SiO₂ Reinforcement of Mechanical Properties for Ebonite from Natural Rubber

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Abstract—To reinforce the mechanical properties of the rubber compounds, the silica was added. In this work, we measured the tensile strength and hardness of the compounds, in which the amounts of sulphur and silica were varied from 45 to 60 phr and 5 to15 phr, respectively. The experimental results showed that the addition of 10 phr silica 10 provides the maximum tensile strength and hardness. However for the amount of silica higher than 10 phr, the tensile strength tended to decrease. We also observe that the amount of sulphur 60 phr with 10 phr silica gives the maximum hardness (73 shore D).

Index Terms—Natural rubber, silica, ebonite, hard rubber, sulphur vulcanization.

I. INTRODUCTION

Hard rubber or Ebonite was rubber vulcanization processed with high amount of sulphur (30-50%). The Ebonite has a glass transition temperature (T_g) higher than the room temperature. It has structured network and high hardness but it is brittle, flammable, non-toxic, high resistant to chemicals, good electrical insulating properties, excellent strength properties, and able to manufacture. The hard rubber is used as storage tanks, reaction vessels, and pump linings [1]. However, hard rubber is produced from natural rubber (NR), styrene-butadiene rubber (SBR), and nitrile-butadiene rubber (NBR).

The natural rubber or Para rubber is very important to the economy of Thailand. The Natural rubber latex has typical composition are skim latex (total solid. content, TSC) is approximately 36 %, water about 60 % by weight rubber (dry rubber content, DRC about 33 %), protein about 1.5%, resin compounds about 1.5 %, Ash is approximately 1 % and Others, such as amino acids, lipids, phospholipids about 1.60 %. The outstanding mechanical properties of natural rubber, such as elasticity and tear resistance. There are more than synthetic rubber from petrochemical industry but natural rubber is easily degraded when exposed to sunlight, heat or non-polar organic solvents. Therefore, natural rubber usages required a modification process to improve its properties and reduce its defects [2]-[6]. However, the use of a natural rubber products is limited due to low physical stability. Therefore in order to improve the mechanical properties such as tensile strength, tear strength, abrasion resistance, stiffness, and hardness of rubber products, fillers were added into natural rubber. The most commonly-used fillers in the rubber

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W. Nattawat and P. Narupon are with the Operation Propulsion System, Research and Development Department, Defence Technology Institute (Public Organization) Ministry of Defence, Thailand (e-mail: nattawat.w@dti.or.th). industry are carbon black and silica, clay, carbon nano-fiber, and mica [7]-[11]. Silica is widely used as reinforcing fillers because it has a high specific surface area and performance to improve the mechanical properties of composite rubber.

Silica is an amorphous material composed of silicon and oxygen atoms connected with silanol (Si-OH) both inside and on the surface. We would like to note that during the mixing process, the chemical reaction occurs between aggregates of silica and natural rubber chains. To avoid the complications, a silane coupling agent is needed to improve silica-rubber interaction and silica dispersion as well as to prevent accelerator adsorption on the silica surface [12]-[16].

Liangliang Qu et al. studied synergistic reinforcement of nanoclay and carbon black in natural rubber. the result revealed that the marked enhancement in tensile strength from 11.4 Mpa for NR to 28.2 MPa for NR composite with 5 wt% nanoclay and 20 wt% carbon black [17]. Sung-Seen Choi found that influence of the modification of silica on reaction behaviors of natural rubber vulcanizates reinforced with silica and carbon black were vulcanizates containing silane coupling agent recovered faster than those without the silane coupling agent. Rattanasom et al. investigated the mechanical properties of natural rubber reinforced with silica/carbon black hybrid filler at vaarious ratios in order to determine the optimum silica/carbon black ratio found than the vulcanizates containing 20 and 30 phr of silica in hybrid filler exhibit the better overall mechanical properties. Hsuen-Huan and Chi-Fang Chu studied Influence of clay, silicate and carbon black on the environmental resistance properties of hard rubber. The result the carbon black has the best hardness and resistivity stability after the immersion test [18].

The objective of this paper is to investigate the influence the mixing amounts between mixing sulphur and silica on the properties of the rubber compound. The composite rubber investigated contains 45, 50, 60 phr of sulphur and 5, 10 and 15 phr of silica. The properties tensile strength and hardness are measured.

II. MATERIALS AND METHODS

A. Materials

NR (natural rubber, STR 5L), Silica (VN-3), Fiber (Aramid-pulp), Antioxidant (Winstay S), Flame retardant (Dechlorane Puls 515), Antimony Oxide, stearic acid, Silane, Sulphur and oil.

B. Measurements

The mechanical properties were measured by tensile TECH 91202 serial no.TBD-2730 according to JIS K6251.

The hardness (Shore D) was measured by Teclock GS-706N according to JIS K6268.

The density measured by METTLER TOLEDO (XS204) according to JIS K6268.

The curing times (t_{90}) of the compounds were obtained by EKTRON at 170 °C.

The compounds were subsequently compression molded by GOTECH (GT-7016) at 170 °C, beased on the respective t_{90} values.

C. Preparation of Compound Rubber

Preparation of compound formulations are natural rubber was mixed at a temperature of 50 °C. Non-vulcaized ebonite composite containing antimony oxide, flame retardant, stearic acid, Silica and silane coupling agents is given in Table I. The composite rubber investigated contains 45, 50, 60 phr of sulphur and 10 and 15 phr of silica. After that will study Curing Characteristics and Mechanical Properties and optimum curing time (tc_{90}) were observed for the reinforced blends. The 50S-10SiO₂ system demonstrated an optimal curing time. The initial decrease in torque.

Fig. 1. displays the maximum torque (M_H) of hard rubber compounds filled with various silica. It was interesting to find out the maximum torque not much different when silica increased in hard rubber compound with sulphur 40, 50 and 60 phr, respectively. However, the maximum torque values of all the samples are higher than soft rubber. The initial decrease in torque is due to the softening of the matrix. The torque then increased due to the crosslinking between the molecular chains. Crosslinks are formed between the unsaturated sites and molecules during vulcanization. The maximum torque increases proportional to the sulphur content, indicating crosslink density enhancement

III.	RESULTS AND DISCUSSION

Table II shows that the curing characteristics of all hard rubber samples. The experimental results show that amount of silica have no significant effect on M_L (minimum torque), t_{s2} (scorch time) and t_{90} (optimum cure time). The table also shows the curing characteristics of the hard rubber under investigation. Regular variations in the maximum torque (Mh)

TABLE II: CURING CHARACTERISTICS OF H	ARD RUBBER
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sample	<i>M</i> _L (Kgf-cm)	M_H (Kgf-cm)	<i>t</i> _{s2} (min)	<i>t</i> ₉₀ (min)	CRI
45S-10Si	7.33	15.88	4.12	12.22	12.3
50S-10Si	9.85	38.84	4.02	11.56	9.5
60S-10Si	8.49	33.78	1.11	11.56	9.6
45S-15Si	6.83	15	3.42	13.59	9.8
50S-15Si	5.47	11.76	4.05	13.5	10.6
60S-15Si	9.07	35.65	1.08	11.26	9.8

TABLE I: THE COMPOUND FORMULATIONS

Raw material and ingredients (phr)	45S-10Si	50S-10Si	50S-10Si	50S-10Si	50S-10Si	50S-10Si
NR	100	100	100	100	100	100
Fiber	20	20	20	20	20	20
Antioxidant	2	2	2	2	2	2
Flame Retardant	40	40	40	40	40	40
Antimony Oxide	20	20	20	20	20	20
filler (Silica)	10	10	10	15	15	15
Stearic acid	1	1	1	1	1	1
Silane	1	1	1	1	1	1
Sulphur	45	50	60	45	50	60
oil	5	5	5	5	5	5



Fig. 1. Maximum torque (M_H) of hard rubber compounds.

The tensile strength of all vulcanizes is shown in Fig. 2. As expected, amounts of sulphur 60 phr give the highest tensile strength while tensile strength of sulphur 40 phr lowest tensile strength when 10 phr of silica is added to the NR. The decrease in tensile strength with silica loading 15 phr occurs because the agglomerate of silica particles

which become difficulty in the flow of molecules of rubber vulcanizes during deformation.

Fig. 3 shows the elongation at break of hard rubber as a decrease elongation at break when increase amount of silica loading. The optimum silica content in hard rubber samples is 10 phr. The tear strength of all vulcanizes is shown in Fig. 4.



Fig. 2. Tensile strength of hard rubber.



Fig. 3. Elongation at break of hard rubber.



Fig. 4. Tear strength of hard rubber.

The tear strength of all vulcanizes is shown in Fig. 4. The 60S-10Si is showing maximum tear strength. This is in exact correlation with the chemical crosslink density values Fig. 5 shows hardness of all vulcanizes is The hardness increase noticeably when increase amount of sulphur loading. However, the ebonite rubber comprising has a Shore D hardness in the range of 70 to 100. In addition, the results show that 60 phr of sulphur is required for vulcanizes to reach highest hardness of hard rubber decrease when increase amount of silica loading.



IV. CONCLUSION

These results showed that the addition of silica 10 phr to the tensile strength and hardness highest. However, Such properties tend to decrease when the amount of silica is higher than 10 phr was the result of a constant process with sulphur found that the amount of sulphur 60 phr to provide the highest hardness (73 shore D). The ebonite rubber comprising has a Shore D hardness in the range of 70 to 100.

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REFERENCES

- H.-H. Lo and C.-F. Chu, "Influence of clay, silicate and carbon black on the environmental resistance properties of hard rubber," China Steel Technical Report, no. 24, pp. 40-47, 2011.
- [2] S. Indra, H. Ismail, and A. R. Azura, "Alkanolamide as an accelerator, filler-dispersant and a plasticizer in silica-filled natural rubber compounds," *Polymer Testing*, vol. 32, issue 8, pp. 1313-1321, December 2013.
- [3] A. Tohsan and Y. Ikeda, "Generating particulate silica fillers in situ to improve the mechanical properties of natural rubber (NR)," *Chemistry, Manufacture and Applications of Natural Rubber*, pp. 168-192, 2014.
- [4] Z. X. Ooi, H. Ismail, and A. A. Bakar, "Study on the ageing characteristics of oil palm ash reinforcednatural rubber composites by introducing a liquid epoxidized," *Polymer Testing*, vol. 37, pp. 156-162, August 2014.
- [5] K. Pal, R. Rajasekar, D. J. Kang, Z. X. Zhang, S. K. Pal, C. K. Das, and J. K. Kim, "Effect of fillers on natural rubber/high styrene rubber blends with nano silica: Morphology and wear," *Materials & Design*, vol. 31, issue 2, pp. 677–686, February 2010.
- [6] S. Uraiwan, N. Charoen, T. Woothichai, and V. Norbert, "Influence of modifying agents of organoclay on properties of nanocomposites based on natural rubber," *Polymer Testing*, vol. 33, pp. 48-56, February 2014.
- [7] K. Sengloyluan, K. Sahakaro, K. Wilma Dierkes, and W. M. Jacques Noordermeer, "Silica-reinforced tire tread compounds compatibilized by using epoxidized natural rubber," *European Polymer Journal*, vol. 51, pp. 69-79, February 2014.
- [8] Q. Pan, B. Wang, Z. Chen, and J. Zhao, "Reinforcement and antioxidation effects of antioxidant functionalized silica in styrene – butadiene rubber," *Materials & Design*, vol. 50, pp. 558-565, September 2013.
- [9] K. Pal, R. Rajasekar, D. J. Kang, Z. X. Zhang, S. K. Pal, C. K. Das, and J. K. Kim, "Effect of fillers on natural rubber/high styrene rubber blends with nano silica: Morphology and wear," *Materials & Design*, vol. 31, issue 2, pp. 677–686, February 2010.
- [10] S. Samarzija-Jovanovic, V. Jovanovića, G. Marković, S. Konstantinović, M. Marinović-Cincović, "Nanocomposites based on silica-reinforced ethylene–propylene–diene–monomer/acrylonitrile–butadiene rubber blends," *Composites Part B: Engineering*, vol. 42, issue 5, pp. 1244–1250, July 2011.
- [11] Y. Li, B. Han, S. Wen, Y. Li, H. Yang, L. Zhang, and L. Liu, "Effect of the temperature on surface modification of silica and properties of modified silica filled rubber composites," *Composites Part A: Applied Science and Manufacturing*, vol. 62, pp. 52-59, July 2014.
- [12] G. Zhao, L. Shi, D. Zhang, X. Feng, S. Yuan, and J. Zhuo "Synergistic effect of nanobarite and carbon black fillers in natural rubber matrix," *Materials & Design*, vol. 35, pp. 847-853, March 2012.
- [13] S. Prasertsri and N. Rattanasom, "Mechanical and damping properties of silica/natural rubber composites prepared from latex system," *Polymer Testing*, vol. 30, issue 5, pp. 515-526, August 2011.
- [14] T. H. Mokhothu, A. S. Luyt, and M. Messori, "Reinforcement of EPDM rubber with in situ generated silica particles in the presence of a coupling agent via a sol - gel," *Polymer Testing*, vol. 33, pp. 97-106, February 2014.
- [15] R. V. Sekharan, B. T. Abraham, and E. T. Thachil, "Utilization of waste expanded polystyrene: Blends with silica-filled natural rubber," *Materials* & *Design*, vol. 40, pp. 221-228, September 2012.
- [16] Y. Jiang, X. Zhang, J. HE, L. Yu, and R. Yang, "Effect of polyphenenylsisesquioxane on the ablative and flame-retardation properties of ethylene propylene diene monomer (EPDM) composite," *Polymer Degradation and Stability*, vol. 96, pp. 949-954, January 2011.
- [17] L. Qu, G. Huang, P. Zhang, Y. Nie, G. Weng and J. Wu, *Polym. Int.*, vol. 59, pp. 1397-1402, 2010.
- [18] N. Rattanason, T. Saowapark, and C. Deeprasertkul, "Reinforcement of natural rubber with silica/carbon black hybrid filler," *Polymer Testing*, vol. 26, issue 3, pp. 369-377, May 2007.

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