the polysulfidic cross-link. The XANES results provide clear evidence supporting the results for the mechanical properties of the rubber vulcanizates. The similarity in the sulfur chemical structures of RS and PS contributes to the comparable mechanical properties of rubber vulcanizates cross-linked with PS and RS.

There is also a weak peak at 2480.3 eV for NBR and at 2481.8 eV for SBR, not noticeable for NR. For NBR-RS and NBR-PS, the absorption peak appears at a photon energy of 2480.3 eV. This feature is attributed to a sulfonate group, as

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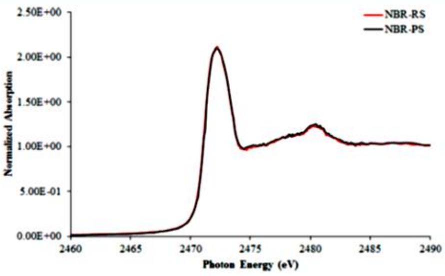

Figure 8. FY sulfur K-edge XANES spectra of NBR vulcanizates prepared with rhombic sulfur (RS) and petroleum-based sulfur (PS).

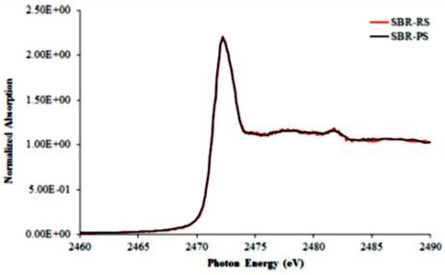

Figure 9. FY sulfur K-edge XANES spectra of SBR vulcanizates prepared with rhombic sulfur (RS) and petroleum-based sulfur (PS).

proposed in previous work.[16,17,26] Likewise, in the case of SBR-RS and SBR-PS, the absorption peak at 2481.8 eV corresponds to the sulfate groups.[16,17,26] These results are also in good agreement with those reported by Modrow et al.[16,17] Typically, these chemical groups are found in synthetic rubbers owing to the oxidative process of sulfur cross-linking, due to the presence of zinc in the compounds.[16,17]

Figure 10 presents a comparison of the sulfur 1s XANES spectra of the three types of rubber vulcanized by PS. It is evident that the three types of rubber exhibit differences in the white-line peak width and a slight shift in this peak position, even though the same type of sulfur was used. These differences might result from variations in the reactivity of sulfur in the cross-linked structure of rubber, independent of the sulfur source. These differences lead to different types of sulfur linkages, namely, mono-, di-, and polysulfidic linkages.[1−6,18] Apart from the reactivity of sulfur in rubber, the chemical groups surrounding the sulfur could play an important role in the absorption spectra.[27,28] Obviously, these results suggest that the XANES technique is efficient in determining the sulfur structure in rubbers.

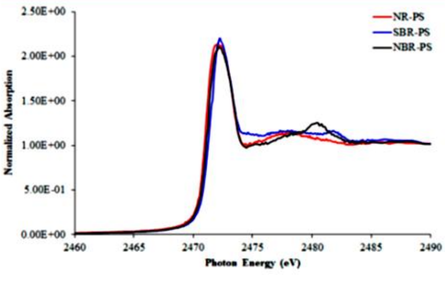

Figure 10. FY sulfur K-edge XANES spectra of PS-vulcanized specimens prepared with petroleum-based sulfur (PS).

The results for PS and RS show that the chemical structures of sulfur in the vulcanized rubbers are similar; therefore, PS has the potential for use as a vulcanizing agent for rubber as an alternative to RS. In other words, it is possible that the PS classified as by-product sulfur from petroleum refining could be used to substitute commercial rhombic sulfur (RS) in the rubber industry. This would increase the value of the PS as a petroleum refining by-product.

■ CONCLUSIONS

Synchrotron-based sulfur K-edge XANES spectroscopy has been employed to study the chemical structures of petroleum-based sulfur (PS) and commercial rhombic sulfur (RS), used as curing agents in a rubber vulcanization process. The results show that RS and PS have similar chemical structures. As evidenced by the results for the mechanical properties of various types of rubber, PS has a strong potential for use as a vulcanizing agent for both natural rubber (NR) and synthetic rubbers with high and low polarities. The present work suggests the possibility of substituting petroleum-based sulfur for commercial rhombic sulfur as a vulcanizing agent in the rubber industry.

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■ ABBREVIATIONS

FY = fluorescent yield
NBR = nitrile rubber
NR = natural rubber
PS = petroleum-based sulfur
RS = commercial rhombic sulfur
SBR = styrene−butadiene rubber
TBBS = *N-tert*-butyl-2-benzothiazole sulfonamide
TEY = total electron yield
XANES = X-ray absorption near-edge structure

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ZnO = zinc oxide

■ REFERENCES

(1) Hofmann, W. *Rubber Technology Handbook*; Hanser: Munich, Germany, 1989.
(2) Coran, A. Y. Vulcanization. In *The Science and Technology of Rubber*, 3rd ed.; Mark, J. E.; Erman, B.; Eirich, F. R., Eds.; Elsevier: San Diego, 2005; Chapter 7, pp 321−366.
(3) Ignatz-Hoover, F.; To, B. H. Vulcanization. In *Rubber Compounding: Chemistry and Applications*; Rodgers, B., Ed.; Marcel Dekker: New York, 2004; Chapter 11, pp 505−568.
(4) Datta, R. N. *Rubber Curing Systems*; Smithers Rapra Publishing: Akron, OH, 2002.
(5) Fisher, H. L. Vulcanization of Rubber. *Ind. Eng. Chem.* **1939**, *31*, 1381−1389.
(6) Vergnaud, J. M.; Rosca, I. D. *Rubber Curing and Properties*; CRC Press: Boca Roton, FL, 2009.
(7) Abi, S. A.; Kuruvilla, J.; Thomas, M.; Volker, A.; Sabu, T. Studies on Accelerated Sulphur Vulcanization of Natural Rubber Using 1-phenyl-2,4-dithiobiuret/tertiary butyl benzothiazole sulphenamide. *Eur. Polym. J.* **2003**, *39*, 1451−1460.
(8) Nehb, W.; Vydra, K.Sulfur. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Dec 15, 2006; available online at http://onlinelibrary.wiley.com/doi/10.1002/14356007.a25_507.pub2/full (accessed Jun 9, 2013).
(9) Chaudhuri, U. R. *Fundamentals of Petroleum and Petrochemical Engineering*; CRC Press: Boca Roton, FL, 2011.
(10) Polian, A.; Itie, J. P.; Dartyge, E.; Fontaine, A.; Tourillon, G. X-ray Absorption Spectroscopy on Solid Krypton up to 20 GPa. *Phys. Rev. B* **1989**, *39*, 3369−3373.
(11) Filipponi, A.; Di Ciico, A. Short-Range Order in Crystalline, Amorphous, Liquid, and Supercooled Germanium Probed by X-ray Absorption Spectroscopy. *Phys. Rev. B* **1995**, *51*, 12322−12336.
(12) Hitchcock, A. P.; Horsley, J. A.; Stöhr, J. Inner Shell Excitation of Thiophene and Thiolane: Gas, Solid, and Monolayer States. *J. Chem. Phys.* **1986**, *85*, 4835−4848.
(13) Prange, A.; Chauvistré, R.; Modrow, H.; Hormes, J.; Trüper, H. G.; Dahl, C. Quantitative Speciation of Sulfur in Bacterial Sulfur Globules: X-ray Absorption Spectroscopy Reveals at Least Three Different Species of Sulfur. *Microbiology* **2002**, *148*, 267−276.
(14) Rosolen, J. M.; Abbate, M. XANES and EXAFS of Chemically Deintercalated $LiCo_{0.5}O_2$. *Solid State Ionics* **2001**, *139*, 83−88.
(15) Chauvistré, R.; Hormes, J.; Brück, D.; Sommer, K.; Engels, H. W. Structural Analysis of Sulfur in Rubber by X-ray Near Edge Absorption Spectroscopy (XANES). *Kautsch. Gummi Kunstst.* **1992**, *45*, 808−813.
(16) Modrow, H.; Hormes, J.; Visel, F.; Zimmer, R. Monitoring Thermal Oxidation of Sulfur Crosslinks in SBR-Elastomers by Quantitative Analysis of Sulfur K-Edge XANES Spectra. *Rubber Chem. Technol.* **2000**, *74*, 281−294.
(17) Modrow, H.; Zimmer, R.; Visel, F.; Hormes, J. Monitoring Thermal Oxidation of Sulfur Crosslinks in SBR-Elastomers Using Sulfur K-Edge XANES: A Feasibility Study. *Kautsch. Gummi Kunstst.* **2000**, *53*, 328−337.
(18) Pattanasiriwisawa, W.; Siritapetawee, J.; Patarapaiboolchai, O.; Klysubun, W. Structural Analysis of Sulfur in Natural Rubber Using X-ray Absorption Near-Edge Spectroscopy. *J. Synchrotron Radiat.* **2008**, *15*, 510−513.
(19) Taweepreda, W.; Limphirat, W.; Songsiririthigul, P. Oxidative Degradation Monitoring of Natural Rubber Using S K-Edge X-ray Absorption Near-Edge Spectroscopy (XANES). *Adv. Mater. Res.* **2013**, *620*, 440−445.
(20) Sperling, L. H. *Introduction to Physical Polymer Science*, 4th ed.; John Wiley & Sons, Inc.: New York, 2006.
(21) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12*, 537−541.
(22) Toki, S.; Hsiao, B. S.; Kohjiya, S.; Tosaka, M.; Tsou, A. H.; Datta, S. Synchrotron X-ray Studies of Vulcanized Rubbers and Thermoplastic Elastomers. *Rubber Chem. Technol.* **2006**, *79*, 460−488.
(23) Hofmann, W. *Vulcanization and Vulcanizing Agents*; MacLaren and Sons: London, 1967.
(24) Steudel, R.; Eckert, B. Solid Sulfur Allotropes. *Top. Curr. Chem.* **2003**, *230*, 1−79.
(25) Speight, J. G. *Handbook of Petroleum Product Analysis*; John Wiley & Sons: New York, 2002.
(26) Wang, M.; Hu, Y.; Wang, J.; Chang, L.; Wang, H. Transformation of Sulfur During Pyrolysis of Inertinite-Rich Coals and Correlation with Their Characteristics. *J. Anal. Appl. Pyrol.* **2013**, *104*, 585−592.
(27) Chauvistré, R.; Hormes, J.; Hartmann, E.; Etzenbach, N.; Hosch, R.; Hahn, J. Sulfur K-Shell Photoabsorption Spectroscopy of the Sulfanes $R{-}S_n{-}R$, $n = 2{-}4$. *Chem. Phys.* **1997**, *223*, 293−302.
(28) Hay, S. J.; Metson, J. B.; Hyland, M. M. Sulfur Speciation in Aluminum Smelting Anodes. *Ind. Eng. Chem. Res.* **2004**, *43*, 1690−1700.

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Pangamol, P.; Sae-oui, P.; Sirisinha, C. Potential Use of Petroleum-based Sulfur in Rubber Industry. 11th Eco-Energy and Materials Science and Engineering Symposium (11th EMSES), Phuket, Thailand, December 18 – 21, 2013. (This manuscript was selected to be published in Energy Procedia Special Issue)

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PUBLICATION

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Pangamol, P.; Sirisinha, C. Use of By-product Sulfur from Petroleum Refinery as Vulcanizing Agent in Natural Rubber. *Chiang Mai Journal of Science.* **Submitted.**

Pangamol, P.; Sae-oui, P.; Sirisinha, C. Dispersion Enhancement of Petroleum-based Sulphur in Natural Rubber by TDAE oil Coating Technique. *Plast. Rubber. Compos.* **Submitted.**