REFERENCES

1. Brydson, J. A. *Rubber Chemistry*. Essex England: Applied Science Publishers; Ltd.: **1978**, pp.11-24.
2. Rubber Research Institute of Thailand: Department of Agriculture. *The Information of Natural Rubber Techniques 2001*, 3rd ed., Bangkok, **2001**, pp. 1-3, 10.
3. Billmeyer, F. W. *Textbook of Polymer Science*. 3rd ed., John Wiley & Sons, **1984**, pp. 372.
4. Robert F. M. *Latex and Foam Rubber*. John Wiley & Sons, **1994**, pp. 50-55.
5. Morton, M. *Rubber Technology*. 2nd ed., New York: Van Nostrand Reinhold Company, **1973**, pp.466-467, 51-84, 87-128.
6. "Rubber Research Institute of Malaysia. RRIM Training Manual on Latex and Rubber Analysis". *Rubber Research Institute of Malaysia, Kuala Lumphur* : **1979**, *24*, pp. 31-32, 44-53, 63.
7. Robert, A. D. *Natural Rubber Science and Technology*. Oxford University Press, New York: **1988**, pp.63-70.
8. James, E. M., Burak E., Frederick. R. E. *Science and Technology of Rubber*, 2nd ed., Academic Press: 1994, pp.420-422, 344-346.
9. Rubber Research Institute of Thailand; Department of Agriculture. *Revision to Thai Technically Specified Rubber Scheme*: **1999**, 2, pp.4-6.
10. Barlow, F. W. *Rubber compounding*. 2nd ed. Marcel Dekker; Inc. New York, **1993**, pp.18-21.
11. Morgan, E. *Chemometrics: Experimental Design*. John Wiley & Sons, **1991**, pp. 92-128.
12. Douglas, C. M. *Design and analysis of Experiments*. 5th ed. John Wiley & Sons, **2001**, pp. 218-244.

13. Kohjiya, S., Murakami, K., Iio, S. *et al.,* "*In situ* filling of silica onto "green" natural rubber by the sol-gel process." *Rubber Chem. Technol.*, **2001**, 74, 16-27.

14. Tanahashi, H., Osani, S., Shigekuni, K. *et al.,* "Reinforcement of acrylonitrile-butadiene rubber by silica generated *in situ*." *Rubber Chem. Technol.*, **1998**, 71, 38-52.

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

16. 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.*, **1997**, 7, 1497-1503.

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

18. 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.*, **1997**, 7, 455-458.

19. Yoshikai, K., Ohsaki, T. and Furukawa, M. "Silica reinforcement of synthetic diene rubbers by sol-gel process in the latex." *J. Appl. Polym. Sci.*, **2002**, 85, 2053-2063.

20. Tong, X., Tang, T., Zhang, Q-L. Feng, Z., Huang, B-T., "Polymer/silica nanoscale hybrids through sol-gel method involving emulsion polymers. I. Morphology of poly(butyl methacrylate)/SiO_2" *J. Appl. Polym. Sci,* **2002**, 83, 446-454.

21. Jan, J.-S. and Park, H.-S., "Formation and structure of polyacrylamide-silica nanocomposites by sol-gel process" *J. Appl. Polym. Sci,* **2002**, 83, 1817-1823.

22. Hsiue, G.-H., Chen, J.-K., and Liu, Y.-L., "Synthesis and characterization of nanocomposite of polyimide-silica hybrid from nonaqueous sol-gel process." *J. Appl. Polym. Sci.*, **2000**, 76, 1609-1618.

APPENDICES

APPENDIX A

Table A-1 Silica contents and mechanical properties data of NR composite filled with *in-situ* generated silica

Exp.	Silica content (%)		Modulus 300% elongation (MPa)		Tear strength (N/mm)		Tensile strength (MPa)	
Set	1	2	1	2	1	2	1	2
ED 1	2.85 ± 0.07	2.52 ± 0.50	1.844 ± 0.147	1.890 ± 0.136	32.80 ± 1.58	34.33 ± 1.25	16.40 ± 1.21	15.33 ± 1.25
ED 2	2.90 ± 0.40	2.73 ± 0.26	1.958 ± 0.220	2.071 ± 0.159	31.34 ± 1.13	33.24 ± 1.20	15.56 ± 1.97	16.88 ± 2.78
ED 3	2.73 ± 0.25	2.62 ± 0.42	2.142 ± 0.115	2.040 ± 0.233	33.42 ± 0.72	31.76 ± 1.40	19.98 ± 1.47	15.54 ± 1.70
ED 4	13.03 ± 0.06	12.96 ± 0.99	2.544 ± 0.294	2.678 ± 0.403	36.06 ± 1.44	36.82 ± 1.91	25.84 ± 1.11	21.12 ± 2.52
ED 5	12.99 ± 0.21	13.35 ± 0.82	2.841 ± 0.486	3.086 ± 0.253	38.28 ± 0.67	37.33 ± 2.23	24.88 ± 1.58	24.91 ± 1.39
ED 6	13.02 ± 0.21	13.56 ± 0.89	2.757 ± 0.137	2.647 ± 0.286	39.52 ± 1.39	36.44 ± 0.87	23.27 ± 1.38	20.86 ± 1.08
ED 7	13.03 ± 0.14	13.98 ± 0.83	2.834 ± 0.318	2.762 ± 0.249	41.95 ± 0.89	39.94 ± 1.95	24.96 ± 1.12	24.30 ± 1.58
ED 8	2.48 ± 0.05	2.60 ± 0.15	2.414 ± 0.294	2.346 ± 0.272	35.41 ± 0.40	32.99 ± 2.20	20.19 ± 1.84	17.40 ± 1.93

APPENDIX B

Experimental designs

Effect on tensile modulus

T effect:

T effect = (y4+y5+y6+y7)/4 - (y1+y2+y3+y8)/4

= (2.611+2.964+2.702+2.798)/4 – (1.867+2.015+2.091+2.380)/4

N effect:

N effect = (y3+y5+y6+y8)/4 - (y1+y2+y4+y7)/4

= (2.091+2.964+2.702+2.380)/4 – (1.867+2.015+2.611+2.798)/4

G effect:

G effect = (y2+y5+y7+y8)/4 - (y1+y3+y4+y6)/4

= (2.015+2.964+2.798+2.380)/4 – (1.867+2.091+2.611+2.702)/4

TN effect:

TN effect = (y1+y2+y5+y6)/4 - (y3+y4+y7+y8)/4

= (1.867+2.015+2.964+2.702)/4 – (2.091+2.611+2.798+2.380)/4

TG effect:

TG effect = (y1+y3+y5+y7)/4 - (y2+y4+y6+y8)/4

= (1.867+2.091+2.964+2.798)/4 – (2.015+2.611+2.702+2.380)/4

NG effect:

NG effect = (y1+y4+y5+y8)/4 - (y2+y3+y6+y7)/4

= (1.867+2.611+2.964+2.380)/4 – (2.015+2.091+2.702+2.798)/4

TNG effect:

TNG effect = (y2+y3+y4+y5)/4 - (y1+y6+y7+y8)/4

= (2.015+2.091+2.611+2.964)/4 – (1.867+2.702+2.798+2.380)/4

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

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

No.	T	N	G	TN	TG	NG	TNG	Tensile modulus 300% (MPa)
ED 1	-	-	-	+	+	+	-	1.867
ED 2	-	-	+	+	-	-	+	2.015
ED 3	-	+	-	-	+	-	+	2.091
ED 4	+	-	-	-	-	+	+	2.611
ED 5	+	+	+	+	+	+	+	2.964
ED 6	+	+	-	+	-	-	-	2.702
ED 7	+	-	+	-	+	-	-	2.798
ED 8	-	+	+	-	-	+	-	2.380
Estimated effect	0.681	0.212	0.221	-0.083	0.003	0.054	-0.017	

Table B-2 Calculation of standard error of estimated effect

Sample No.	Results from individual runs		Average response value	Difference	Standard deviation of each run (SD)
	1	2			
1	1.844	1.890	1.867	0.046	0.0011
2	1.958	2.071	2.015	0.113	0.0064
3	2.142	2.040	2.091	0.102	0.0052
4	2.544	2.678	2.611	0.134	0.0090
5	2.841	3.086	2.964	0.245	0.0300
6	2.757	2.647	2.702	-0.110	0.0061
7	2.834	2.762	2.798	0.072	0.0026
8	2.414	2.346	2.380	0.068	0.0023
				Σ SD =	0.0626

Standard error of estimated effect = $\{(\Sigma\ SD)/\ 2(N)^{1/2} = (0.0626 / 32)^{1/2} = 0.044$

Effect on tensile strength

Table B-3 Estimated effect for the 2^3 factorial design on tensile strength

No.	T	N	G	TN	TG	NG	TNG	Tensile strength (MPa)
ED 1	-	-	-	+	+	+	-	15.87
ED 2	-	-	+	+	-	-	+	16.22
ED 3	-	+	-	-	+	-	+	17.76
ED 4	+	-	-	-	-	+	+	23.48
ED 5	+	+	+	+	+	+	+	24.90
ED 6	+	+	-	+	-	-	-	22.07
ED 7	+	-	+	-	+	-	-	24.63
ED 8	-	+	+	-	-	+	-	18.80
Estimated effect	6.61	0.83	1.34	-1.41	0.65	0.59	0.25	

Table B-4 Calculation of standard error of estimated effect

Sample No.	Results from individual runs		Average response value	Difference	Standard deviation of each run (SD)
	1	2			
1	16.40	15.33	15.87	-1.07	0.57
2	15.56	16.88	16.22	1.32	0.87
3	19.98	15.54	17.76	4.44	9.86
4	25.84	21.12	23.48	-4.72	11.14
5	24.88	24.91	24.90	0.03	0.00
6	23.27	20.86	22.07	-2.41	2.90
7	24.96	24.30	24.63	0.66	0.22
8	20.19	17.40	18.80	2.79	3.89
				Σ SD =	29.45

Standard error of estimated effect = $\{(\Sigma SD)/ 2(N)\}^{1/2} = (29.45 / 32)^{1/2} = 0.96$

Effect on tear strength

Table B-5 Estimated effect for the 2^3 factorial design on tear strength

No.	T	N	G	TN	TG	NG	TNG	Tear strength (N/mm)
ED 1	-	-	-	+	+	+	-	33.57
ED 2	-	-	+	+	-	-	+	32.29
ED 3	-	+	-	-	+	-	+	32.59
ED 4	+	-	-	-	-	+	+	36.44
ED 5	+	+	+	+	+	+	+	37.81
ED 6	+	+	-	+	-	-	-	37.98
ED 7	+	-	+	-	+	-	-	40.95
ED 8	-	+	+	-	-	+	-	34.20
Estimated effect	5.13	-0.17	1.17	-0.63	1.00	-0.45	-1.89	

Table B-6 Calculation of standard error of estimated effect

Sample No.	Results from individual runs		Average response value	Difference	Standard deviation of each run (SD)
	1	2			
1	32.80	34.33	33.57	1.53	1.17
2	31.34	33.24	32.29	1.90	1.81
3	33.42	31.76	32.59	1.66	1.38
4	36.06	36.82	36.44	0.76	0.29
5	38.28	37.33	37.81	-0.95	0.45
6	39.52	36.44	37.98	-3.08	4.74
7	41.95	39.94	40.95	-2.01	2.02
8	35.41	32.99	34.20	-2.42	2.93
				Σ SD =	14.78

Standard error of estimated effect = $\{(\Sigma SD)/ 2(N)^{1/2} = (14.78 / 32)^{1/2} = 0.68$

APPENDIX C

Table C-1 Cure time (min) of NR-silica composite

Silica content (%)	Mechanically mixed silica	*In situ* silica
0	9.45	6.96
2	11.04	6.48
5	11.30	5.04
7	11.14	5.27
10	11.49	6.19
13	11.10	6.55
16	11.47	4.58
19	10.36	5.20

Table C-2 Mooney viscosity (MV) of NR-silica composite

Silica content (%)	Mechanically mixed silica	*In situ* silica
0	43.05	29.66
2	50.69	33.04
5	55.57	30.91
7	59.88	34.16
10	59.88	40.48
13	63.26	42.92
16	53.50	36.00
19	65.88	40.38

Table C-3 Tensile modulus at 300% elongation (MPa) of NR-silica composite

Silica content (%)	Mechanically mixed silica	*In situ* silica
0	1.749 ± 0.084	1.812 ± 0.117
2	1.884 ± 0.181	2.071 ± 0.159
5	2.257 ± 0.333	2.243 ± 0.178
7	2.277 ± 0.184	2.446 ± 0.139
10	2.315 ± 0.154	2.651 ± 0.138
13	2.334 ± 0.061	2.762 ± 0.249
16	2.482 ± 0.364	3.106 ± 0.211
19	2.434 ± 0.323	3.726 ± 0.292

Table C-4 Tensile strength (MPa) of NR-silica composite

Silica content (%)	Mechanically mixed silica	*In situ* silica
0	12.71 ± 6.07	13.69 ± 1.31
2	17.58 ± 1.65	16.88 ± 2.78
5	21.95 ± 0.99	20.10 ± 1.12
7	24.61 ± 1.61	23.40 ± 0.78
10	24.17 ± 1.07	22.83 ± 0.83
13	23.69 ± 1.65	24.30 ± 1.58
16	23.44 ± 0.98	24.40 ± 1.70
19	22.42 ± 1.22	24.26 ± 1.65

Table C-5 Tear strength (N/mm) of NR-silica composite

Silica content (%)	Mechanically mixed silica	*In situ* silica
0	29.96 ± 1.26	31.68 ± 1.54
2	29.73 ± 0.51	33.24 ± 1.20
5	32.33 ± 1.07	32.97 ± 1.88
7	33.75 ± 3.00	35.10 ± 2.24
10	32.09 ± 1.13	36.43 ± 2.54
13	31.58 ± 1.73	39.94 ± 1.95
16	35.09 ± 2.07	36.98 ± 1.29
19	33.52 ± 1.64	40.57 ± 2.50

Table C-6 Stress (MPa) and strain (%) value of eight experiments in experimental designs

Sample	Stress at n% elongation (MPa)					Elongation at break (%)	Tensile strength (MPa)
	100%	200%	300%	400%	500%		
ED 1	0.74	1.27	1.89	2.87	4.98	685	15.33
ED 2	0.84	1.37	2.07	3.15	4.97	662	16.88
ED 3	0.85	1.38	2.04	2.99	4.18	737	15.54
ED 4	1.04	1.69	2.68	4.39	7.36	764	21.12
ED 5	1.12	1.78	2.84	4.66	7.09	728	24.88
ED 6	1.02	1.68	2.65	4.19	7.00	731	20.86
ED 7	1.10	1.79	2.83	4.61	7.97	717	24.96
ED 8	0.99	1.57	2.35	3.61	6.77	696	17.40

Table C-7 Stress (MPa) and strain (%) value of NR-silica composites

Sample	Stress at n% elongation (MPa)					Elongation at break (%)	Tensile strength (MPa)
	100%	200%	300%	400%	500%		
I0	0.81	1.27	1.81	2.55	3.74	718	13.96
I2	0.84	1.37	2.07	3.15	4.97	711	16.88
I5	0.89	1.47	2.24	3.46	5.89	687	20.10
I7	0.93	1.55	2.45	3.94	7.04	705	23.40
I10	0.99	1.64	2.65	4.40	7.51	743	22.83
I13	1.03	1.71	2.76	4.59	7.80	809	24.30
I16	1.16	0.91	3.11	5.10	8.76	708	24.40
I19	1.32	2.24	3.73	6.16	10.53	679	24.26
M0	0.74	1.21	1.75	2.54	3.97	706	12.71
M2	0.80	1.29	1.88	2.74	4.39	767	17.58
M5	0.93	1.50	2.26	3.53	5.45	740	21.95
M7	0.94	1.53	2.28	3.42	5.69	759	24.60
M10	0.95	1.54	2.32	3.58	6.21	754	24.17
M13	0.95	1.54	2.33	3.63	6.16	769	23.69
M16	1.00	1.60	2.48	3.96	6.43	794	23.44
M19	0.99	1.53	2.43	3.73	6.04	812	22.44

VITAE

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