REFERENCES

[1] Kohjiya, S. and Ikeda, Y. Reinforcement of general-purpose grade rubbers by silica generated *in situ*. Rubber Chem. Technol. 73 (2000): 534-550.

[2] Jesionowski, T. and Krysztafkiewicz, A. Influence of silane coupling agents on surface properties of precipitated silica. Appl. Surf. Sci. 172 (2001): 18-32.

[3] Park, S. J. and Cho, K. S. Filler-elastomer interactions: influence of silane coupling agent on crosslink density and thermal stability of silica/rubber composites. J. Colloid Interface Sci. 267 (2003): 86-91.

[4] Saeoui, P., Sirisinha, C., Thepsuwan, U., and Hatthapanit, K. Roles of silane coupling agents on properties of silica-filled polychloroprene. Eur. Polym. J.42 (2006): 479-486.

[5] Kohjiya, S., Murakami, K., Iio, S., Tanahashi, T. and Ikeda, Y. *In situ* filling of silica onto "Green" natural rubber by the sol-gel process. Rubber Chem. Technol. 74 (2001): 16-27.

[6] Kohjiya, S. and Ikeda, Y. *In situ* formation of particulate silica in natural rubber matrix by the sol-gel reaction. J. Sol-Gel Sci. Technol. 26 (2003): 495-498.

[7] Bokobza, L. and Chauvin, J. Reinforcement of natural rubber: use of *in situ* generated silicas and nanofibres of sepiolite. Polymer. 46 (2005): 4144-4151.

[8] Landry, C. J. T., Coltrain, B. K. and Brady, B. K. *In situ* polymerization of tetraethoxysilane in poly (methyl methacrylate): morphology and dynamic mechanical properties. Polymer 33 (1992): 1495-1486.

[9] Bandyopadhyay, A., Bhowmick, A. K. and Sarkar, M. D. Synthesis and characterization of acrylic rubber/silica hybrid composites prepared by sol-gel technique. J. Appl. Polym. Sci. 93 (2004): 2579-2589.

[10] Hashim, A. S., Kawabata, N. and Kohjiya, S. Silica reinforcement of epoxidized natural rubber by the sol-gel method. J. Sol-Gel Sci. Technol. 5 (1995): 211-218.

[11] Sengupta, R., Bandyopadhyay, A., Sabharwal, S., Chaki, T. K. and Bhowmick, A.K. Polyamide-6,6/*in situ* silica hybrid nanocomposites by sol-gel

technique: synthesis, characterization and properties. Polymer 46 (2005): 3343-3354.

[12] Bandyopadhyay, A., Sarkar, M. D. and Bhowmick, A. K. Epoxidised natural rubber/silica hybrid nanocomposites by sol-gel technique: Effect of reactants on the structure and the properties. J Mater. Sci. 40 (2005): 53-62.

[13] Bandyopadhyay, A., Sarkar, M. D., and Bhowmick, A. K. Structure-property relationship in sol-gel derived polymer/silica hybrid nanocomposites prepared at various pH. J. Mater. Sci. 41 (2006): 5981-5993.

[14] Brinker, C. J. and Scherer, G. W. Sol-gel science: The physics and chemistry of sol-gel processing. Boston: Academic Press, 1990.

[15] Ikeda, Y., Poompradub, S., Morita, Y. and Kohjiya, S. Preparation of high performance nanocomposite elastomer: effect of reaction conditions on *in situ* silica generation of high content in natural rubber. J. Sol-Gel Sci. Technol. 45 (2008): 299-306.

[16] Ikeda, Y., Tanaka, A. and Kohjiya, S. Effect of catalyst on *in situ* silica reinforcement of styrene-butadiene rubber vulcanizate by the sol-gel reaction of tetraethoxysilane. J. Mater. Chem. 7 (1997): 455-458.

[17] Tangpasuthadol, V., Intasiri, A., Nuntivanich, D., Niyompanich, N. and Kiatkamjornwong, S. Silica-reinforced natural rubber prepared by the sol–gel process of ethoxysilanes in rubber latex. J. Appl. Polym. Sci. 109 (2008): 424-433.

[18] Sirimanont, J. Reinforcement of natural rubber by silica generated from sol-gel process of silane in latex. Master's Thesis, Petrochemistry and Polymer Science, Faculty of Science, Graduate School, Chulalongkorn University, 2005.

[19] Ikeda, Y. and Kameda, Y. Preparation of "Green" Composites by the Sol-Gel Process: *In situ* Silica Filled Natural Rubber. J. Sol-Gel Sci. Technol. 31 (2004): 137-142.

[20] Poompradub, S., Kohjiya, S. And Ikeda, Y. Natural rubber/*In situ* silica nanocomposite of a high silica content. Chem. Lett. 34 (2005): 672-673.

[21] Yoshikai, K., Ohsaki, T. and Furukawa, M. Silica reinforcement of synthetic diene rubbers by sol-gel process in the latex. J. Appl. Polym. Sci. 85 (2002): 2053-2063.

[22] Brydson, J. A. Rubber chemistry. London: Applied science, 1978.

[23] Williams, P.H. The science of rubber. Malaysia: Dunlop, 1975.

[24] Aziz, A. Advance in natural rubber production. Rubber Chem. Technol. 67 (1994): 537-547.

[25] Mark, J. E., Erman, B. and Eirich, F. Science and technology of rubber. 3rd ed. London: Academic Press, 2005.

[26] Mark, H. F. Encyclopedia of polymer science and technology. 3rd ed. USA: Wiley & Sons, 2004.

[27] Odian, G. Principles of polymerization. 4th ed. New Jersey: Wiley & Sons, 2004.

[28] Rodgers B. Rubber compounding: Chemistry and applications. New York: Marcel Dekker, 2004.

[29] Medalia, A. I. and Kraus, G. Reinforcement of elastomers by particulate fillers. 2nd ed. San Diego: Academic Press, 1994.

[30] Ciullo, P. A. and Hewitt, N. The rubber formulary. New York: Noyes /William Andrew, 1999.

[31] Hepburn, C. Rubber compounding ingredients need: Theory and innovation part I. England: Rapra technology, 1981.

[32] Bergna, H. E. and Roberts, W. O. Colloidal silica: fundamentals and applications. New York: Taylor & Francis, 2006.

[33] Kohijiya, S., Katoh, A., Shimanuki, J., Hasegawa, T. and Ikeda, Y. Three dimensional nano-structure of *in situ* silica in natural rubber as revealed by 3D-TEM/electron chromatography. Polymer 46 (2005): 4440-4446.

[34] Aucher, J. F., Kalin, T. and Sakuma Y. Chemical Economics Handbook. USA: SRI International, 2002.

[35] Ikeda, Y. and Kohjiya, S. *In situ* formed silica particles in rubber vulcanizate by the sol-gel method. Polymer 38, 17 (1997): 4417-4423.

[36] Poh, B. T. and NG, C. C. Effect of silane coupling agents on the Mooney scorch time if silica-filler natural rubber compound. Eur. Polym. J. 34, (1998): 975-979.

[37] Ono, S., Kiuchi, Y., Sawanoburi, K. and Ito, M. Structure development in silica-filled rubber composites. Polym. Int. 48 (1999): 1035-1041.

[38] Ansarifara, A., Azhar, A., Ibrahim, N., Shiah, S. F. and Lawton, J. M. D. The use of a silanised silica filler to reinforce and crosslink natural rubber. Int. J. Adhes. 25 (2005): 77–86.

[39] López, B. L., *et al*. Use of mesoporous silica as a reinforcing agent in rubber compounds. e-Polymers 2005, 18.

[40] Rattanasom, N., Saowapark, T. and Deeprasertkul, C. Reinforcement of natural rubber with silica/carbon black hybrid filler. Polym. Test 26 (2007): 369–377.

[41] Conant, F. S. Physical testing of vulcanizates. New York: Van norstrand reinhold, 1973.

[42] Dick, J. S. Vulcanizate physical properties: Performance characteristics, and testing. Rubber technology compounding and testing for performance. Munich: Hanser, 2001.

[43] Bayer material science. Compression set [Online]. Available from: http://tpe-u.com/tpu/emea/en/products/product_properties/Compression_set/Compression_set.html [2008, December 5].

[44] Ferry, J. Viscoelastic properties of polymers. 3rd ed. New York: Wiley and Sons, 1980.

[45] Sperling, L.H. Introduction to Physical Polymer Science 4th ed. USA: Wiley & Sons, 2006.

[46] Osseo, A. K. and Arriagada, F. J. Growth kinetics of nanosize silica in a nonionic water-in-oil microemulsion: a reverse micellar pseudophase reaction model. J. Colloid Interface Sci. 218 (1999): 68–76

[47] Debuigne, F., Jeunieau, L., Wiame, M. and Nagy, J. B. Synthesis of organic nanoparticles in different W/O microemulsions. Langmuir. 16 (2000): 7605-7611.

[48] Sae-oui, P. Rubber Chemicals. Bangkok: MTEC, 2005.

[49] Wagner, H. D. Encyclopedia of Polymer Science and Technology 3rd ed. New York: Wiley & Sons, 2003.

[50] Sae-oui, P., Sirisinha, C., Wantana, T and Hatthapanit, K. Influence of silica loading on the mechanical properties and resistance to oil and thermal aging of CR/NR blends. J. Appl. Polym. Sci. 104 (2007): 3478-3483.

[51] Horn, J.B. Materials for Compounding and Reinforcement. England: Newnes-Butter worths, 1980.

[52] Sae-oui, P., Sirisinha, C., Thepsuwan, U. and Hatthapanit, K. Dependence of mechanical and aging properties of chloroprene rubber on silica and ethylene thiourea loadings. Eur. Polym. J. 43 (2007): 185–193.

[53] Murakami, K., *et al.* Effect of silane-coupling agent on natural rubber filled with silica generated *in situ*. J. Mater. Sci. 38 (2003): 1447-1455.

[54] Sae-oui, P., Thepsuwan U. and Hatthapanit K. Effect of curing system on reinforcing efficiency of silane coupling agent. Polym. Test 23 (2004): 397–403.

[55] Martinsa, M. A., *et al.* Thermooxidative study of raw natural rubber from Brazilian IAC 300 series clones. Thermochim Acta 474 (2008): 62-66.

[56] Chen, Y., Peng, Z., Kong, L. X., Huang, M. F. and Li, P. W. Natural rubber nanocomposite reinforced with nano silica. Polym. Eng. Sci. 48 (2008): 1674-1677.

[57] Gilman, J. W., *et al.* Flammability properties of polymer-layered-silicate nanocomposites polypropylene and polystyrene nanocomposites. Chem. Mater. 12 (2000): 1866

[58] Vyazovkin, S., Dranca, I., Fan, X. W. and Advincula, R. Kinetics of the thermal and thermo-oxidative degradation of a polystyrene-clay nanocomposite. Macromol. Rapid. Commun. 25 (2004): 498.

[59] Horowitz, H. H. and Metzger, G. A. New analysis of thermogravimetric traces. Anal Chem 35 (1963): 1464-1468.

[60] Park, S. J. and Cho K. S. Filler–elastomer interactions: influence of silane coupling agent on crosslink density and thermal stability of silica/rubber composites. J Colloid Interface Sci. 267 (2003): 86-91.

APPENDICES

APPENDIX A

- **Determination of NR degree swelling**

The degree swelling of natural rubber in TEOS was calculated according to following equation.

$$\text{Degree of swelling} = \frac{\text{weight of TEOS} + \text{weight of NR}}{\text{weight of NR}} \times 100 \qquad \text{(A.1)}$$

This study used 360% degree swelling with 10 g of natural rubber. The TEOS density is 0.933g/ml

Substituting in the equation A.1

$$360 = \frac{\text{weight of TEOS} + 10}{10} \times 100$$

$$\text{weight of TEOS} = 26\,\text{g}$$

From

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \qquad \text{(A.2)}$$

$$0.933 = \frac{26}{\text{volume}}$$

$$\text{Volume of TEOS} = 27.87\ \text{ml}$$

- **Determination of Network chain density**

Substituting equation (3.2) by

$W_D = 0.9015$ g, $W_S = 2.3234$ g, $W_F = 0.1265$ g, $\rho_D = 0.9688$ g/cm^3, $\rho_S = 0.867$ g/cm^3.

$$V_r = \frac{\left[\frac{0.9015-0.1265}{0.867}\right]}{\left[\left(\frac{0.9015+0.1265}{0.9688}\right)+\left(\frac{2.3234}{0.867}\right)\right]}$$

$$V_r = 0.2542$$

Substituting equation (3.1) by $V_l = 106.3$, $\chi_1 = 0.393$

$$\nu_e = \frac{-\left[\ln(1-0.2542)+0.2542+(0.393\times 0.2542^2\right]}{\left[106.3\left(.02542^{\frac{1}{3}}-\frac{0.2542}{2}\right)\right]}$$

$$\nu_e = 2.55\times 10^{-4}$$

Network chain density of *in situ* 30 phr filled NR vulcanizate is 2.55×10^{-4} mol/cm^3.

APPEMDIX B

Table B-1 Mechanical Properties of Natural Rubber Composites

Sample	Stress (MPa)				Elongation at break (%)	Hardness	Abrasion Resistance (mm^3)	Compression Set (%)
	50 % Elongation	100 % Elongation	300 % Elongation	Tensile Strength				
NR	0.51±0.11	0.78±0.04	1.65±0.30	20.3±0.58	841±50	36.3±0.3	235±44	34±2.0
In-15	0.55±0.08	0.79±0.10	2.02±0.83	19.3±0.69	799±36	38.4±0.2	223±15	27±0.4
In-30	0.60±0.01	0.88±0.01	2.82±0.16	19.2±0.32	743±10	40.2±0.3	231±13	38±2.0
In-45	0.63±0.02	0.92±0.03	3.11±0.22	16.5±0.63	672±15	41.2±0.3	542±20	43±0.3
In-65	0.67±0.10	0.96±0.03	4.40±0.12	14.8±2.06	559±20	42.7±0.4	666±18	45±0.8
In-30-C	0.47±0.05	0.73±0.06	4.71±0.08	22.5±2.43	723±16	45.5±0.0	192±9	32±4.0
Si-30	0.83±0.06	1.16±0.08	2.57±0.21	26.9±1.30	850±28	51.8±0.3	234±8	62±2.0
Si-30-C	0.73±0.04	1.07±0.08	3.34±0.34	28.9±2.11	811±49	55.3±0.3	190±2	57±3.0
CB-30	0.89±0.03	1.47±0.09	6.23±0.50	27.2±0.49	710.±44	58.5±0.5	194±6	30±4.0
Ca-30	0.57±0.06	0.89±0.05	2.30±0.14	17.5±0.63	779±33	42.5±0.0	245±19	42±1.0

APPENDIX C

Table C-1 Material Specification of Calcium Carbonate: CNANO P-62.

Properties	Specification
Appearance	White Powder
Moisture content	< 0.5%
Specific Gravity	2.55
Particle size average	40-60 nm
Surface area (BET)	> 20 m^2/g
pH	8.5 - 10

Table C-2 Material specification of carbon black: N550.

Properties	Specification
Average Particle Diameter	24 nm
Iodine Number	90 mg/g
N_2Surface area	100 m^2/g
DBP Absorption	114 ml/100g
Tint	115 % ITRB
Pour Density	345 kg/m^3

Table C-3 Material specification of silica: Hi-Sil 255.

Properties	Specification
Physical form	Granules
Moisture content	< 8 %
SiO_2	≥ 97 %
DBP/Absorption	190
Surface area (BET)	150 - 180 m^2/g
Loss on ignition	14 %
Bulk density	0.20 – 0.24 g/ml

CURRICULUM VITAE

Benjawan Chaichua was born on May 16, 1983 in Songkhla, Thailand. She received a Bachelor's degree of Engineering, majoring in Petrochemicals and Polymeric Materials from Silpakorn University in 2005. She has pursued Master's degree in Petrochemistry and Polymer, Faculty of Science, Chulalongkorn University, Bangkok, Thailand since 2005 and finished her study in 2008.

Publication

Sirilux Poompradub, Benjawan Chaichua, Chosita Kanchanaamporn, Tanaporn Boosalee, Pattarapan Prasassarakich "Synthesis of silica in natural rubber solution via sol-gel reaction", Journal Kautschuk Gummi Kunststoffe, 2008,152-155.

Presentations

1. 12-13 March 2009 Oral presentation "Natural rubber reinforced by in situ silica generated in rubber solution by sol-gel process" The 17 th Science Forum 2009 at Chulalongkorn University, Bangkok, Thailand.

2. 8-9 May 2008 Oral presentation "Natural rubber reinforced by in situ silica" The sixth PSU Engineering Conference (PEC-06) at Prince of Songkhla University, Songkhla, Thailand.

3. 12-14 December 2007 Poster Presentation "Natural Rubber Reinforced by In Situ Silica Generated In Rubber Solution by Sol-Gel Process" The 3rd Mathematics and Physical Science Graduate Congress (MPSGC) at University of Malaya, Kuala Lumpur, Malaysia.