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**APPENDICES**

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## APPENDIX A

### Model Studies

**Table A-1** Water contact angle data and layer thickness of VDMS-Si.

Sample	Time (h)	Layer thickness (Å)	$\theta_A/\theta_R(^{\circ})$
Clean Si-Surface	-	22.6±2.15	46/31
VDMS-Si	0.083	6.0±1.59	54/47
	0.167	6.0±0.67	58/43
	0.5	6.4±0.96	60/52
	1	6.5±0.67	66/57
	2	6.5±0.70	75/68
	6	6.0±0.66	80/70
	12	7.0±1.26	82/75
	24	6.5±1.59	93/84
	48	7.1±2.07	94/88

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**Table A-2** Water contact angle data and layer thickness of TVS-Si.

Sample	Time (h)	Layer thickness (Å)	$\theta_A/\theta_R(^{\circ})$
Clean Si-Surface	-	22.6±2.15	46/31
TVS-Si	0.083	11.25±0.77	50/32
	0.167	13.25±0.82	55/41
	0.5	11.06±1.70	60/58
	1	13.00±1.85	79/68
	2	12.16±2.11	82/73
	6	12.50±1.27	83/77
	12	12.55±1.85	85/73
	24	11.80±1.45	90/80
	48	12.20±1.37	93/81

**Table A-3** The thickness of crosslinked layer at VDMS-Si/SqE interface as a function of *p*-TsOH using SqE 10% (mole/mole), at 40 °C for 6h.

<i>p</i> -TsOH : SqE (w/w)	Layer thickness (Å)
0.25 %	8.20±1.83
0.5 %	10.43±1.29
1.0 %	9.20±0.98
5.0 %	15.67±0.74
10.0 %	15.00±1.00
20.0 %	16.40±1.95

**Table A-4** The thickness of the crosslinked layer at VDMS-Si/SqE interface as a function of SqE using *p*-TsOH 5% (mole/mole) at 40°C for 6 h.

% SqE in Toluene	Layer thickness (Å)
5	15.01±1.05
10	15.67±0.74
20	20.67±1.37
35	22.67±0.94
50	21.20±1.03
75	21.70±1.03
100	21.67±1.24
% 100 SqA in Toluene	6.40±1.28

**Table A-5** The thickness of VDMS-Si/SqE interface using *p*-TsOH 5% (mole/mole).

Time (h)	Layer thickness (Å)		
	40°C	70°C	150°C
1	8.00±1.29	15.25±2.16	16.60±1.85
3	14.30±1.30	17.80±2.31	23.25±0.83
6	22.67±0.94	28.33±1.69	26.60±0.80
12	25.20±1.89	34.50±1.11	-
24	30.50±1.50	39.75±2.38	-



**Table A-6** The thickness of TVS-Si/SqE interface using *p*-TsOH 5% (mole/mole).

Time (h)	Layer thickness (Å)		
	40°C	70°C	150°C
1	10.00±1.73	12.40±1.10	18.60±1.35
3	15.75±1.38	15.50±2.44	23.20±2.31
6	23.60±1.74	27.30±1.09	26.75±2.77
12	30.30±1.09	38.25±0.83	-
24	35.80±1.12	43.75±1.41	-

**Table A-7** The thickness of VDMS-Si/SqE and TVS-Si/SqE interfaces using sulfur 5% (mole/mole) at 150°C.

Time (h)	Layer thickness (Å)	
	VDMS-Si/SqE	TVS-Si/SqE
1	20.50±1.65	18.80±2.48
3	22.80±1.93	22.20±2.92
6	28.25±2.30	25.88±2.11

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## APPENDIX B

### Curing Behavior and Mechanical Properties of Natural Rubber Composites

**Table B-1** Cure time (min) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	8.50	8.50	8.50	8.50	8.50	8.50
5	9.47	8.47	11.07	11.31	8.56	8.28
10	9.47	7.40	8.15	9.45	8.05	9.17
20	9.50	5.56	7.53	8.40	12.20	6.43
30	7.29	4.38	7.20	6.41	10.31	5.43

**Table B-2** Scorch time (min) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	5.32	5.32	5.32	5.32	5.32	5.32
5	6.22	5.48	5.17	6.58	4.51	4.53
10	6.13	5.00	4.27	5.48	4.52	5.19
20	6.06	4.03	3.52	6.07	5.44	3.37
30	4.15	2.43	3.03	4.30	4.40	3.16

**Table B-3** Mooney viscosity (MV) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	39.16	39.16	39.16	39.16	39.16	39.16
5	49.47	37.04	38.81	36.97	36.14	35.81
10	54.49	27.76	44.77	37.49	36.97	36.84
20	49.66	34.78	43.74	25.19	46.96	36.46
30	88.31	28.15	40.45	44.51	27.25	45.35

**Table B-4** Hardness (Shore A) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	40.6	40.6	40.6	40.6	40.6	40.6
5	38.9	42.0	39.9	39.3	46.0	45.3
10	40.0	42.0	41.3	41.4	46.7	45.5
20	39.7	46.7	46.1	45.8	49.0	49.6
30	43.9	50.0	50.8	51.1	51.4	55.1

**Table B-5** Tensile strength (MPa) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	23.48±2.05	23.48±2.05	23.48±2.05	23.48±2.05	23.48±2.05	23.48±2.05
5	22.29±2.65	25.33±2.16	12.44±0.42	16.63±2.56	19.00±1.12	17.49±3.63
10	26.05±1.11	20.08±1.75	15.05±6.20	19.20±1.69	13.19±3.61	20.66±0.59
20	25.56±2.13	27.79±1.01	25.41±1.77	28.16±0.91	24.05±4.59	27.99±2.03
30	18.42±1.13	29.55±1.33	27.40±0.88	29.41±0.86	29.92±0.87	31.11±0.46

**Table B-6** Tear strength (N/mm) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	36.97±4.40	36.97±4.40	36.97±4.40	36.97±4.40	36.97±4.40	36.97±4.40
5	37.10±1.67	33.94±1.94	35.78±3.27	32.95±4.70	39.67±1.35	36.30±2.14
10	34.66±1.85	35.13±1.24	39.10±2.09	41.20±2.00	37.13±4.53	31.76±3.06
20	37.22±1.47	40.58±2.14	59.27±5.74	39.22±1.22	52.26±4.21	48.14±9.85
30	26.72±1.09	51.41±6.71	78.96±14.3	68.81±5.56	63.42±8.5	80.22±2.21

**Table B-7** Tensile modulus (M100) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	0.959±0.07	0.959±0.07	0.959±0.07	0.959±0.07	0.959±0.07	0.959±0.07
5	0.836±0.07	0.958±0.19	0.977±0.23	0.987±0.92	1.278±0.27	1.331±0.06
10	1.081±0.29	0.910±0.17	1.181±0.17	1.251±0.38	1.355±0.12	1.309±0.14
20	0.951±0.10	1.169±0.08	1.436±0.16	1.315±0.18	1.38±0.06	1.399±0.18
30	0.952±0.04	1.274±0.05	1.763±0.19	1.590±0.14	1.519±0.13	1.778±0.11

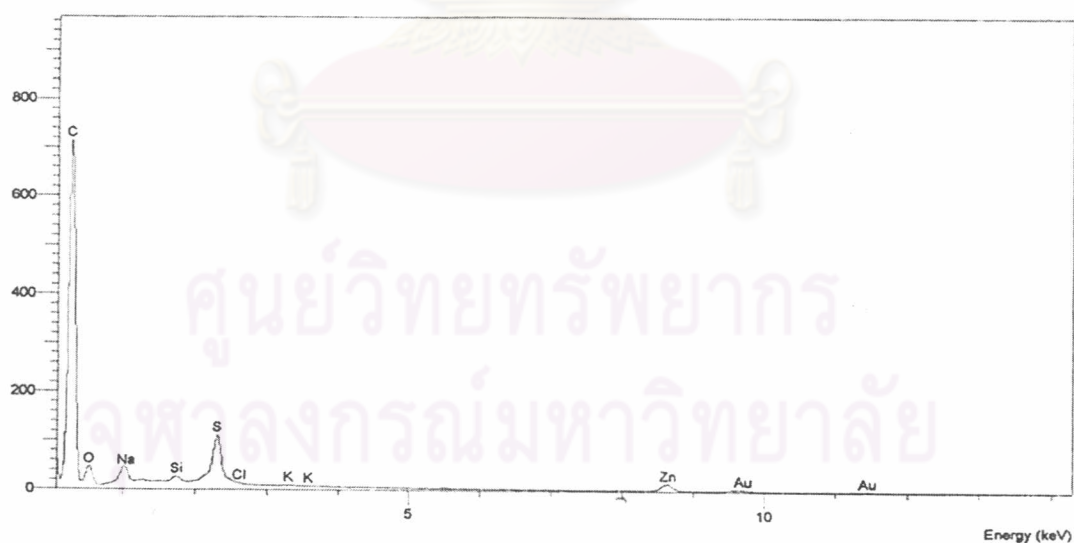


**Table B-8** Tensile modulus (M300) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	2.39±0.17	2.39±0.17	2.39±0.17	2.39±0.17	2.39±0.17	2.39±0.17
5	2.337±0.37	2.691±0.31	2.834±0.30	2.698±0.23	4.616±0.75	4.22±0.42
10	2.781±0.44	2.703±0.44	3.810±0.61	3.548±1.10	4.378±0.56	3.579±1.10
20	2.550±0.30	3.004±0.30	4.874±0.53	4.031±0.72	5.925±0.35	5.166±0.35
30	2.891±0.27	3.713±0.25	6.533±1.26	5.205±0.76	6.088±0.68	6.212±0.50

**Table B-9** Elongation at break (%) of natural rubber composites filled with silica.

Phr	Silica	VDMS-Si	Si-69 mix	TVS-Si	Si-69 Pre	VDMS-Si+ Si69mix
0	707.1±47.0	707.1±47.0	707.1±47.0	707.1±47.0	707.1±47.0	707.1±47.0
5	713.1±69.9	917.9±561	513.5±157	588.1±26.6	530.7±29.9	513.3±41.9
10	1390.0±746	1018.0±580	524.1±127	591.4±62.7	478.4±48.9	249.9±44.3
20	721.0±72.2	760.0±50.8	849.6±426	297.0±645	573.9±62.5	1518.0±403
30	718.7±49.2	760.6±36.1	654.3±83.9	1261±598.4	656.7±38.9	1046.0±566

**Figure B-1** Elemental scan of natural rubber composites without silica.

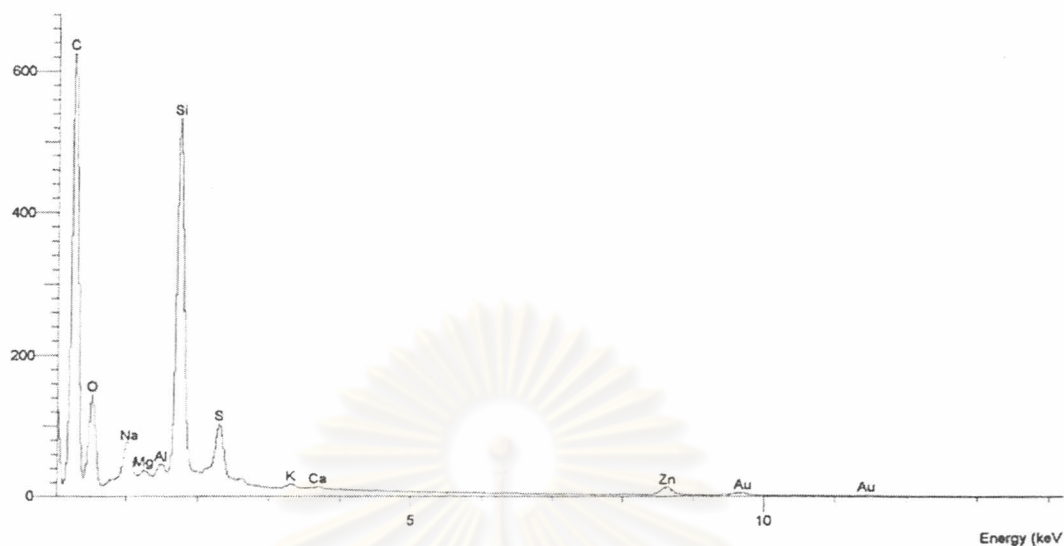
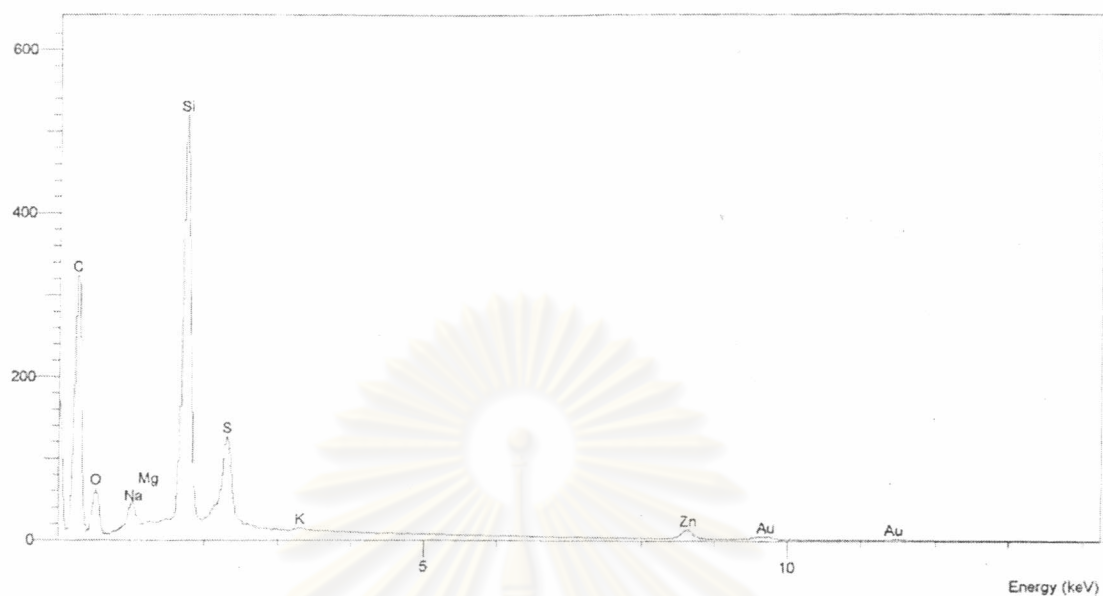


Figure B-2 Elemental scan of natural rubber composites filled with 30 phr silica.



Figure B-3 Elemental scan of natural rubber composites filled with VDMS-Si.





**Figure B-4** Elemental scan of natural rubber composites filled with silica and mixed with Si-69.



**Figure B-5** Elemental scan of natural rubber composites filled with TVS-Si.

## VITAE

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