Effect of 3-Aminopropyltriethoxysilane (APTS), Aging Process and Ozone Exposure on Mechanical Properties of Vulcanized Natural Rubber

Emil Budianto[1], Bambang Soegijono[2*], Mahendra Anggaravidiya[1,3], Chandra Lizq[1,4], Sudirman [2,5]

[1] Departement of Chemistry, University of Indonesia

[2] Departement of Physics, Materials Science, University of Indonesia

[3] Industrial Assessment Center Process, Agency for the Assesment and Application of Technology, Indonesia

[4] Center of Polymer Technology, Agency for the Assessment and Application of Technology, Indonesia

[5] Center for Technology of Nuclear Industry Materials-National Nuclear Energy Agency, Indonesia

[*]*Corresponding author's email: bambangsg11 [AT] yahoo.com*

ABSTRACT— ***Mechanical properties, heat and ozone resistances of vulcanized natural rubber thin pale crepee types can be improved by addition of 3-aminopropyltriethoxysilane (APTS). Addition of APTS improves interaction between polymer filler in rubber and vulcanized. Vulcanized that have been added 2, 6 and 10 phr APTS characterized by Fourier-Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy (SEM-EDS), while mechanical properties were tested by using a Universal Testing Machine. Ozone testing was performed by using Ozone Aging Tester. The results showed that APTS addition on vulcanized rubber can increase value bound, aging resistance and ozone resistance, and also mechanical properties such as tensile strength, elongation at break and 100% modulus.***

Keywords—natural rubber, APTS, ozone and aging

---

1. INTRODUCTION

Silanes as coupling agents were first discovered in the 1940s and then used for developing of composites to improve bond between matrixes and filler, also to prevent decrease of strength because of time.

Several studies have been conducted on polymeric materials and rubber. Some results showed that addition of 3-aminopropyltriethoxysilane and formamide in carbon black is decrease resistivity of polymers made [1]. On the other hand some other studies showed that reaction between styrene butadiene rubber (SBR) and 3-aminopropyltriethoxysilane increased thermal stability properties [2]. Other studies also showed that carbon nanotubes that were treated with 3-aminopropyltriethoxysilane in acidic conditions have changed crystal structure of carbon nanotubes and improved modulus and tensile strength properties of the vulcanized rubber product [3].

Mixing of silane type of bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) with SBR rubber type and NR-SBR blend have changed mechanical properties of vulcanized rubber[4]. In addition, use of silanes have also led to better filler dispersion [5, 6], and increase adhesion between carbon and polymer [7] as well as increased in tensile strength, modulus and ductility of carbon fiber cement-matrix composites [8]. This paper shows effect of 3-aminopropyltriethoxyxilane (APTS) addition on properties of vulcanized natural rubber such as aging resistance and ozone resistance, and also mechanical property and bound rubber.

2. MATERIALS AND METHODS

Materials used were TPC type natural rubber (Indonesian Plantation Company) with mooney viscosity value of 83.59, 101 Type Stearic Acid (Cisadane Raya Chem Company, Indonesia), ZnO (Red Seal Banana Brand, China), CBS (N-Cyclohexyl-2-benzothiazyl Sulphenamide) of Flexy Chem granules (China) and sulfur of Ground Sulfur type 325 mesh. Carbon black N-660 is from Cabot-Starling Company (Indonesia). 3-Aminopropyltriethoxysilane (APTS) was obtained from Sigma-Aldrich.

APTS was added as 0, 2, 6, and 10 phr (henceforth coded T0, T2, T6 and T10). Mixing process between APTS and carbon black has been performed using a mixer for 5 minutes, and then added to the mixture in accordance with the formula as shown in Table 1 below.

Table 1. Sample formulation with variation of phr APTS

Materials	**Phr**			
	T0	**T2**	**T6**	**T10**
TPC	100.0			
Stearic Acid	2.0			
ZnO-Red Seal	5.0			
Carbon black	40.0			
APTS	**0**	**2**	**6**	**10**
CBS	1.4			
Sulfur	2.5			

Bound Rubber

Percentage of bound rubber was obtained by soaking 1.0 g of sample into 100 ml of toluene at room temperature for 48 hours. The solvent was then filtered, and the remaining samples were dried at 40^{o}C for 24 hours in a vacuum until constant weight. Percentage of bound rubber can be calculated using the equation:

$$BR\ (\%) = 100\ x\ \frac{(M_o - M_b) - \left[\frac{CPD}{100(M_o - M_e)}\right]}{(M_o - M_b)} \qquad (1)$$

where M_o is initial weight of container and sample, M_b is weight of container, CPD is phr of used carbon black, and M_e is final weight of container and sample.

Fourier-Transform Infrared Spectroscopy (FTIR-ATR)

FTIR-ATR Spectroscopy was used to determine nature of functional groups presented in APTS on vulcanizates surfaces. Measurements were performed using FTIR Microscope Hyperion 3000. Spectra were made up of 32 scans with a resolution of 4 cm^{-1}.

Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM-EDS)

SEM-EDS - A JSM-6510 Jeol, Tokyo, Japan was utilized to observe morphologies of fracture surface of composite. Specimens with a thickness of 2 mm were cryogenically fractured in liquid nitrogen and then sputter coated with gold before observation under an accelerating voltage of 20 kV.

Mechanical Properties

U-CAN-UT2800 Universal Testing Machine was used for testing of tensile strength, elongation and modulus 100%, with crosshead speed of 5 ~ 600 mm/min for 250 kgf and crosshead speed accuracy of $\pm$1,5%. Testing of tensile strength, elongation and modulus of 300% has been conducted in accordance with ASTM D 412.

Ozone Aging Tester

Ozone resistance testing was performed using an ozone aging tester with reference to ASTM D-1149. Ozone concentration used was 25 pphm with temperature of 40^{o}C

3. RESULTS AND DISCUSSION

Bound *Rubber*

Bound rubber measurements indicate that carbon black particles interact physically with polymer chains of polyisoprene. Consequently, percent bound rubber will be directly proportional to the surface activity of carbon black used. Addition of APTS increases bound rubber values in the ranges from 13.16% to 71.90% as shown in Table 2 and Figure 1. These results confirm formation of bonding between carbon black with the polymer [9].

Table 2. Bound rubber content (%).

Bound Rubber	**T0**	**T2**	**T6**	**T10**
Value	45.510	51.497	72.076	78.231
% compare T0		13.16%	58.37%	71.90%

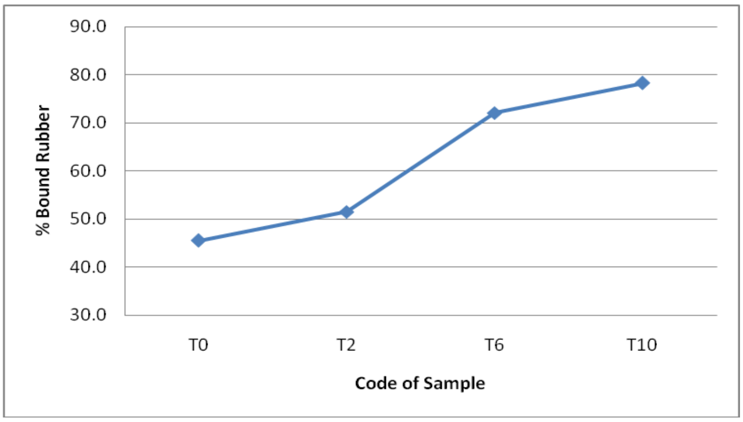


Figure 1. The effect of APTS amount (phr) on bound rubber values

Ozone Exposure

Ozone exposure has been carried out using ozone aging equipment tester. Samples were exposed to 25 PPHM ozone at 40°C for 21 days. Figure 2 shows crack in the sample. Addition of APTS with greater phr causes samples to be more resistant to ozone, which is indicated by small crack in the sample. Increased ozone resistance was caused by the formation of a bond between rubber and APTS in samples. Number of double bond C = C decreased as shown in FTIR results in Figure 3, where peak at 1597 cm^{-1} showing C = C group is much reduced.

Fig.2. Morphology of the samples after ozone process.

Fourier-Transform Infrared Spectroscopy

Figure 3 shows FTIR spectrum of sample without addition of APTS and samples with addition of 10 phr APTS, before and after ozone exposure. The figure shows that after ozone process there are changes of peaks around the wave number 824 cm^{-1}, 1600 cm^{-1} and 3000-3600 cm^{-1}. Peak at a wavelength of 3437 cm^{-1} indicates NH stretching of aminosilane on the surface of carbon black. This result is supported by appearance of peaks at 2926 cm^{-1} and 2856 cm^{-1}, which indicate >CH2 group asymmetric and symmetric stretching [3].

Peak at 824 cm^{-1}indicates the C= CH bending of isoprene, and at 1597 cm^{-1} shows group C = C stretching vibration of isoprene units at natural rubber, were reduced after ozone process. This indicates that double bond in the carbon atoms oxidized by the presence of ozone, and lead to a new peak at wave number of 1095 cm^{-1}, which indicates the oxidation process of C-O-C. The wave numbers at 3000-3600 cm^{-1} are also observed, which indicates the OH group, which is derived from the ozonisation process and caused the termination of the rubber polymer chains.

Addition of APTS on ozone mixture is able to improve robustness of resulting vulcanized, as indicated by low value of transmittance at wave number of 1095 cm^{-1} and 3000-3600 cm^{-1}.

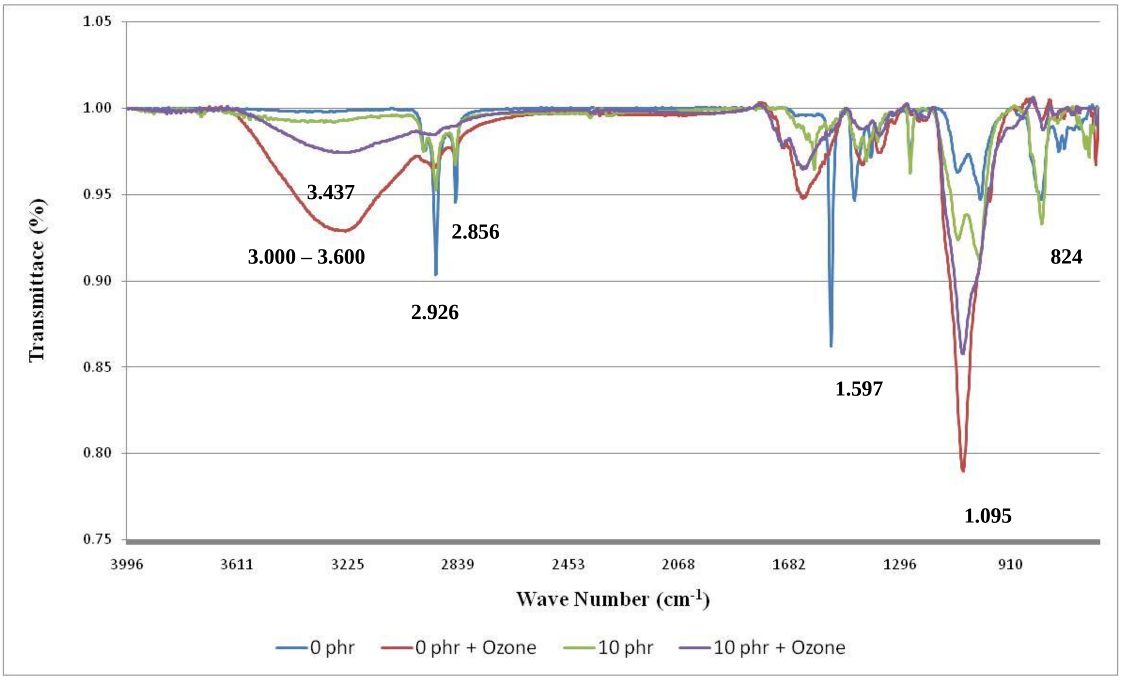


Figure 3. FTIR spectrum of natural rubber without APTS and natural rubber with 10 phr APTS, before and after ozonisation

Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM-EDS)

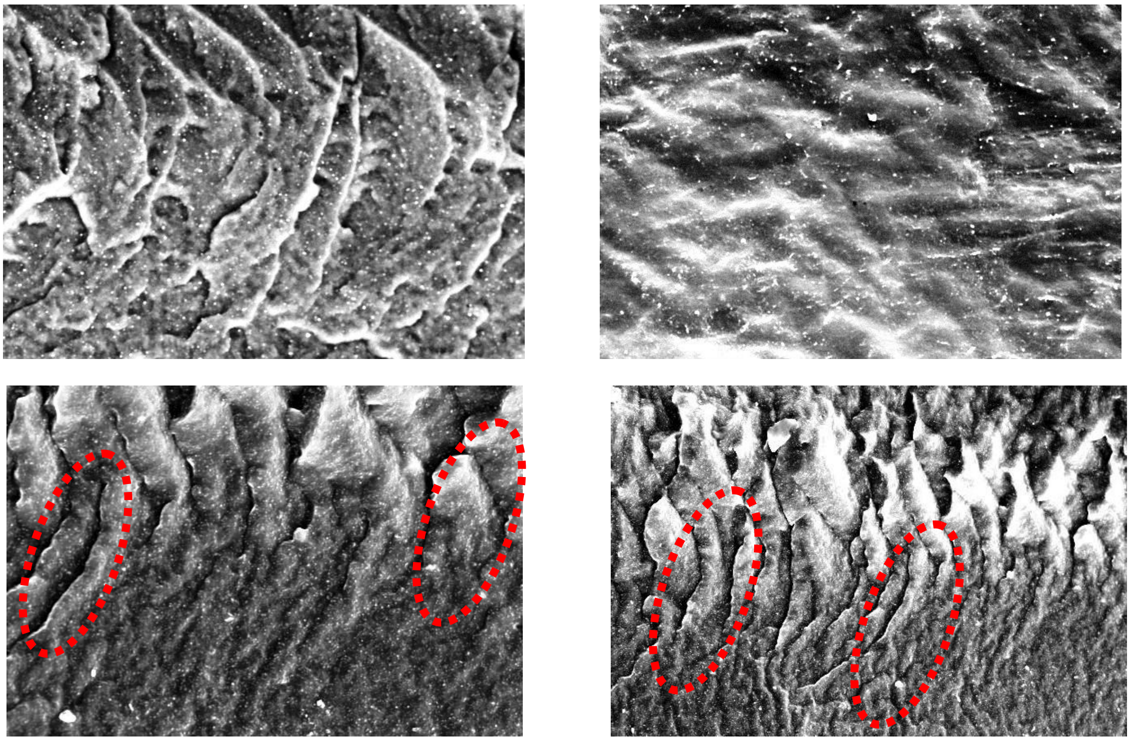
SEM-EDS characterization has been performed to observe distribution of carbon black and APTS before and after ozone process. The results as shown in Figure 2 show that crack in sample was formed after ozone process because of polymer chain termination process by ozone (marked area). This result is consistent with the FTIR results which showed an increase in the content of the C-O-C functional groups related to the process of oxidation caused by exposure to ozone.

Effect of Aging to Mechanical Properties

Aging process refers to the ASTM D-572 in which the sample was heated at temperature of 70 °C for 24 hours, and then tested for mechanical properties. Test results showed a decrease in mechanical properties of sample (retention), as shown in Table 3 and Figure 4.

After aging process, tensile strength of sample without addition of APTS (T0) decreased by 26.31%. Meanwhile, for sample with addition of APTS, it is found that the tensile strength decreased by 22.43% (T2), 14.05% (T6) and 6.80% (T10). Improvement of these properties is due to modification of filler surface due to presence of APTS [10, 11].

Elongation at break of samples T0, T2, T6 and T10 was changed by 16.15%, 37.16%, 34.97%, and 28.33% respectively; while 100% modulus of samples were changed by -195.52%, - 43.57%, -33.17% and -1.83%, respectively. Test results indicate that samples with addition of APTS showed larger stiffness properties due to presence of more polysulfide bonds in the mixture [13].



T0 after ozone process **T10 after ozone process**

Figure 2. SEM-EDS images of fracture surfaces of T0 and T10 before and after ozone processes

Table 3. Mechanical properties before and after aging process

Testing	T0		T2		T6		T10	
	F	**A**	**F**	**A**	**F**	**A**	**F**	**A**
Tensile strength(Kg/Cm2)	167.3	123.3	196.9	152.7	217.7	187.1	211.8	197.4
Elongation at Break(%)	351.8	295.0	412.2	259.0	474.7	308.7	410.6	294.3
Modulus 100% (%)	30.3	89.6	27.6	39.6	27.4	36.4	36.0	36.7

F : Fresh ; A : After aging

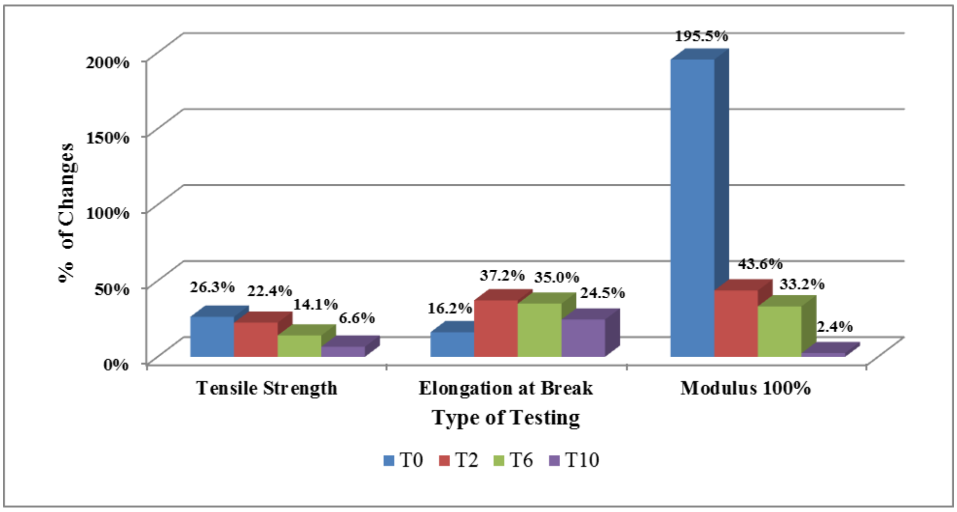


Figure 4. Mechanical Properties before and after Aging Process

4. CONCLUSION

Addition of APTS on TPC type natural rubber mixture resulted better bonding between rubber and carbon black, which is indicated by an increase in value of bound rubber. The bonding is proportional to amount of APTS phr, at 13.16%, 58.37%, 71.90%. Increasing bound rubber values were correlated with aging and ozone resistance of vulcanized. Samples with addition of APTS showed smaller percentage change of mechanical properties after experiencing aging process. Addition of APTS was also able to increase endurance properties of ozone, which is indicated by the small crack that occurs in vulcanized after ozone process

5. REFERENCES

[1]. Ozcan Koysuren, Sertan Yesil, Goknur Bayram.. *Effect of Surface Treatment on Electrical Conductivity of Carbon Black Filled Conductive Polymer Composites*, Journal of Applied Polymer Science, vol. 104:3427–3433, 2007

[2]. Maria Augusta de Luca, Marly Maldaner Jacobi, Lisia Floriani Orlandini, (2009). *Synthesis and characterisation of elastomeric composites prepared from epoxidised styrene butadiene rubber, 3-aminopropyltriethoxysilane and tetraethoxysilane*, Journal of Sol-Gel Science and Technology, vol. 49:150–158, 2009

[3]. A.M. Shanmugharaj, J.H. Bae, Kwang Yong Lee, Woo Hyun Noh, Se Hyoung Lee, Sung Hun Ryu. *Physical and chemical characteristics of multiwalled carbon nanotubes functionalized with aminosilane and its influence on the properties of natural rubber composites*, Composites Science and Technology 67 : 1813–1822, 2007

[4]. Sung-Seen Choi, Jong-Chul Kim, Ji-Eun Ko, Yi Seok Cho, Wae Gi Shin. *Influence of Coupling Agent on Properties of Carbon Black-Reinforced SBR and NR/SBR Vulcanizates*, Journal of Industrial and Engineering Chemistry, vol. 13, No. 6:1017-1022, 2007

[5]. Nabil A.N. Alkadasi, D.G. Hundiwale and U.R. Kupandi. *Studies on the Effect of Silane Coupling Agent (2.0 per cent) on the Mechanical Properties of Flyash Filled Polybutadiene Rubber.* Journal of Scientific & Industrial Research, vol.63: 603-609, 2004

[6]. C. Thongpin, C. Sangnil, P. Suerkong, A. Pongpilaiprertti and N. Sombatsompop. *The Effect of Excess Silane-69 used for Surface Modification on Cure Characteristic and Mechanical Properties of Precipitated Silica filled Natural Rubber (PSi/NR)*. Advanced Materials Research, vols. 79-82:2171-2174,2009

[7]. Ji-Hoon Le, John Kathi, Kyomg Yop Rhee, Joong Hee Lee. *Wear Properties of 3-Aminopropyltriethoxysilane Functionalized Carbon Nanotubes Reinforced Ultra High Molecular Polyethylene Nanocomposites*. Polymer Engineering & Science; vol. 50:7:1433-1439, 2010

[8]. Yunsheng Xu, D.D.L. Chung. *Silane-Treated Carbon Fiber for Reinforcing Cement*, Carbon 39:1995–2001

[9]. Sumanda Bandyopadhyay, P. P. De, D. K. Tripathy, S. K. De. (1996). *3-Aminopropyltriethoxysilane as a Promoter in the Crosslinking of Carboxylated Nitrile Rubber by Surface- Oxidized Carbon Black*. Journal of Applied Polymer Science, vol. 63:1833–1839, 2001

[10]. P.A. Nelson and S.K.N. Kutty. *Effect of Silane Coupling Agent on Cure Characteristics and Mechanical Properties of Nitrile Ubber/Reclaimed Rubber Blend*. Progress in Rubber, Plastic and Recycling Technology, 20:3:213-228, 2004.

[11]. H. Ismail, Z. A. A. Hamid, S. Ishak. *Effect of Silane Coupling Agent on the Curing, Tensile, Thermal, and Swelling Properties of EPDM/Mica Composites*. Advanced Materials Research, vol. 626: 641-651, 2013.

[12]. Pang Ai Ling and Hanafi Ismail. *The Effects of Kenaf Loadings and 3-aminopropyltriethoxysilane (APTES) coupling agent on Mechanical Properties of Polypropylene/Waste Tire Dust/Kenaf (PP/WTD/KNF) Composites*. Advanced Materials Research, vol. 626:828-833, 2013

[13]. M. Sabri, F. Hafiz, K. Shahril, A. Siti Rohana, dan H. Salmah. *Effects of Silane Coupling Agent on Mechanical Properties and Swelling Behaviour of Coconut Fiber Filled Polypropylene Composite*. Advanced Materials Research, vol. 626:657-661, 2013.