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APPENDIX A

Co-monomer Loading Calculation

Table A1 Calculation of the amount of co-monomer loading for the surface modification.

Monomer	Styrene	Isoprene
Mole ratio	1	3
Molecular weight	104.15	68.12
Density (ml/g)	0.906	0.681

Mole factor	Weight (g)		Total weight (g)	Volume (ml)	
	Styrene	Isoprene		Styrene	Isoprene
0.01621	1.6880	3.3120	5	0.0147	0.0331
0.06483	6.7518	13.2482	20	0.0587	0.1324
0.09724	10.1277	19.8723	30	0.0881	0.1987

Pump Flow Rate Determination

Table A2 Calculation of pump flow rate for various retention times of the surface modification.

Reactor size	1 liter	(V)
Total run volume	12.5 liters	

(τ)	$(v = V / \tau)$		$(t = \tau / v)$		
Mean resident time (min)	Flow rate		Total run time		
	ml / sec	ml / min	min	hr	hr : Min
30	0.556	33.33	375	6.25	6:15
45	0.370	22.22	562.5	9.375	9: 22.5
60	0.278	16.67	750	12.5	12:30

Calculation is based on a ratio of 80 grams silica per liter of CTAB solution, and for one-kilogram silica modification per a run.

APPENDIX B

Pulse Test Results

Table B1 Pulse test results of reactor by injection of NaOH to water feed at 30 ml/min, 30°C.

Min	Sec	Time (min)	PH	Delta pH
-	0	-	8.23	-
-	10	0.17	8.23	0.00
-	20	0.33	8.25	0.02
-	40	0.67	8.57	0.34
1	0	1.00	8.67	0.44
1	20	1.33	8.71	0.48
1	40	1.67	8.73	0.50
2	0	2.00	8.75	0.52
2	20	2.33	8.75	0.52
2	40	2.67	8.76	0.53
3	0	3.00	8.76	0.53
3	20	3.33	8.75	0.52
3	40	3.67	8.72	0.49
4	30	4.50	8.71	0.48
5	10	5.17	8.70	0.47
5	40	5.67	8.72	0.49
6	20	6.33	8.63	0.40
7	10	7.17	8.68	0.45
8	10	8.17	8.67	0.44
9	0	9.00	8.67	0.44
10	15	10.25	8.66	0.43
11	5	11.08	8.66	0.43
12	50	12.83	8.63	0.40
13	30	13.50	8.63	0.40
15	30	15.50	8.58	0.35
16	30	16.50	8.54	0.31
18	5	18.08	8.56	0.33

Table B1 (Continued).

Min	Sec	Time (min)	PH	Delta pH
19	20	19.33	8.54	0.31
20	20	20.33	8.52	0.29
21	20	21.33	8.53	0.30
25	30	25.50	8.47	0.24
27	0	27.00	8.44	0.21
29	10	29.17	8.44	0.21
30	30	30.50	8.45	0.22
32	50	32.83	8.43	0.20
33	40	33.67	8.41	0.18
36	10	36.17	8.39	0.16
38	20	38.33	8.38	0.15
41	10	41.17	8.37	0.14
43	40	43.67	8.40	0.17
45	0	45.00	8.37	0.14
48	20	48.33	8.34	0.11
49	40	49.67	8.36	0.13
51	10	51.17	8.33	0.10
52	30	52.50	8.35	0.12
56	30	56.50	8.32	0.09
60	40	60.67	8.31	0.08
66	0	66.00	8.27	0.04
72	20	72.33	8.27	0.04
79	7	79.12	8.27	0.04
84	50	84.83	8.27	0.04
90	30	90.50	8.26	0.03
106	40	106.67	8.25	0.02

Product Consistency Consideration

Table B2 Carbon content from TOC at different time after startup.

Time (Hr:min)	Time (min)	C content (ppm)
0:00	0	2924
0:15	15	2879
0:30	30	2758
0:45	45	2795
1:00	60	2790
1:15	75	2807
2:00	120	2800
2:30	150	2811
3:00	180	2817

Modification condition is 40-gram styrene-isoprene charged per kilogram silica at 120-minute retention time. Polymerization was carried on at 70°C.

The carbon content at various startup time of product come out from reactor was determined by using a Total Organic Carbon analyzer (TOC). The carbon content value represents the amount of CTAB and monomers dissolving in liquid filtered from product.

BET Raw Data

Table B3 BET surface area raw data with various retention times and styrene-isoprene loading.

Sample		BET		
Monomer loading (g/kg silica)	Retention time*	m ² / g		% Changed
5	S	130.45	-	-23.51
	M	133.65	-	-21.64
	L	117.60	-	-31.05
20	S	136.90	-	-19.73
	M1	151.30	143.23	-11.29
	M2	135.15		-20.76
	L	130.60	-	-19.93
30	S	140.57	-	-17.58
	M	135.43	-	-35.12
	L	133.00	-	-22.02
Silica Hi-Sil®255		170.55	-	-
Average			-22.26	

*S = 30 min

M= 45 min

L = 60 min

Silica Hi-Sil®255 was outgased at 200°C in N₂ environment. All modified silicas were outgased at 150°C for at least three hours, then, analyzed with program of 10 points adsorption and 10 points desorption. The calculation is based on silica Hi-Sil®255.

Particle Size Raw Data

Table B4 Particle size raw data with various retention times and styrene-isoprene loadings.

Sample		Particle size (μ m)			
Monomer loading (g/kg silica)	Retention time*	1 st	2 nd	Average	% Changed
5	S	55.85	-	55.85	0.14
	M	64.18	62.87	63.53	13.91
	L	59.83	-	59.83	7.28
20	S	63.38	-	63.38	13.65
	M1	74.21	-	70.86	33.06
	M2	67.51	-		21.05
	L	68.02	-	68.02	21.97
30	S	63.27	-	63.27	13.45
	M	64.88	-	64.88	16.33
	L	65.00	63.79	64.40	15.47
Silica Hi-Sil®255		55.77	-	55.77	-
Average					15.63

*S = 30 min

M= 45 min

L = 60 min

Calculation of the Amount of Polymer from TGA

Table B5 Calculation of the amount of polymer from TGA data of the modified silica.

Sample		TGA (%wt. loss)						% Extracted polymer	
		Before THF extraction			After THF extraction				
		1st step * losing	2nd step # losing	Calculated polymer	1st step * losing	2nd step # losing	Calculated polymer		
5	S	6.198	2.595	1.220	6.793	2.519	1.013	20.74	
	M	7.228	2.611	1.008	7.230	2.545	0.942	6.64	
	L	6.421	3.1005	1.677	6.6975	3.0055	1.520	15.63	
20	S	7.001	2.805	1.253	8.294	2.955	1.116	13.67	
	M1	4.547	1.915	0.907	4.689	1.845	0.805	10.20	
	M2								
30	S	4.099	1.648	0.739	4.323	1.590	0.631	10.77	
	M	7.053	3.020	1.456	7.592	2.946	1.263	19.35	
	L	5.681	2.461	1.201	6.242	2.345	0.961	24.00	
Silica-CTAB		9.404	2.488						
		11.86	2.227						
Average		10.632	2.3575						

* Disappear at 150°C

Disappear at 300°C

% wt of calculated polymer = the % wt lose at the second lose of modified silica - (the % wt lose at the first lose of modified silica \times 10.632 / 2.3575)

% wt of extracted polymer = (% wt of calculated polymer at before THF extraction - % wt of calculated polymer at after THF extraction) \times 100



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