

## REFERENCES

1. Adamson A.W. Physical chemistry of surfaces. 5<sup>th</sup> ed. New York : John Wiley & Sons, 1990.
2. Akelah A., Salahuddin N., Hiltner A., Baer E. and Moet A., Morphological hierarchy of butadieneacrylonitrile/montmorillonite nanocomposite, Nanostructured Materials 4, (1994) : 965-978.
3. Alexander B.M., Joseph D.H., Effects of organoclay Soxhlet extraction on mechanical properties, flammability properties and organoclay dispersion of polypropylene nanocomposites, Polymer 44, (2003) : 2313–2320.
4. Ammann L. Cation exchange and adsorption on clays and clay minerals. Dissertation Submitted for the degree “Dr. rer. nat.” Faculty of mathematics and natural sciences Christian-Albrechts-Universität Kiel, 2003.
5. Bergaya F. and Lagaly G. Surface modification of clay minerals. Applied Clay Science 19,1-6 (2001) : 1-3.
6. Cases J.M. and Villieras F. Thermodynamic model of ionic and nonionic surfactants adsorption-abstraction on heterogeneous surfaces. Langmuir 8, (1992) : 1251-1264.
7. Chales M.B. Compositional Analysis by Thermo-gravimetry. Philadelphia : ASTM, 1988.
8. Chen G., Pan J., Han B. and Yan H. Adsorption of methylene blue on montmorillonite. Journal of Dispersion Science and Technology 20, 4 (1999) : 1179–1187.
9. Cho G.C., and Santamarina J.C. Unsaturated particulate materials — particle level studies. Journal of Geotechnical and Geoenvironmental Engineering, ASCE, 127,1 (2001) : 84–96.
10. Deer W.A., Howie R.A. and Zussman J. An Introduction to The Rock-Forming Minerals. China : Addison Wesley Longmann Ltd., 1996.
11. Duncan J.S. Introduction to colloid and surface chemistry. 3<sup>rd</sup> ed. London : Butterworths, 1980.
12. Farrar D.M., and Coleman J.D. . The correlation of surface area with other properties of nineteen British clays. Journal of Soil Science, 18,1 (1967) : 118–124.

13. Fukushima Y. and Ingaki S. Synthesis of an intercalate compound of montmorillonite and 6-polyamide. Journal of Inclusion Phenomena 5, (1987) : 473-482.
14. Fu X. and Qutubuddin S., "Polymer-clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene" Polymer 42, (2001) : 807-813.
15. Gerry C., Industrial clays a special review. Industrial Minerals Division of Metal Bulletin (1989) : 78-79.
16. Gilman J.W., et al. Nanocomposites : a revolutionary new flame retardant approach. SAMPE Journal 33, (1997) : 40-46.
17. Grim R.E. Clay Mineralogy. 2<sup>nd</sup> ed., New York : Mc Graw-Hill, 1968.
18. Han B. et.al. "Preparation and characterization of nylon 66/montmorillonite nanocomposites with co-treated montmorillonites" European Polymer Journal 39, (2003) : 1641-1646.
19. Hang P.T. and Brindley G.W. Methylene blue absorption by clay minerals: determination of surface areas and cation exchange capacities (clay-organic studies XVIII). Clays and Clay Minerals 18, (1970) : 203–212.
20. Hay J.N. and Shaw S.J., A review of nanocomposites 2000, Technology Chief, Polymers and Adhesives, DERA, Farnborough, UK.
21. Hwhner G., Marti, A., Spencer N.D. and Caseri W.R. Orientation and electronic structure of methylene blue on mica: a near edge X-ray adsorption fine structure spectroscopy study. Journal of Chemical Physics 104, 19 (1996.) : 7749–7757.
22. James S.R. Introduction to the principles of ceramic processing. Singapore : John Wiley & Sons, 1989.
23. Joann E.W. SEM Petrology Atlas. New York : The American Association of Petroleum Geologist, 1984.
24. Kandhal P.S. and Parker F. Aggregate tests related to asphalt concrete performance in pavements. National Cooperative Highway Research Program NCHRP Report 405, 1998.
25. Klein K. Electromagnetic properties of high specific surface minerals. Ph.D. thesis, Department of Civil and Environmental, 1999.
26. Kojima Y., et al. Mechanical properties of nylon 6-clay hybrid. Journal of Materials Research 8, (1993) a : 1185-1189.

27. Kojima Y., et al. Sorption of water in nylon 6-clay hybrid. Journal of Applied Polymer Science 49, (1993) b : 1259-1264.
28. Kornmann X. Synthesis and Characterisation of Thermoset-Clay Nanocomposites, Division of Polymer Engineering. Luleå University of Technology, 2003.
29. Lagaly G., Wilson A.D. and Posser H.T. Smectic clay as ionic macromolecules in developments in ionic polymer. London : Applied Science Publishers, 1986.
30. LeBaron P.C., et al. Polymer-layered silicate nanocomposites : an overview. Applied Clay Science 15, (1999) : 11–29.
31. Lee S.Y. and Kim S.J. Delamination Behavior of Silicate Layers by Adsorption of Cationic Surfactants. Journal of Colloid and Interface Science 248, (2002) : 231–238.
32. Mitchell J.K. Fundamentals of soil behavior. 2<sup>nd</sup> ed. New York : John Wiley & Sons, 1993.
33. Moore D.M., Robert C. and Reynolds Jr., “Identification of Mixed-layered Clay Mineral” X-ray Diffraction and the Identification and Analysis of Clay Minerals, 2<sup>nd</sup> ed. New York: Oxford University Press. 1997.
34. Paul F.L. and Sylvia R. The colloidal and rheological properties of bentonite suspensions. Advances in Colloid and Interface Science 82, (1999) : 43-92.
35. Santamarina J.C., Klien K.A., Wang Y.H. and Prencke E. Specific surface: determination and relevance. Canadian Geotechnical Journal 39, (2002) : 233–241.
36. Shinoda K., Nakagawa T., Tamamushi B. and Isemura T. Colloidal Surfactants. New York: Academic Press, 1963.
37. Vaia R. et al., Thermal Degradation Chemistry of Alkyl Quaternary Ammonium Montmorillonite, Chemistry of Materials. 13, 2001 : 2979-2990.
38. Vaia R.A., Ishida H. and Giannelis E.P. Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. Chemistry of Materials. 5, (1993) : 1694-1696.
39. Whitting L.D. “X-ray Diffraction technique for minerals identification and mineralogical composition” Methods of Soil Analysis Part I Agronomy No.9, C.A. Black,ed. Wisconsin: Amer. Soc. Agron, 1965.

40. Xie W. et al., Singh in Thermal Characterization of Organically Modified Montmorillonite, Thermochimica Acta, 367-368, 2001 : 339-3
41. Xu S. and Boyd S.A. Cationic surfactant adsorption by swelling and non-swelling layer silicates. Langmuir 11, (1995) : 2508.
42. Zerwer A. and Santamarina J.C. Double layers in pyrometamorphosed bentonite : index properties and complex permittivity. Applied Clay Science 9, (1994) : 283–291.





## APPENDICES

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

## Appendix A

### Particle size separation

The sedimentation is the method to settle out the particles, basis on the Stoke's law. The ability of the settling particles depending on the several factors as following:

1. Particle size
2. Particle specific gravity
3. Viscosity of suspension
4. Specific gravity of liquid medium.

The large particle will settle faster than small particle in the same liquid as follow by

$$t = \frac{18 \eta h}{(\rho_2 - \rho_1) g D^2}$$

Where :

- $t$  = minutes of time particle settling,
- $\eta$  = viscosity of medium
- $\rho_1$  = density of liquid
- $\rho_2$  = density of clay
- $g$  =  $980 \text{ cm/s}^2$
- $D$  = diameter of particle

For centrifugal sedimentation, The centrifugal time can be calculated by

$$t = \frac{63 \times 10^8 \eta \log_{10}(R/S)}{N_m^2 - D_\mu^2 \Delta S}$$

Where :

$N_m$  is the speed of centrifuge in rpm.;  $\Delta S$  is the difference specific gravity;  $D_\mu$  is the diameter of particle in micron and  $R, S$  is the distance from the rotation axis to sediment and to suspension, respectively.

## Appendix B

### CEC calculation by methylene blue method

The methylene blue method follow as the ASTM C837-91 (1992) covers the measurement of absorption methylene blue dye in the clay. The methylene blue index can be calculated by this equation

$$\text{MBI} = \frac{V \times 0.01 \times 100}{W}$$

Where :

- MBI = methylene blue index for the clay in meq/100 g. of clay,
- V = milliliters of methylene blue solution increment, and
- W = grams of dried clay.

The result in the part IV was average form three experiments

Experiment	Volume of methylene blue (ml)	MBI
1	205.00	102.50
2	195.00	97.50
3	190.00	95.00
average	196.67	98.33

## Appendix C

### Molecular formula calculation

The molecular formula of clay mineral can be calculated from the chemical content. This experiment should be get rid the SiO<sub>2</sub> around 30% for cristoballite content. The factor ( $f$ ) =  $44/\text{total charge equivalent}$ , for unknown structural water content.

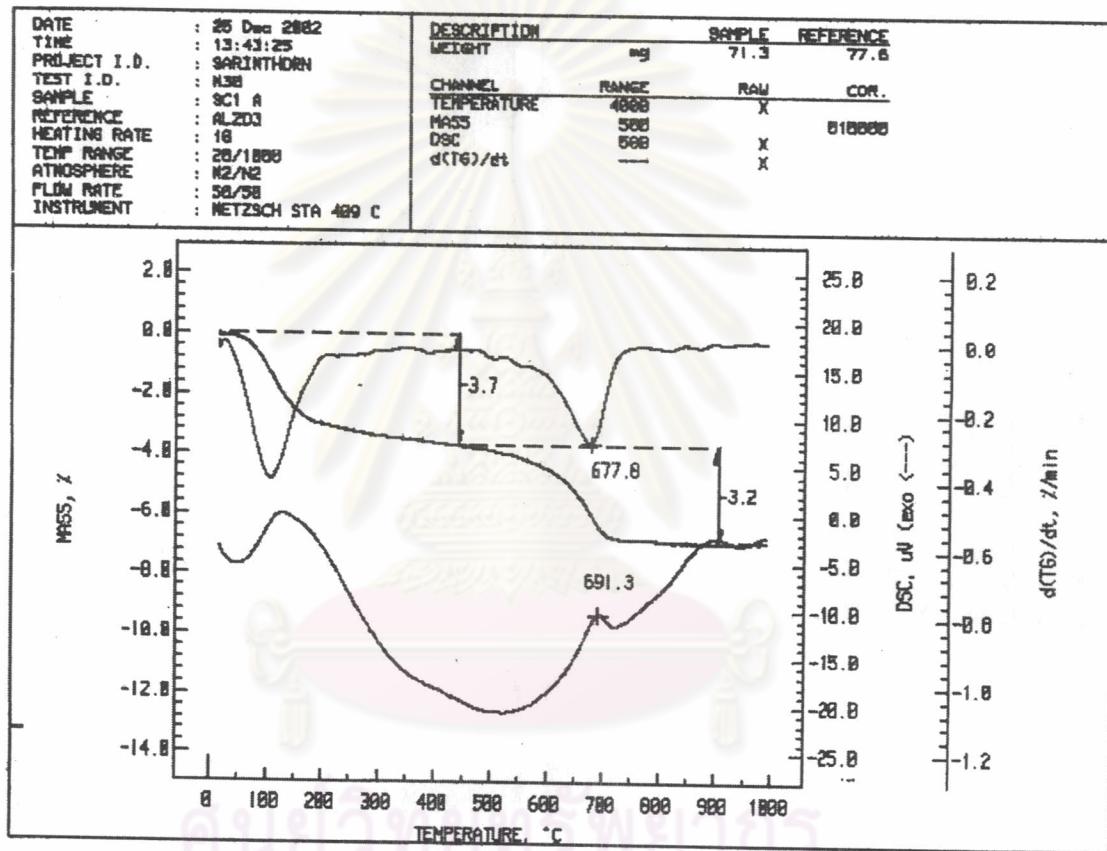
The chemical content calculated as follow :

Clay	Weight of oxide (%)							
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	TiO <sub>2</sub>	MgO	K <sub>2</sub> O	CaO
Oxide wt.	16.53	75.80	1.42	2.64	0.18	2.75	0.34	0.25
Formula wt.	101.96	60.08	159.69	30.99	79.89	40.31	47.10	56.07
Atom%	0.32	0.90	0.01	0.17	0.002	0.06	0.01	0.004
Atom per unit	2.87	8.00	0.16	1.51	0.02	0.60	0.13	0.04

## Appendix D

### Absorption of surfactant calculation

The amount absorption of surfactant were calculated from weight loss which eliminated the amount of water (3.7%) and dehydroxylation (3.2%) of Na-clay as the Figure



**Figure of Thermal analysis of Na-clay in N<sub>2</sub> atmosphere from room temperature to 1000 °C**

The total weight loss has been estimated as weight of clay which excluded water and hydroxyl group in the clay structure.

Octadecyltrimethyl ammonium chloride (S18) MW =340.5						area/molecule =19.95 Å <sup>2</sup>			area/mmole = 1.2E+22 Å <sup>2</sup>			area occupied	
conc.	%wt loss	%water	%OH	mw. S18 free Cl	%wt alkyl	mmol	wt.clay include OH and water	mmol/g clay	% efficiency	Å <sup>2</sup>	m <sup>2</sup>		
0	6.9	3.7	3.2										
0.25	11.90	3.41	3.03	305.00	5.00	0.16	94.62	0.1733	69.30	2.11E+21	21.15		
0.50	15.80	3.26	2.89	305.00	8.90	0.29	90.43	0.3227	64.54	3.76E+21	37.64		
1.00	21.20	3.05	2.71	305.00	14.30	0.47	84.63	0.5540	55.40	6.05E+21	60.48		
1.50	25.70	2.87	2.55	305.00	18.80	0.62	79.80	0.7724	51.50	7.95E+21	79.52		
2.00	29.20	2.74	2.43	305.00	22.30	0.73	76.04	0.9615	48.08	9.43E+21	94.32		
2.50	32.10	2.63	2.33	305.00	25.20	0.83	72.92	1.1330	45.32	1.07E+22	106.59		

Octadecyltrimethyl ammonium chloride (S18) after wash Chloride						wt.clay include OH and water			mmol/g clay			% efficiency		Å <sup>2</sup>		m <sup>2</sup>	
conc.	%wt loss	%water	%OH	mw. S18 free Cl	%wt alkyl	mmol	wt.clay include OH and water	mmol/g clay	% efficiency	Å <sup>2</sup>	m <sup>2</sup>						
0.50	15.37	3.27	2.91	305.00	8.47	0.28	90.89	0.31	61.11	3.67E+21	36.69						
1.00	18.81	3.14	2.79	305.00	11.91	0.39	87.20	0.45	44.78	5.38E+21	53.78						
1.50	23.03	2.98	2.65	305.00	16.13	0.53	82.67	0.64	42.65	7.68E+21	76.83						
2.00	29.57	2.72	2.42	305.00	22.67	0.74	75.64	0.98	49.13	1.18E+22	118.01						
2.50	27.23	2.81	2.50	305.00	20.33	0.67	78.15	0.85	34.11	1.02E+22	102.43						

di-octadecyltrimethyl ammonium chloride (D18)  
MW =573.0

conc.	%wt loss	%water	%OH	mw. D18 free Cl	area/molecule =51.01 Å <sup>2</sup>			area/mmole = 3.07E+22 Å <sup>2</sup>	area occupied		
					%wt alkyl	mmol	wt.clay include OH and water	mmol/g clay	%efficiency	Å <sup>2</sup>	m <sup>2</sup>
0	6.9	3.7	3.2								
0.25	20.94	3.06	2.72	537.50	14.04	0.26	84.91	0.3076	123.05	9.45E+21	94.46
0.50	31.17	2.66	2.37	537.50	24.27	0.45	73.92	0.6108	122.16	1.88E+22	187.55
1.00	44.44	2.15	1.91	537.50	37.54	0.70	59.67	1.1704	117.04	3.59E+22	359.38
1.50	49.53	1.95	1.73	537.50	42.63	0.79	54.20	1.4632	97.55	4.49E+22	449.27
2.00	45.88	2.09	1.86	537.50	38.98	0.73	58.12	1.2477	62.38	3.83E+22	383.10
2.50	53.26	1.81	1.61	537.50	46.36	0.86	50.20	1.7182	68.73	5.28E+22	527.57

di-octadecyltrimethyl ammonium chloride (D18) after wash treatments

conc.	%wt loss	%water	%OH	mw. D18 free Cl	area/molecule =51.01 Å <sup>2</sup>			area/mmole = 3.07E+22 Å <sup>2</sup>	area occupied		
					%wt alkyl	mmol	wt.clay include OH and water	mmol/g clay	%efficiency	Å <sup>2</sup>	m <sup>2</sup>
1.00	44.44	2.15	1.91	537.50	37.54	0.70	59.67	1.17	117.04	3.59E+22	359.38
EtOH	33.10	2.59	2.30	537.50	26.20	0.49	71.85	0.68	67.84	2.08E+22	208.31
reflux	35.00	2.51	2.23	537.50	28.10	0.52	69.81	0.75	74.89	2.30E+22	230.04
Reflux (2.5 mmol)	35.70	2.49	2.21	537.50	28.80	0.54	69.06	0.78	77.59	2.38E+22	238.24

Tricaprylyl methyl ammonium chloride (T8) MW =404.17							area/molecule =80.12 Å <sup>2</sup>	area/molecule =4.28E+22 Å <sup>2</sup>	area occupied		
conc.	%wt loss	%water	%OH	mw. T8 free Cl	%wt alkyl	mmol	wt.clay include OH and water	mmol/g clay	%efficiency	Å <sup>2</sup>	m <sup>2</sup>
0	6.9	3.7	3.2								
0.50	20.10	3.09	2.75	368.67	13.20	0.36	85.81	0.4172	83.45	2.01E+22	201.24
1.00	27.60	2.80	2.49	368.67	20.70	0.56	77.76	0.7221	72.21	3.48E+22	348.27
1.50	32.50	2.61	2.32	368.67	25.60	0.69	72.50	0.9578	63.86	4.62E+22	461.98
2.00	35.50	2.49	2.22	368.67	28.60	0.78	69.27	1.1199	55.99	5.40E+22	540.12

Methyl polyoxyethylene(15)octadecanammonium chloride (EO18) MW =979.5							area/molecule =80.12 Å <sup>2</sup>	area/molecule =4.82E+22 Å <sup>2</sup>	area occupied		
conc.	%wt loss	%water	%OH	mw. EO18 free Cl	%wt alkyl	mmol	wt.clay include OH and water	mmol/g clay	%efficiency	Å <sup>2</sup>	m <sup>2</sup>
0	6.9	3.7	3.2								
0.50	34.80	2.52	2.24	944.00	27.90	0.30	70.02	0.42	84.41	2.04E+22	203.57
1.00	42.50	2.22	1.98	944.00	35.60	0.38	61.76	0.61	61.07	2.95E+22	294.53
1.50	41.60	2.26	2.01	944.00	34.70	0.37	62.72	0.59	39.07	2.83E+22	282.66
2.00	41.60	2.26	2.01	944.00	34.70	0.37	62.72	0.59	29.30	2.83E+22	282.66

**VITAE**

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