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APPENDICES

Appendix A Continuous Stirred Tank Reactor

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	0.906	0.681

Mole factor	Weight (g)		Total weight (g)	Volume (ml)	
	Styrene	Isoprene		Styrene	Isoprene
0.01621	1.688	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 l	(V)
Total run volume	12.5 l	

Mean resident time (min)	Flow rate ($v = V / \tau$)		Total run time ($t = \tau / v$)		
	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
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.

Product Consistency Consideration**Table A3** Carbon content from TOC at different time after startup

Time (h:min)	Time (min)	C content (ppm)
0:00	0	2011
0:15	15	2219
0:30	30	2401
0:45	45	2228
1:00	60	2316
1:30	90	2353
2:00	120	2012
2:30	150	2116
3:00	180	2380
3:30	210	2085
4:00	240	2085

Modification condition is 20 g styrene-isoprene charged per kg silica at 30 min retention time. Polymerization was carried on at 70°C.

The carbon content at various startup time of product from the reactor was determined by a TOC. The carbon content value represents the amount of CTAB and monomers dissolving in the liquid filtered from product.

Appendix B Adsorption Isotherm

Surfactant Adsorption Isotherms Calculation

CTAB adsorption isotherm was constructed by plotting the amount of CTAB adsorbed per gram silica versus equilibrium concentration of CTAB.

Conditions : Silica 0.5 g, Solution 20 ml, MW of CTAB

1. Finding CTAB adsorbed concentration (ppm).

$$[\text{Adsorbed CTAB}] = [\text{Initial CTAB}] - [\text{Equilibrium CTAB}]$$

$$[\text{Initial CTAB}] = 149.70 \text{ ppm.}$$

$$[\text{Equilibrium CTAB}] = 32.00 \text{ ppm.}$$

$$[\text{Adsorbed CTAB}] = 149.70 - 32.00 = 117.70 \text{ ppm.}$$

2. To convert unit of ppm to micromolar by parameter from calibration curve.

$$\text{Micromolar} = \text{ppm}/0.3137$$

$$\text{Adsorbed concentration } (\mu\text{M}) = \text{Adsorbed concentration (ppm)}/0.3137$$

$$\text{Adsorbed concentration } (\mu\text{M}) = 117.70/0.3137 = 477.21$$

$$\text{Equilibrium concentration } (\mu\text{M}) = \text{Equilibrium concentration (ppm)}/0.3137$$

$$\text{Equilibrium concentration } (\mu\text{M}) = 32.00/0.3137 = 102.01$$

3. To convert adsorption concentration to moles of adsorption.

$$\text{Mole} = \frac{(\text{concentration} \times \text{volume})}{1000}$$

$$\text{Adsorbed } (\mu\text{moles}) = \frac{(\text{Adsorbed } (\mu\text{M}) \times \text{volume of solution})}{1000}$$

$$\text{Adsorbed } (\mu\text{moles}) = (477.21 \times 20)/1000 = 9.54$$

4. Finding CTAB adsorbed per gram silica.

$$\text{CTAB adsorbed } (\mu\text{moles/g silica}) = \frac{\text{Adsorbed } (\mu\text{moles})}{0.5 \text{ g}}$$

$$\text{CTAB adsorbed } (\mu\text{moles/g silica}) = 9.54/0.5 = 19.09$$

Adsorption Isotherm**Table B1** Adsorption isotherm of CTAB at pH 5 and 8

Adsorbed CTAB ($\mu\text{mol/g}$ silica)	Eq conc.(μM)
1.45	26.72
10.23	36.35
13.74	46.74
18.21	41.19
22.16	38.86
28.76	71.63
33.04	60.91
120.66	47.84
383.66	179.44
435.79	160.65
633.10	595.74
697.30	791.97
688.15	1101.25
718.03	2487.62
730.23	1776.83
747.27	3353.39
674.37	30622.98
618.46	38282.76
716.59	44738.54

Appendix C Surface Characterization

BET Raw Data

Table C1 BET surface area raw data with various retention times and styrene-isoprene loading.

Sample		BET surface area		Pore Volume		Pore Diameter	
Monomer Loading (g/kg silica)	Retention Time*	m ² / g	% Changed	(cc/g)	% Changed	(A°)	% Changed
5	L	119.0	-30.21	1.144	-23.83	365.6	15.66
	M	141.0	-17.30	1.582	5.33	428.4	35.53
	H	124.0	-27.27	1.176	-21.70	377.7	19.49
20	L	129.2	-24.22	0.896	-40.35	260.9	-17.46
	M	143.0	-16.13	1.216	-19.04	348.0	10.09
	H	135.0	-20.82	1.205	-19.77	354.7	12.21
30	L	139.0	-18.48	1.210	-19.44	348.3	10.19
	M	157.0	-7.92	1.579	5.13	399.8	26.48
	H	153.0	-10.26	1.136	-24.37	314.3	-0.57
Silica Hi-Sil [®] 255		170.5	-	1.502	-	316.1	-
Average			-18.78		-17.56		12.40

*L = 30 min, M = 45 min, H = 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 C2 Particle size raw data with various retention times and styrene-isoprene loading.

Sample		Particle size (μm)				
Monomer Loading (g/kg silica)	Retention time*	1 st	2 nd	3 rd	Average	% Changed
5	L	93.15	92.36	-	92.76	82.409
	M	98.11	98.53	-	98.32	93.353
	H	100.69	104.66	-	102.68	101.917
20	L	73.97	79.14	83.70	78.94	55.2343
	M	90.54	71.79	-	81.17	59.6165
	H	69.97	72.26	66.93	69.72	37.1091
30	L	84.84	85.45	-	85.15	67.4435
	M	80.99	79.47	-	80.23	57.7778
	H	69.59	70.91	-	70.25	38.1514
Silica Hi-Sil [®] 255		52.44	49.25	-	50.85	-
Average						65.8902

*L = 30 min

M = 45 min

H = 60 min

Calculation of Amount of Polymer from TGA

Table C3 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			
		1 st step* losing	2 nd step** losing	Calculated % carbon of polymer	1 st step* losing	2 nd step** losing	Calculated % carbon of polymer	
5	L	2.250	1.600	1.101	3.698	1.043	0.223	87.810
	M	2.977	1.567	0.907	3.715	1.140	0.316	59.078
	H	2.314	1.540	1.027	3.338	1.055	0.315	71.217
20	L	2.294	1.413	0.904	3.395	1.060	0.307	59.724
	M	2.227	1.251	0.757	3.856	1.025	0.170	58.731
	H	2.306	1.356	0.845	3.482	0.956	0.184	66.087
30	L	2.574	1.477	0.906	3.696	1.081	0.262	64.491
	M	2.248	1.350	0.852	3.424	0.980	0.221	63.087
	H	1.764	1.284	0.893	3.511	0.990	0.212	68.146
Silica_CTAB [#]		9.404	2.488					
		11.86	2.227					
Average		10.632	2.357					

* Disappear at 180°C

** Disappear at 327°C

[#] (Chaisirimahamorakot, 2001)

%wt of calculated polymer = the % wt lose at the second lose of modified silica – (the %wt loss at the first lose of modified silica / 10.632 x 2.3575)

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

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