REFERENCES

1. Choi, S. S. Influence of storage time and temperature and silane coupling agent on bound rubber formation in filled styrene–butadiene rubber compounds. Polym. Test. 21 (2002): 201-208.

2. Hashim, A. S., Azahari, B., Ikeda, Y., and Kohjiya, S. The effect of bis(3-triethoxysilylpropyl)tetrasulfide on silica reinforcement of styrene-butadiene rubber. Rubber Chem. Technol. 71 (1998): 289-299.

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

4. 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.

5. Ikeda, Y., Tanaka, A., and Kohjiya, S. Reinforcement of styrene-butadiene rubber vulcanizate by *in situ* silica prepared by the sol-gel reaction of tetraethoxysilane. J. Mater. Chem. 7 (1997): 1497-1503.

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

7. Tanahashi, H., Osanai, S., Shigekuni, M., Murakami, K., Ikeda, Y., and Kohjiya, S. Reinforcement of acrylonitrile-butadiene rubber by silica generated *in situ*. Rubber Chem. Technol. 71 (1998): 38-52.

8. Manna, A. K., De, P. P., Tripathy, D. K., De, S. K., and Feiffer, D.G. Bonding between precipitated silica and epoxidized natural rubber in the presence of silane coupling agent. J. Appl. Polym. Sci. 74 (1999): 389-398.

9. 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.

10. Nuntivanich, D., and Tangpasuthadol, V. Silica reinforcement of natural rubber by sol-gel process in latex. Master's Thesis, Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2003.

11. Billmeyer, F. W., Jr. Textbook of polymer science. 3 rd ed. New York: John Wiley & Sons, 1984.

12. Robert, F. M. Latex and foam rubber. New York: John Wiley & Sons, 1994.

13. Brydson, J. A. Rubber chemistry. England: Applied Science, 1978.

14. Rogers, T. H., and Hecker, K. C. Latex and foam rubber. In M. Morton (ed.), Rubber technology, pp. 459-466. New York: Van Nostrand Reinhold, 1973.

15. Malaysia, R. R. I. O. Rubber research institute of malaysia. RRIM training manual on latex and rubber analysis. Kuala Lumphu: Rubber Research Institute of Malaysia, 1979.

16. Gazeley, K. F., Gorton, A. D. T., and Pendle, T. D. Latex concentrates: Properties and composition. In A. D. Roberts (ed.), Natural rubber science and technology, pp. 63-72. New York: Oxford University Press, 1988.

17. Ciullo, P. A., and Hewitt, N. The rubber formulary. New York: Noyes Publications/ Willium Andrew Publising, 1999.

18. Boonstra, B. B. Fillers: Carbon black and nonblack. In M. Morton (ed.), Rubber technology, pp. 51-85. New York: Van Nostrand Reinhold, 1973.

19. Barbin, W. W., and Rodgers, M. B. The science of rubber compounding. In J. E. Mark, B. Erman, and F. R. Eirich (eds.), Science and technology of rubber, pp. 437-442. San Diego: Academic Press, 1994.

20. Wagner, M.P. Reinforcing silicas and silicates. Rubber Chem. Technol. 49 (1976): 703-774.

21. Weng, S.S., Mun, S. S., Cheong, S. Y., Leong, S. Y., and Kwong, L. A. Silane Coupling Agents[Online]. 2000. Available from: http://www.sinrubtech.com.my/short%20notes/Short%20Notes%205.1.htm[2004, July 10]

22. Wang, M. J. Effect of polymer-filler and filler-filler interactions on dynamic properties of filled vulcanizates. Rubber Chem. Technol. 71 (1998): 520-589.

23. Wise, R. W. Processing and vulcanization tests. In M. Morton (ed.), Rubber technology, pp. 87-113. New York: Van Nostrand Reinhold, 1973.

24. Coran, A. Y. Vulcanization. In J. E. Mark, B. Erman, and F. R. Eirich (eds.), Science and technology of rubber, pp. 339-386. San Diego: Academic Press, 1994.

25. Conant, F. S. Physical testing of vulcanizates. In M. Morton (ed.), Rubber technology, pp. 119-146. New York: Van Nostrand Reinhold, 1973.

26. Sperling, L. H. Introduction to physical polymer science. 2 nd ed. New York: John Wiley & Sons, 1992.

27. Morgan, E. Chemometrics: Experimental design. Chichester: John Wiley & Sons, 1991.

28. Montgomery, D. C. Design and analysis of experiments. New York: John Wiley & Sons, 2001.

29. Brinke, J. W. T., Debnath, S. C., Reuvekamp, L. A. E. M., and Noordermeer, J. W. M. Mechanistic aspects of the role of coupling agents in silica–rubber composites. Comp. Sci. Tech. 63 (2003): 1165-1174.

30. Sae-oui, P., Sirisinha, C., Thepsuwan, U., and Hatthapanit, K. Comparison of reinforcing efficiency between Si-69 and Si-264 in a conventional vulcanization system. Polym. Test. 23 (2004): 871-879.

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

32. Kohjiya, S., and Ikeda, Y. Reinforcement of natural rubber by silica generated *in situ*. Proc. Japan Acad. 76 (2000): 29-34.

33. Tissue, B. M. Q-test for rejection of outliers[Online]. 1996. Available from: http://elchem.kaist.ac.kr/vt/chem-ed/data/q-test.htm[2005, March 21]

34. Loy, D. A., Baugher, B. M., Baugher, C. R., Schneider, D. A., and Rahimian, K. Substituent Effects on the Sol-Gel Chemistry of Organotrialkoxysilanes. Chem. Mater. 12 (2000): 3624-3632.

35. Shea, K. J., and Loy, D. A. A mechanistic investigation of gelation. The sol-gel polymerization of precursors to bridged polysilsesquioxanes. Acc. Chem. Res. 34 (2001): 707-716.

36. Simonutti, R., Comotti, A., Negroni, F., and Sozzani, P. ^{13}C and ^{29}Si solid-state NMR of rubber-silica composite materials. Chem. Mater. 11 (1999): 822-828.

37. Bauer, F., et al. Trialkoxysilane grafting onto nanoparticles for the preparation of clear coat polyacrylate systems with excellent scratch performance. Prog. Org. Coatings 47 (2003): 147-153.

APPENDICES

APPENDIX A

Experimental designs

Effect on tensile modulus

$$T\ Effect = \frac{-y_1 + y_2 - y_3 + y_4 - y_5 + y_6 - y_7 + y_8}{4}$$

$$= \frac{-2.47 + 3.46 - 2.93 + 4.17 - 2.38 + 3.78 - 2.78 + 4.43}{4}$$

$$C\ Effect = \frac{-y_1 - y_2 + y_3 + y_4 - y_5 - y_6 + y_7 + y_8}{4}$$

$$= \frac{-2.47 - 3.46 + 2.93 + 4.17 - 2.38 - 3.78 + 2.78 + 4.43}{4}$$

$$N\ Effect = \frac{-y_1 - y_2 - y_3 - y_4 + y_5 + y_6 + y_7 + y_8}{4}$$

$$= \frac{-2.47 - 3.46 - 2.93 - 4.17 + 2.38 + 3.78 + 2.78 + 4.43}{4}$$

$$TC\ Effect = \frac{+y_1 - y_2 - y_3 + y_4 + y_5 - y_6 - y_7 + y_8}{4}$$

$$= \frac{+2.47 - 3.46 - 2.93 + 4.17 + 2.38 - 3.78 - 2.78 + 4.43}{4}$$

$$TN\ Effect = \frac{+y_1 - y_2 + y_3 - y_4 - y_5 + y_6 - y_7 + y_8}{4}$$

$$= \frac{+2.47 - 3.46 + 2.93 - 4.17 - 2.38 + 3.78 - 2.78 + 4.43}{4}$$

$$CN\ Effect = \frac{+y_1 + y_2 - y_3 - y_4 - y_5 - y_6 + y_7 + y_8}{4}$$

$$= \frac{+2.47 + 3.46 - 2.93 - 4.17 - 2.38 - 3.78 + 2.78 + 4.43}{4}$$

$$TCN\ Effect = \frac{-y_1 + y_2 + y_3 - y_4 + y_5 - y_6 - y_7 + y_8}{4}$$

$$= \frac{-2.47 + 3.46 + 2.93 - 4.17 + 2.38 - 3.78 - 2.78 + 4.43}{4}$$

All main and interaction effects are listed in Table A-1.

Table A-1 Estimated effect for 2^3 factorial design on tensile modulus at 300 %elongation

Entry.	T	C	N	TC	TN	CN	TCN	Tensile modulus 300 %elongation (MPa)
1	-	-	-	+	+	+	-	2.47
2	+	-	-	-	-	+	+	3.46
3	-	+	-	-	+	-	+	2.93
4	+	+	-	+	-	-	-	4.17
5	-	-	+	+	-	-	+	2.38
6	+	-	+	-	+	-	-	3.78
7	-	+	+	-	-	+	-	2.77
8	+	+	+	+	+	+	+	4.43
Estimated effect	1.322	0.553	0.083	0.125	0.208	-0.030	-0.002	

Table A-2 Calculation of standard error of estimated effect

Entry.	Result from individual runs			Average response value	Estimated variance at each set of conditions
	1	2	3		
1	2.52	2.24	2.66	2.47	0.05
2	3.51	2.82	4.04	3.46	0.37
3	3.27	2.73	2.79	2.93	0.09
4	4.02	4.40	4.09	4.17	0.04
5	2.35	2.14	2.64	2.38	0.06
6	4.18	3.79	3.37	3.78	0.16
7	2.81	2.62	2.90	2.77	0.02
8	5.01	4.28	3.99	4.43	0.28
				Σ (variance) =	1.07

Standard error of estimated effect (E) $= \left(\frac{\sum V}{2N}\right)^{1/2} = \left(\frac{1.07}{2*24}\right)^{1/2} = 0.149$

Table A-3 Estimated effect for 2^3 factorial design on tear strength

Entry.	T	C	N	TC	TN	CN	TCN	Tear strength (N/mm)
1	-	-	-	+	+	+	-	34.04
2	+	-	-	-	-	+	+	44.80
3	-	+	-	-	+	-	+	33.67
4	+	+	-	+	-	-	-	47.22
5	-	-	+	+	-	-	+	35.50
6	+	-	+	-	+	-	-	42.23
7	-	+	+	-	-	+	-	35.89
8	+	+	+	+	+	+	+	38.66
Estimated effect	8.453	-0.283	-1.858	-0.295	-3.705	-1.305	-1.686	

Table A-4 Calculation of standard error of estimated effect

Entry.	Result from individual runs			Average response value	Estimated variance at each set of conditions
	1	2	3		
1	36.50	35.01	30.60	34.04	9.41
2	45.31	43.16	45.93	44.80	2.12
3	40.11	25.43	35.46	33.67	56.26
4	48.79	44.31	48.55	47.22	6.35
5	38.60	35.17	32.73	35.50	8.68
6	43.33	43.00	40.36	42.23	2.65
7	39.35	37.38	30.96	35.89	19.23
8	40.53	39.63	35.83	38.66	6.20
				Σ (variance) =	110.89

Standard error of estimated effect (E) $= \left(\frac{\sum V}{2N}\right)^{1/2} = \left(\frac{110.89}{2*24}\right)^{1/2} = 1.520$

Table A-5 Estimated effect for 2^3 factorial design on hardness

Entry.	T	C	N	TC	TN	CN	TCN	Hardness
1	-	-	-	+	+	+	-	40.6
2	+	-	-	-	-	+	+	43.8
3	-	+	-	-	+	-	+	41.5
4	+	+	-	+	-	-	-	46.2
5	-	-	+	+	-	-	+	41.2
6	+	-	+	-	+	-	-	44.1
7	-	+	+	-	-	+	-	43.0
8	+	+	+	+	+	+	+	44.4
Estimated effect	3.083	1.333	0.117	0.000	-0.917	-0.300	-0.767	

Table A-6 Calculation of standard error of estimated effect

Entry.	Result from individual runs			Average response value	Estimated variance at each set of conditions
	1	2	3		
1	41.6	38.3	41.9	40.6	3.99
2	43.7	42.4	45.4	43.8	2.26
3	42.3	41.0	41.1	41.5	0.52
4	46.9	46.7	45.1	46.2	0.97
5	41.9	39.4	42.2	41.2	2.36
6	46.0	42.9	43.4	44.1	2.77
7	44.6	41.3	43.0	43.0	2.72
8	46.5	44.0	42.6	44.4	3.90
				Σ (variance) =	19.51

Standard error of estimated effect (E) $= \left(\frac{\sum V}{2N}\right)^{1/2} = \left(\frac{19.51}{2*24}\right)^{1/2} = 0.638$

APPENDIX B

Table B-1 The tensile modulus at 300 %elongation of NR-silica vulcanizates

Sample	1	2	3	Average
NR/10 phr TEOS	2.29 ± 0.24	2.59 ± 0.19	-	2.44 ± 0.21
NR/10 phr TEOS/ 1 phr TESPT	2.52 ± 0.47	2.24 ± 0.04	2.66 ± 0.24	2.47 ± 0.22
NR/10 phr TEOS/ 5 phr TESPT	3.26 ± 0.52	2.73 ± 0.30	2.79 ± 0.22	2.93 ± 0.29
NR/10 phr TEOS/ 10 phr TESPT	4.02 ± 0.88	3.11 ± 0.37	-	3.57 ± 0.65
NR/50 phr TEOS	2.70 ± 0.34	3.97 ± 0.85	-	3.33 ± 0.90
NR/50 phr TEOS/ 1 phr TESPT	3.51 ± 0.81	2.82 ± 0.31	4.04 ± 0.18	3.46 ± 0.61
NR/50 phr TEOS/ 5 phr TESPT	4.02 ± 0.56	4.40 ± 0.10	4.09 ± 0.22	4.17 ± 0.20
NR/50 phr TEOS/ 10 phr TESPT	5.60 ± 0.31	5.06 ± 0.87	-	5.33 ± 0.38

Table B-2 The tear strength of NR-silica vulcanizates

Sample	1	2	3	Average
NR/10 phr TEOS	32.77 ± 1.45	36.34 ± 1.21	-	34.56 ± 2.53
NR/10 phr TEOS/ 1 phr TESPT	36.50 ± 2.36	35.01 ± 1.42	30.60 ± 9.51	34.04 ± 3.07
NR/10 phr TEOS/ 5 phr TESPT	40.11 ± 6.71	25.43 ± 6.39	35.46 ± 5.97	33.67 ± 7.50
NR/10 phr TEOS/ 10 phr TESPT	42.98 ± 1.59	43.08 ± 11.65	-	43.03 ± 0.07
NR/50 phr TEOS	35.88 ± 1.31	41.22 ± 1.95	-	38.55 ± 3.78
NR/50 phr TEOS/ 1 phr TESPT	45.31 ± 2.12	43.16 ± 4.13	45.93 ± 1.85	44.80 ± 1.45
NR/50 phr TEOS/ 5 phr TESPT	48.79 ± 7.63	44.31 ± 4.83	48.55 ± 6.11	47.22 ± 2.52
NR/50 phr TEOS/ 10 phr TESPT	40.96 ± 3.92	45.78 ± 3.94	-	43.37 ± 3.40

Table B-3 The hardness of NR-silica vulcanizates

Sample	1	2	3	Average
NR/10 phr TEOS	40.9 ± 0.59	42.5 ± 0.53	-	41.7 ± 1.13
NR/10 phr TEOS/ 1 phr TESPT	41.6 ± 0.64	38.3 ± 0.70	41.9 ± 0.76	40.6 ± 2.00
NR/10 phr TEOS/ 5 phr TESPT	42.3 ± 0.23	41.0 ± 0.67	41.1 ± 0.69	41.5 ± 0.72
NR/10 phr TEOS/ 10 phr TESPT	43.2 ± 0.44	45.1 ± 0.19	-	44.2 ± 1.34
NR/50 phr TEOS	42.0 ± 0.62	43.3 ± 0.99	-	42.7 ± 0.92
NR/50 phr TEOS/ 1 phr TESPT	43.7 ± 0.46	42.4 ± 0.58	45.4 ± 1.20	43.8 ± 1.50
NR/50 phr TEOS/ 5 phr TESPT	46.9 ± 0.99	46.7 ± 0.36	45.1 ± 0.87	46.2 ± 0.99
NR/50 phr TEOS/ 10 phr TESPT	46.6 ± 0.85	48.4 ± 0.41	-	47.5 ± 1.27

Table B-4 The swelling ratio of NR-silica vulcanizates

Sample	1	2	3	Average
NR/10 phr TEOS	317.93	320.82	319.04	319.26 ± 1.46
NR/10 phr TEOS/ 1 phr TESPT	282.62	278.54	276.12	279.09 ± 3.29
NR/10 phr TEOS/ 5 phr TESPT	257.71	253.84	255.93	255.83 ± 1.94
NR/10 phr TEOS/ 10 phr TESPT	246.37	245.69	245.57	245.88 ± 0.43
NR/50 phr TEOS	272.69	274.07	273.96	273.57 ± 0.77
NR/50 phr TEOS/ 1 phr TESPT	268.14	260.48	269.72	266.11 ± 4.94
NR/50 phr TEOS/ 5 phr TESPT	228.30	232.15	235.77	232.07 ± 3.73
NR/50 phr TEOS/ 10 phr TESPT	214.94	218.22	204.14	212.43 ± 7.37

VITAE

Miss Nantida Niyompanich was born in Chachoengsao, Thailand, on November 3rd, 1980. She received Bachelor Degree of Science in 2002 from Department of Chemistry, Faculty of Science, Burapha University. In the same year she was admitted as a Master Degree student in Petrochemistry and Polymer Science Program, Faculty of Science, Chulalongkorn University, and completed the program in 2005.