11th Eco-Energy and Materials Science and Engineering (11th EMSES)

Potential use of petroleum-based sulfur in rubber industry

Pathompong Pangamol[a], Pongdhorn Sae-oui[b], Chakrit Sirisinha[a,c]*

a Department of Chemistry and Center of Excellence for Innovation in Chemstry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
b National Metal and Materials Technology Center, 114 Thailand Science Park Paholyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand
c Rubber Technology Research Centre (RTEC), Faculty of Science, Mahidol University Salaya Campus, Nakhon Pathom 73170, Thailand

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.

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

---

* Corresponding author. Tel.: +66-2441-9816-20 ext. 1142; fax: +66-2441-0511.
  E-mail address: chakrit.sir@mahidol.ac.th

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

2.1 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].

2.2 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

2.3 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.

2.4 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].

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

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.

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

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. 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].

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

3. Results and discussion

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 (x10^{-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.
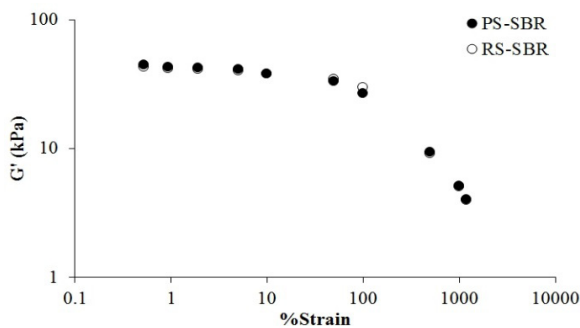

Fig. 1. Viscoelastic properties of SBR compounds incorporated
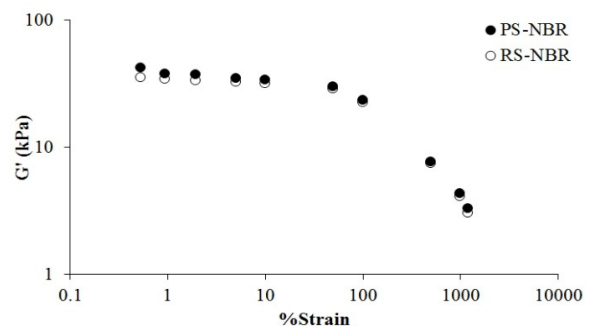

Fig. 2. Viscoelastic properties of NBR compounds incorporated with

with different sulfurs   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.
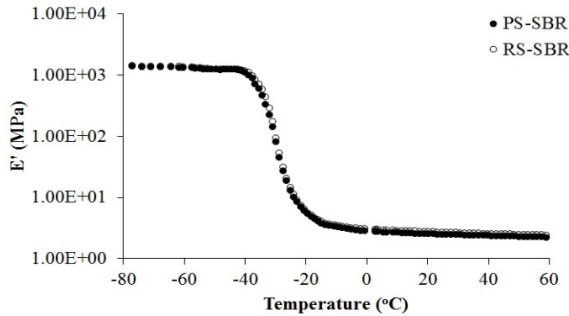
Fig. 3. Storage modulus of SBR vulcanizates incorporated with different sulfurs
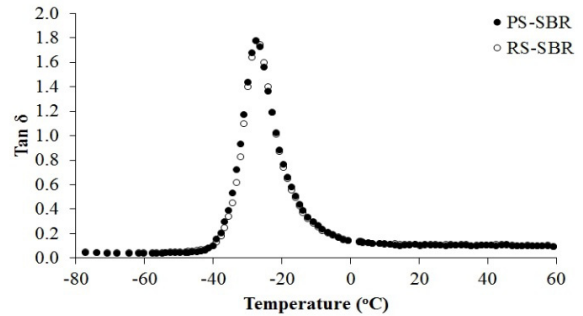
Fig. 4. Tan δ of SBR vulcanizates incorporated with different sulfurs
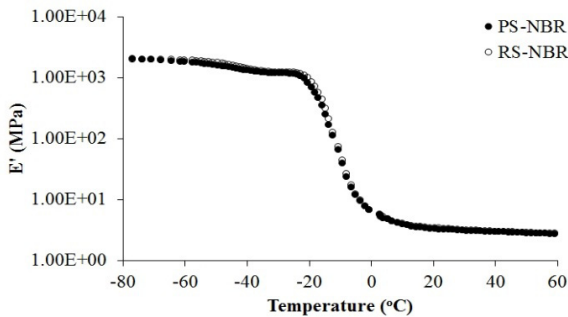
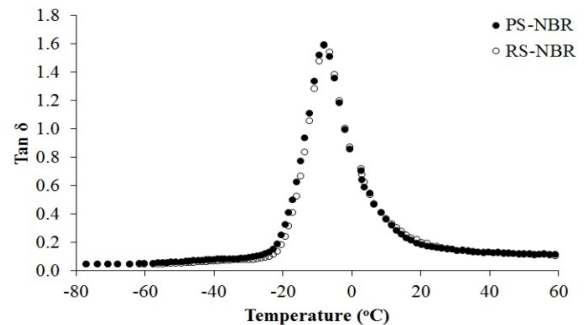Fig. 5. Storage modulus of NBR vulcanizates incorporated with different sulfurs

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.
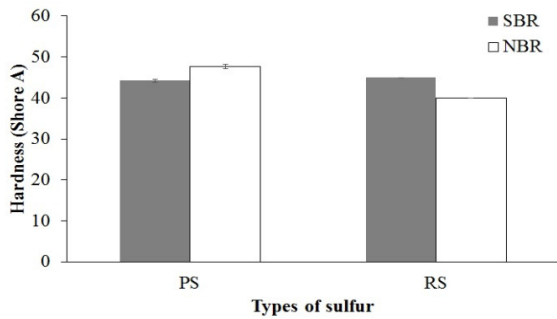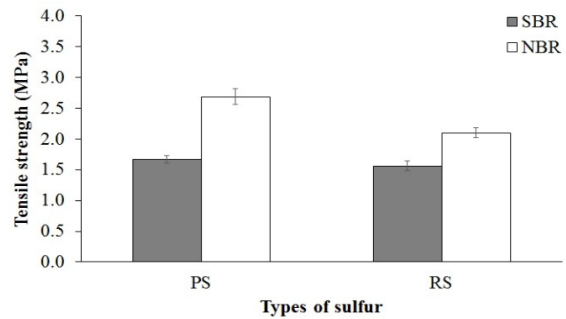
Fig. 7. Hardness of vulcanizeates
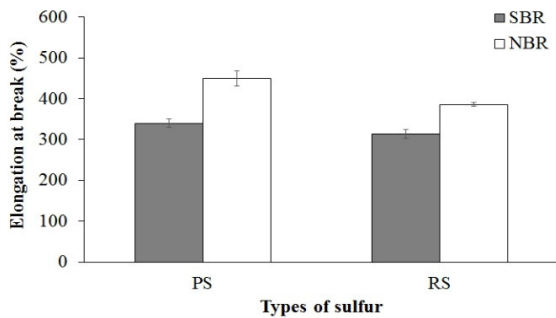

Fig.8. Tensile strength of vulcanizates

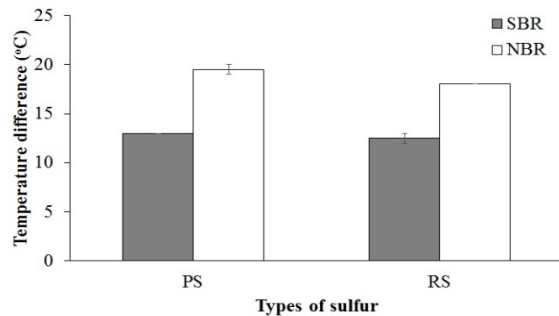Fig. 9. Elongation at break of vulcanizates

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.

Acknowledgements

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. *J. Appl. Polym. Sci.* 2001; **79**(1): 1-8.
[6] Debnath SC, Mandal SK, Basu DK. *J. Appl. Polym. Sci.* 1995; **57**(5): 555-562.
[7] Aprem AS, Joseph K, Mathew T, Altstaedt V, Thomas S. *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. *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, Hu Y, Urquhart SG. *Ind. Eng. Chem. Res.* 2013; **52**: 17179-17183
[16] Zhan Y, Wu J, Xia H, Yan N, Fei G. Yuan G. *Macromol. Mater. Eng.* 2011; **296**(7): 590-602.