PROPERTIES OF SULPHUR IN COLLOIDAL SYSTEM: A REVIEW

MOHAMAD FIRDAUS OMAR[1, 2], NURIAH MOHAMAD[2], AZLIN SUHAIDA AZMI[1] AND FATHILAH ALI[1]*

[1]*Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia.*

[2]*Top Glove Sdn. Bhd., R&D Centre, Lot 64593, Jalan Dahlia KU/8, 41050 Klang, Selangor.*

**Corresponding author: fathilah@iium.edu.my*

ABSTRACT: Sulfur has been highly sought by many industries everywhere around the world for various applications. This exceptionally useful element has been largely manufactured especially in powder form each year reflecting its increase in demand in line with technological advancement and uses for various product applications. The manufacturing processes include mining as well as chemical reactions in Claus Process. Rubber industries normally use abundance of sulfur in their latex compound to introduce vulcanization. The geneal concern of sulfur for rubber vulcanization is dispersibility in the rubber matrix due to improper optimization of its preparation process prior to latex compounding. Another crucial issue is crystallization of soluble sulfur from its insoluble origin, either during or post-rubber vulcanization that constitutes to formation of sulfur bloom that grows on the surface of the rubber articles. It is known that both issues are related to the process conditions and compounding recipe that could not be fully solved. Various studies have been conducted to minimize such occurences – from process optimization to sulfur chemistry itself – and of continuous improvement and innovation to solve various threats in sulfur applications. This paper reviews on detailed description on elemental sulfur, of respective industrial applications, and most importantly highlights on sulfur trends and issues normally encountered.

KEY WORDS: *sulfur; vulcanizing agent; dispersion; soluble; sulfur bloom;*

1. INTRODUCTION

The earth is richly equipped with various chemical elements in different regions in land and in the sea. As the elements naturally exist, their usage is exceptionally important for living things. Examples of elements include carbon, oxygen, zinc, magnesium, calcium and so much more. Sulfur (S) is one of the elements abundantly present in bulk on the earth – both naturally and by chemical means – and its usage is exceptionally important in different industrial applications.

Today, in some regions of the world, sulfur (S) (in its powder or derived form) or interchangeably spelled as sulphur, has been widely manufactured and used in many industrial applications [1,2]. United States of America (US) was the largest producer of elemental sulfur in the world, followed by Canada, in 2013. Apparently, China increased its sulfur production until the year 2015, then continued throughout until 2018 and became the world's largest manufacturer of sulfur [3]. Figure 1 shows the graph of sulfur production from the year 2013 to 2018, by country.

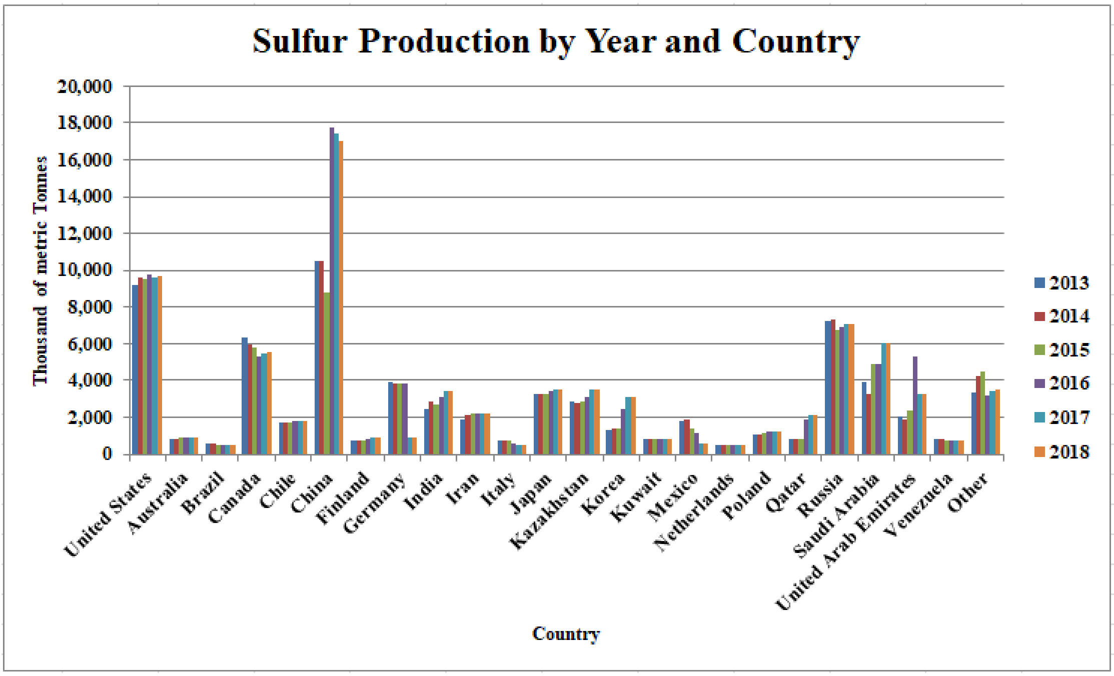

Fig. 1. Sulfur production by year and country (2013 until 2018) [4]

Kurtney added that Canada has never manufactured sulfur through the antique mining process [3]. Apparently, Canadian sulfur originates from the gas purification process in petroleum, coal and oils industries. In relation to this, around 9,000,000 tons/year of sulfur are recovered from the gases produced via metal ores processes in the US. Upon removal of hydrogen sulfide (H_2S) from the complex mixture of organic compounds, the compound will then be converted into sulfur, which derivatively known as Claus process. The process involves hydrogen sulfide burning to become sulfur dioxide (SO_2) with additional reaction of those two to produce sulfur as element. Thus, the dominance and abundance sources of sulfur obtained today are the results of the recovered sulfur from the process [5,6]. Figure 2.2 summarizes the Claus process used to yield sulfur element.

Based on Figure 2, in the burner, H_2S is partially oxidized to produce water (H_2O) and SO_2 from the burner. Consequently, the burner product SO_2 reacts with the excess H_2S in the reactor converter in order to produce final product sulfur element together with water as its side product. Precisely, the final products should ideally consist only of sulfur element and water without the presence of H_2S or SO_2 compound, as summarized in below reaction equation [6,7].

Main reaction inside the burner: $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$

Main reaction inside the reactor and converter: $2H_2S + SO_2 \rightarrow 2H_2O + 3\mathbf{S}$

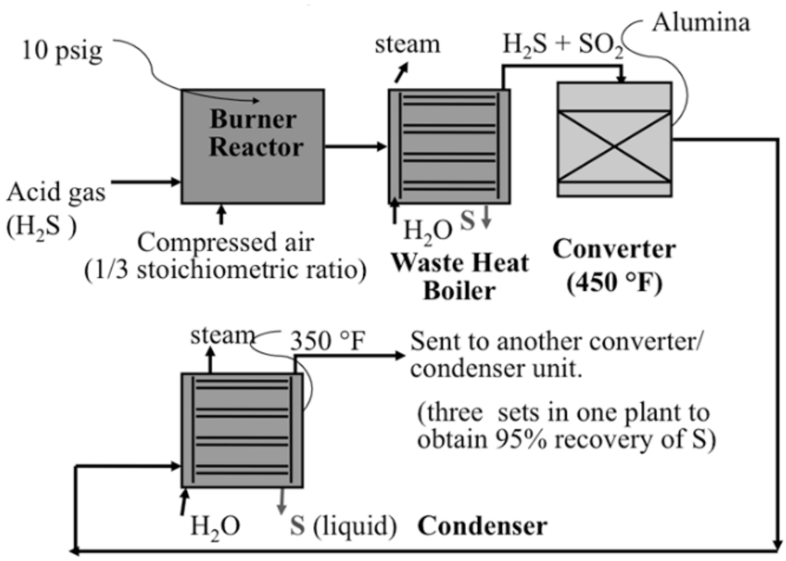

Fig. 2. Claus process used to yield sulfur element [7]

2.0 Properties of Sulfur

Basically, sulfur is an element with S as atomic symbol and with atomic number of 16. At room temperature, it is a yellow crystalline solid. It is a crucial element in all living things and is in the organic molecules of all fossil fuels. Plus, elemental sulfur does not only occur naturally in its underived form or in a variety form of derived minerals – i.e. sulfides or sulfates, that contains sulfur but it also can be produced such as those in petroleum industry's by-product, mainly from the process called hydro-desulfurization [8]. Although sulfur is insoluble in water, it is considered as one of the most versatile elements at forming compounds [9]. However, sulfur cannot react with gold, platinum, tellurium, and other inert gases to form a compound [5]. Table 1 shows the general properties of sulfur element in nature.

Preferentially under normal ambient conditions, orthorombic sulfur represented in the form of an S_8 ring, is the form of sulfur that is the most stable thermodynamically form of sulfur. When introduced to heat and under atmospheric pressure, the orthorhombic sufur S_8 will be eventually converted into monoclinic S_8 at 95.6 °C. Prolong introduction of heat towards the S_8 rings will contribute in the melting of solid state sulfur – which mainly are S and S residual crystals that eventually will be directed towards obtaining a yellow liquid S at a melting point temperature of near 119 °C. This S will consist abundance of S_8 rings. A deep-red liquid sulfur from S_8 monomer rings may be obtained at temperatures above 159 °C that will be able to form polymeric sulfur, S_w from the ring-opening polymerization (ROP) process that eventually polymerize the formed diradicals of linear sulfur. From here, immediate quenching of the polymerized sulfur at ambient temperature will form another classification of sulfur product called "plastic sulfur". The sulfur-polymer product apparently contains unreacted sulfur, S_8 as well as some ratio of insoluble sulfur (IS) that over the time this product will become brittle and employs low mechanical properties as a result of the depolymerization process of the polymeric phase that leads to the re-formation of S_8 rings and consequent recrystallization of S_8 to orthorhombic form, S [8,10,15].

Table 1: Basic properties of sulfur element [5], [9]

Chemical Classification	Native Element
Chemical Composition	S
Atomic Number	16
Atomic Weight	32.064
Mohs Hardness	1.5 to 2.5
Specific Gravity	2.0 to 2.1
Boiling Point	444.6 °C (832 °F)
Oxidation States	−2, +4, +6
Electron Configuration	$1s^2 2s^2 2p^6 3s^2 3p^4$
Color	Yellow. Brownish yellow to greenish yellow. Red when molten at over 200 degrees Celsius. Burns with a flame that can be difficult to see in daylight but is blue in the dark.
Luster	Crystals are resinous to greasy. Powdered sulfur is dull or earthy.
Diaphaneity	Transparent to translucent
Diagnostic Properties	Yellow color, low hardness, low specific gravity, extremely flammable burning with a blue flame, low melting temperature
Crystal System	Orthorhombic

However, the insoluble sulfur may be stabilized during polymerization process when the sulfur diradicals are synthesised in a high thermal condition which is via copolymerization of elemental sulfur with unsaturated organic compounds such as dicyclopentadiene, styrene or limonene via a bulk copolymerization process that will eventually lead to sulfur/organic copolymers synthesis that is currently being sought for a lot of advanced material applications. [2, 8, 10, 12].

2.1 Sulfur Usage

In relation to the previous explanation on sulfur, Table 2 summarizes the different forms of sulfur used for different industrial applications those of which found in the literature with their respective usage. As summarized in Table 2, it can be seen that a lot of researches and findings have been done for different kinds and forms of sulfur element in different industries deemed to suit with respective sulfur applications. Precisely, one of the most commonly use of sulfur is as vulcanizing agent in rubber when in dispersion or colloidal form.

2.1.1 Sulfur Dispersion as Rubber Vulcanizing Agent

Generally, amorphous and cyclic or orthorhombic S_8 sulfur are two basic kinds of sulfur for rubber vulcanizing agent, while other kinds of chemicals prior to vulcanizing also includes selenium, tellurium, thiuram disulfides, peroxides, oxides metal, as well as quinone dioxides. Typically, the solids content for sulfur dispersion or colloid is around 30 to 60% and the dispersion must be ball-milled to undergo reduction in its particle size as well as to stabilize the dispersed solids in their suspension manner. The sulfur solids are normally mixed with surfactants or emulsifiers at significant dosage to make them dissolve in water to ensure better dispersion of the solids [20-22].

Vulcanizing agents can be defined as a chemical which must be there in a process to initiate chemical reaction, in terms of cross-linking of the elastomer molecules. At a significant temperature, vulcanizing agent will form stable covalent carbon-carbon double bonding when it is used together with an accelerator and activator. Sulfur is considered the most frequent used vulcanizing material for rubber but it must contain around 99.5% purity with considerably not more than 0.5% ash content [23,24].

2.1.2 Issues with Sulfur in Rubber System and Causes

Often, sulfur is prepared as colloid or dispersion via mixing and/or chemical grinding process that will produce fine sulfur particle size that rarely settle or sediment that is suitable to be used in latex compounds. Several studies have been done with different sulfur types and optimal ball-milling process conditions that is proven could comparatively give obvious changes in rubber vulcanizates‘ mechanical properties [19]. Thus, it is suggested that improper optimization of process conditions such as ball-milling to effectively reduce the particle size and/or their distributional behaviour could remarkably affect its stability or dispersibility in the rubber matrix.

Another crucial aspect to look at is solubility of sulfur inside the rubber system. It is important to understand the sulfur distribution between rubber and the best solvent for the sulfur in which rubber is insoluble. As such, it is necessary to optimize the recipe with process conditions i.e. temperature and time, upon blending of sulfur inside the rubber matrix with other compound ingredients. Typically, insoluble sulfur type is preferebaly used over soluble sulfur as a solution to overcome or hinder “sulfur blooms” issue in unvulcanised rubber. This blooming can minimize the adhesion of rubber to the adjacent layer of rubber or substrate and consequently hinders the performance of the resulting molded rubber articles. Upon mixing of the compound ingredients which include insoluble sulfur, complete dissolution normally is achievable because the mixing temperature is high enough to melt sulfur and to prevent crystallization. However, when subjected to actual processing at industrial practice, normally unexpected blooms still occur due to the revertion of insoluble sulfur to the orthorhombic soluble sulfur well before the rubber is cured. Eventually, the sulfur supersaturates the rubber when the stock is cooled at long period of time and thus the soluble portion of the sulfur forms crystals within the bulk rubber and initiates growth towards the surface and crystallize there due to the lack of interference. As such, a lot of literatures and patents proposed on inhibiting or minimizing such blooming events studies, which comprises of process study in rubber compound blending temperature and time effects on sulfur bloom; and as well towards chemistry studies such as new sulfur products which are treated or reacted with olefin/ unsaturated hydrocarbons, or interpolymers/copolymers or special surfactants and additives; optimizing on recipe and dosage that constitutes to sulfur vulcanization i.e. fillers, carbon black and accelerators; and so on [25-31].

Table 2: Different forms of sulfur, industry applications and their usage

Form of Sulfur	**Industry**	**Remarks**
Methylsulfonylmethane (MSM)	Medicine	Treatment of allergy, pain syndromes, athletic injuries, and bladder disorders [16].
Sulfonamide (organo-sulfur compounds)	Pharmaceutical	As an antibacterial drug [16].
Sulfur Concrete	Building	Applied both for non-reinforced elements (weights, channels, drainage elements) and for reinforced elements (tanks, plates). To the wide range of usage, can also add its usefulness in renovations works (coatings with fiber extenders) and restoration works [17].
High Volatile Sulfur Compounds (HVFCs) such as dimethylsulfur (DMS), dimethyldisulfur (DMDS), dimethyltrisulfur (DMTS)	Biotechnology	As fundamental for the characterization and definition of the wine sensory properties, obtained throughout the fermentation of strains of S. *cerevisiae* [18].
Petroleum-based Sulfur (PS) in Dispersion/Slurry form	Rubber	The ground PS (GPS) exhibits significant improvement in mechanical properties of rubber vulcanizates to be comparable to the conventional rhombic sulfur [19].

2. CONCLUSIONS

Sulfur production over the world is considerably increasing over the past years to date, reflecting its high demand by different industrial applications. The sulfur element may undergo many distinguish processes to yield different forms of sulfur that are deemed suit for the end-user's respective usage objective. Additionally, tackling issues with sulfur especially on the sulfur bloom as in rubber vulcanization is crucial to maintain the quality of their end-products. Rubber industry has been considerably consuming abundance of sulfur in their production, during the compounding of the latex. Promising studies are possible to be done so as to highly utilize the exceptionally precious sulfur element without wastages.

ACKNOWLEDGEMENT

The authors would like to thank IIUM Faculty of Engineering and Department of Biotechnology Engineering for the supports in accomplishing this review article.

REFERENCES

[1] W. Nehb and K. Vydra, “Vol. 35 Sulfur,” *Ullmann’s Encycl. Ind. Chem.*, pp. 5–71, 2012.

[2] L. Blight, B. R. Currell, B. J. Nash, R. A. M. Scott, and C. Stillo, “Preparation and Properties of Modified Sulfur Systems,” no. 3, pp. 13–30, 1978.

[3] G. Kutney, *Sulfur. History, Technology, Applications & Industry*, 2nd ed. Toronto: ChemTec Publishing, 2013.

[4] U.S. Geological Survey, *Mineral Commodity Summaries 2019*, vol. 3. U.S. Geological Survey, 2019.

[5] R. C. Brasted, “Sulfur | Definition, Properties, Uses, & Facts,” *Encyclopedia Britannica*. Encyclopaedia Britannica, Inc., 2019.

[6] J. S. Eow, “Recovery of sulfur from sour acid gas: A review of the technology,” *Environ. Prog.*, vol. 21, no. 3, pp. 143–162, 2002.

[7] S. Eser, “Modified Claus Process,” pp. 2–5, 2018.

[8] J. Wręczycki, D. M. Bieliński, and R. Anyszka, “Sulfur/organic copolymers as curing agents for rubber,” *Polymers (Basel).*, vol. 10, no. 8, 2018.

[9] H. M. King, “Sulfur: Chemical Element. Native Mineral. Essential to All Living Things.,” *Geology and Earth Science News, Articles, Photos, Maps and More.*, 2005. [Online]. Available: https://geology.com/minerals/sulfur.shtml.

[10] W. J. Chung *et al.*, “The use of elemental sulfur as an alternative feedstock for polymeric materials,” *Nat. Chem.*, vol. 5, no. 6, pp. 518–524, 2013.

[11] H. Colvin and C. B. Jr., “Sulfur/Olefin Copolymers as Vulcanizing Agents for Rubber,” *Rubber Chem. Technol.*, vol. 68, pp. 746–756, 1995.

[12] B. R. Currell, A. J. Williams, A. J. Mooney, and B. J. Nash, “Plasticization of Sulfur.,” *Adv Chem Ser*, vol. 140, pp. 1–17, 1974.

[13] A. H. Johansson, Y. Pa, S. K. Flanders, Woodstock, and Ill, “Rubber Vulcanizing Agents Comprising Reaction Products of Sulfur and Unsaturated Hydrocarbons,” 4752507, 1988.

[14] G. Rosen and W. D. Helmer, “Vulcanizing Agent Prepared from Sulfur, Linseed Oil and Dicyclopentadiene,” 3264239, 1966.

[15] J. Schenk, “On the Molecular Constitution of Liquid and Amorphous Sulfur,” *Phys. XXIII*, pp. 546–550, 1957.

[16] Z. Haque, T. Ahmed, D. Mand, K. Asma, M. Rumman, and A. Alam, “Gandhak (Sulphur) and its medicinal importance described in Unani Medicine : Mini review,” vol. 4, no. 4, pp. 191–192, 2015.

[17] N. Ciak and J. Harasymiuk, “Sulphur concrete’s technology and its application to the building industry,” *Tech. Sci. / Univ. Warm. Maz. Olsztyn*, vol. nr 16(4), no. 4, pp. 323–331, 2013.

[18] F. Patrignani *et al.*, "Production of volatile and sulfur compounds by 10 Saccharomyces cerevisiae strains inoculated in trebbiano must," *Front. Microbiol.*, vol. 7, no. MAR, pp. 1–11, 2016.

[19] P. Pangamol, P. Sae-Oui, and C. Sirisinha, "Use of by-product sulfur from petroleum refinery as vulcanizing agent in natural rubber," *Chiang Mai J. Sci.*, vol. 43, no. 3, pp. 569–576, 2016.

[20] M. Porter, R. Rawi, and S. A. Rahim, "Chemistry of the latex prevulcanization process. Part 1. Migration of reactants from the solid phase into rubber particles.," *J. Nat. Rubber Res.*, vol. 7, no. 2, pp. 85–101, 1992.

[21] T. F. Tadros, *Polymeric Surfactants : Dispersion Stability and Industrial Applications*. 2017.

[22] K. Landfester, *Polymer Dispersions and Their Industrial Applications*, vol. 204, no. 3. 2003.

[23] Y. K. Peng, "The Effect of Carbon Black and Silica Fillers on Cure Characteristics and Mechanical Properties of Breaker Compounds," University Science Malaysia, 2007.

[24] C. X. Viet, "Curing Characteristics , Mechanical Properties and Morphology of Surface Modified Montmorillonite Filled Natural Rubber Nanocomposites," *Curing Charact. Mech. Prop. Morphol. Surf. Modif. Montmorillonite Fill. Nat. Rubber Nanocomposites*, p. 113, 2008.

[25] G. B. Brands, Wilmette, and I. (US), "Stabilized Dispersion of Insoluble Sulfur and Method of Stabilizing," US6291569B1, 2001.

[26] B. Rodgers, *Rubber Compounding: Chemistry and Applications*. New York: Marcel Dekker, Inc., 2004.

[27] C. Aziz, Y.B. ; Hepbrun, "Problems of Bloom Experienced When Insoluble Sulphur is used in Natural Rubber," *Journal of the Rubber Research Institute of Malaysia*, vol. 2, no. 2. pp. 57–67, 1979.

[28] B. Jurkowski and B. Jurkowska, "On the Mechanism of Sulfur Behavior in Rubber Compounds," *J. Macromol. Sci. - Phys.*, vol. 37, no. 2, pp. 135–142, 1998.

[29] "Behaviour of Sulphur in Rubber," *Nature Publishing Group*, vol. 150, no. 3792. Nature Publishing Group, p. 31, 1942.

[30] W. J. Kelly and K. B. Ayers, "The Solubility of Sulphur in Rubber," *Ind. Eng. Chem.*, vol. 16, no. 2, pp. 1922–1924, 1924.

[31] M. N. Katun, "Non-Sulphur Vulcanization Of Rubber - A Brief Overview," *J. Teknol.*, vol. 25, no. 1, pp. 19–25, 1996.