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APPENDICES

Appendix I : Stoichiometric Calculation of Organophilic-Clay

The stoichiometric calculation of starting material in preparation of organophilic-clay filler can be shown by the chemical equation :

$$NH_2(CH_2)_{11}CH_3 + HCl \longrightarrow Cl^-NH_3^+(CH_2)_{11}CH_3 \quad \textbf{(I.1)}$$

Dodecylamine	Hydrochloric acid	Dodecylammonium chloride
M.W.= 185 g/mol	M.W.= 36.5 g/mol	M.W.=221.5 g/mol

$$Na(Al_2Si_4O_{10}(OH)_2) + Cl^-NH_3^+(CH_2)_{11}CH_3 \longrightarrow$$

Sodium-montmorillonite	Dodecylammonium chloride
M.W.= 383 g/mol	

$$[NH_3(CH_2)_{11}CH_3](Al_2Si_4O_{10}(OH)_2) + NaCl \quad \textbf{(I.2)}$$

Dodecylamine-montmorillonite

M.W.=545 g/mol

The dodecylamine was first reacted with hydrochloric acid resulting in dodecylammonium chloride. Afterwards, one mole of sodium-montmorillonite was reacted by one mole of dodecylammonium ion to yield one mole of dodecylamine-montmorillonite. In order to yield 13 g of dodecylamine-montmorillonite (0.024 mole), 4.42 g of dodecylamine and 2.4 ml of concentrated hydrochloric acid as well as 10 g of sodium-montmorillonite would be reacted.

Appendix II : Determination of Sodium Ions in Montmorillonite by Atomic Absorption Spectrometry (AAS)

(1) Apparatus

a) Flame Atomic Absorption Spectrometer, air-C_2H_2 flame
: Varian Model : SpectrAA

b) Glassware : All of glasswares were rinsed with 1+15 HNO_3 and followed by several portions of deionized water.

(2) Reagents

a) Stock sodium solution (1000ppm) : Carlo Erba Standard

b) Potassium chloride : Carlo Erba, AR grade

c) Hydrochloric acid (37 %w/w) : Merck

d) Deionized water

(3) Procedure

a) Preparation of Standard Sodium Solution for the Calibration Curve

A 1000 ppm of stock sodium solution was diluted to 10 ppm of an intermediate solution using deionized water as a diluent. A blank and sodium standards were prepared by transferring of 0, 2, 5 and 10 ml of an intermediate sodium solution to volumetric flasks and increased the volume of each containers to 100 ml with deionized water. All containers were added 0.4 g of KCl in order to remove some interfered ions and 10 ml of 1+1 HCl as a conditioning solvent prior to increase the volume. A diagram of preparation method is shown in Figure II.1.

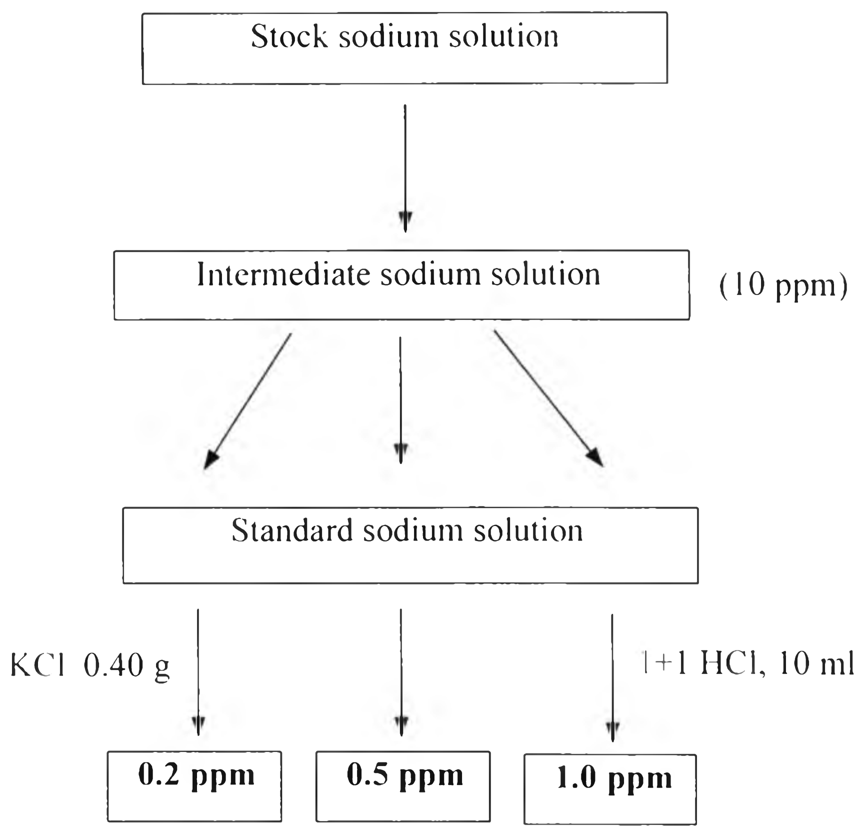

Figure II.1 A preparation diagram of standard sodium solution for a calibration curve.

b) Preparation of Unknown Solution

A mixture of 0.10 g of montmorillonite, 10 ml of 1+1 HCl and 10 ml of deionized water was stirred at 80 °C for 2 hours, yielding an acidic unknown solution. The solution was then cooling down to 30 °C. A precipitate was isolated by filtering with a 0.45 μm cellulose acetate filter membrane and washing with deionized water. The supernatant with 0.40 g of KCl was transferred to a volumetric flask and increased the volume to 100 ml by deionized water. The unknown solution was taken to analyze by the AAS. A diagram of preparation method is shown in Figure II.2.

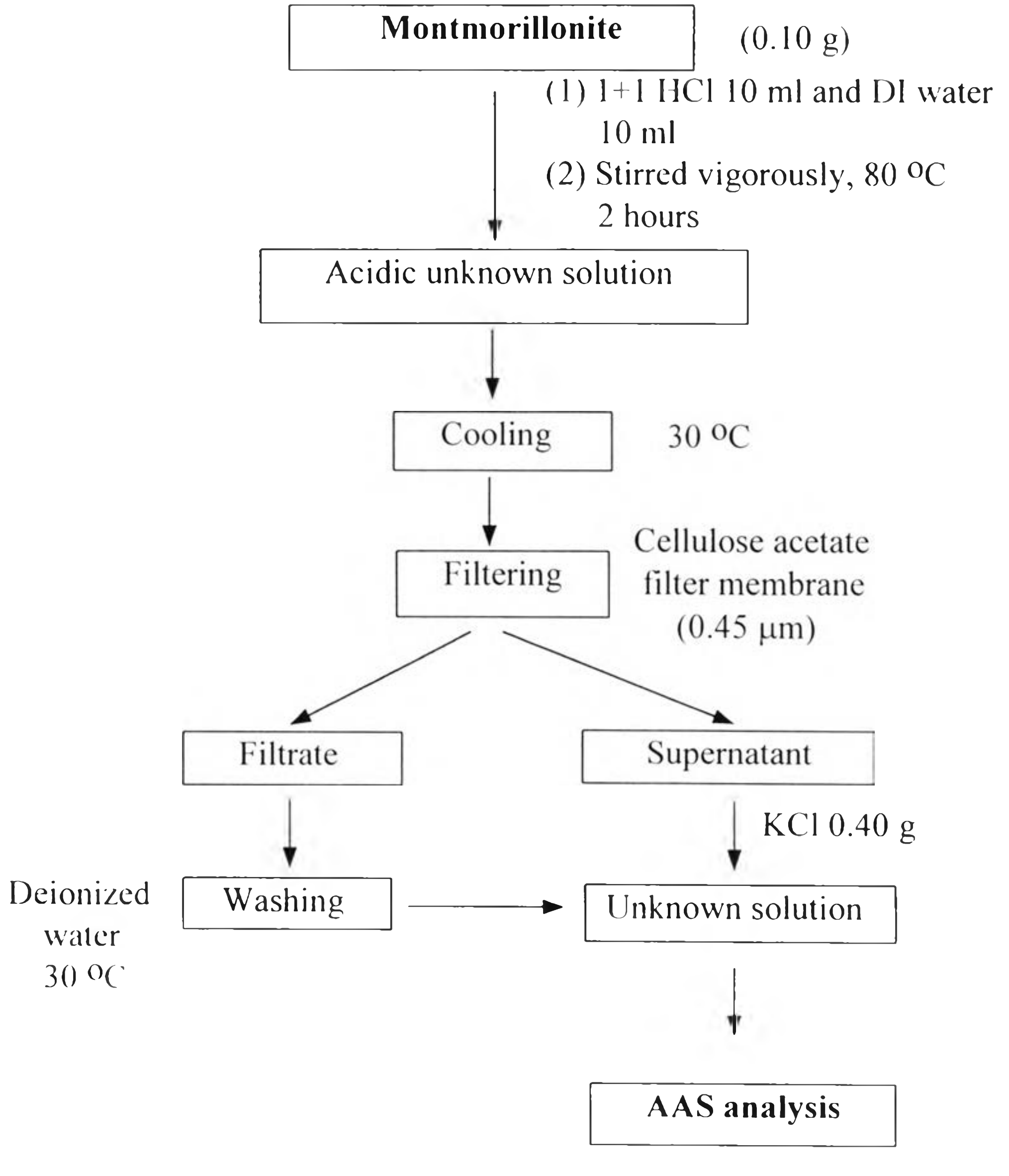

Figure II.2 A preparation diagram of the AAS unknown solution.

c) Determination of Sodium Ions by AAS

The sodium ions in acidic unknown solution were measured using an air-C_2H_2 flame mode with a sodium hollow cathode lamp. The wavelength of a specific lamp was set at 589 nm to produce a maximum absorption. The chamber inside the nebulizer was exposed to a continuous flow of acetylene gas with a flow rate of 2.2 L/min and air with a flow rate of 13.5 L/min. The amount of sodium ions in an atomizer unit were monitored and recorded using the controller software. The average value of absorbance from 3 measurements were reported as a representative value of each sample.

(4) The Recovery Percentage of Sodium Ions as Measured by AAS

(Table 4.4)

No.	Na^+ content (%wt)	
	Sodium-montmorillonite	Dodecylamine-montmorillonite
1	2.87	0.22
2	2.84	0.20
3	2.89	0.20
Average	2.87$\pm$0.02*	0.21$\pm$0.01

* The exact value from Kunimine's technical data sheet is 3.15 %wt.

Appendix III : Thermogravimetric Data of BPDA/PDA Polyimide Film and Its Clay Nanocomposites

(Figure 4.9)

Materials	Clay content (%wt)	Decomposition temperature* (°C)			
		#1	#2	#3	Average
PI2610	0	584	576	580	580.0±4.0
PI2610-Clay 1 %	1.17	598	600	595	597.7±2.5
PI2610-Clay 3 %	2.89	602	603	595	600.0±4.4
PI2610-Clay 6 %	6.19	608	602	601	603.7±3.8
PI2610-Clay 9 %	8.87	613	604	608	608.3±4.5
PI2610-Clay 11 %	10.86	615	603	609	609.0±6.0

* Measured by using a scanning rate of 10 ml/min.

Appendix IV : Thermomechanical Data of Polyimide Films and Their Clay Nanocomposites

Testing Conditions : (1) Annealed from 30 to 300 °C with a rate of 10 °C/min

(2) Cooled down to 30 °C with a rate of 5 °C/min

(3) Held for 1 hour

(4) Heated up from 30 to 400 °C with a rate of 5 °C/min and measured the change in length

(5) Cooled down to 30 °C

Remark : All steps were performed under a constant force of 30 mN.

(1) In-Plane CTE (α_{50-250})

BPDA/PDA (PI2610) (Figure 4.14)

Materials	Clay content (%wt)	α_{50-250} (ppm/°C)			Average thickness (μm)
		#1	#2	Average	
PI2610	0	45.20	33.76	39.48±8.08	28.0±1.3
PI2610-Clay 1 %	1.00	42.66	40.30	41.48±1.67	25.5±1.6
PI2610-Clay 3 %	2.67	33.12	34.78	33.95±1.17	23.2±3.0
PI2610-Clay 6 %	5.96	32.63	37.25	34.94±3.27	23.3±3.6
PI2610-Clay 9 %	8.85	35.70	35.47	35.59±0.16	24.0±3.6

BTDA/ODA-MDA (PI2579) (Figure 4.14)

Materials	**Clay content (%wt)**	**α_{50-250} (ppm/°C)**			**Average thickness (μm)**
		#1	**#2**	**Average**	
PI2579	0	73.24	-	73.24±0.00	21.0±0.0
PI2579-Clay 1 %	1.04	74.80	71.92	73.36±2.04	23.0±1.4
PI2579-Clay 3 %	3.04	66.28	69.01	67.64±1.93	23.5±2.1
PI2579-Clay 6 %	5.86	63.19	61.40	62.34±1.20	20.0±1.4
PI2579-Clay 9 %	8.79	62.30	62.10	62.20±0.14	24.0±0.0
PI2579-Clay 11%	10.95	60.38	59.16	59.77±0.86	21.0±0.0

(2) Expansion Temperature (T_e)

a) Definition

The temperature at inflection point on the plot of in-plane CTE as function of temperature as shown in Figure IV.1. At this point, the film starts to expand dramatically with an in-plane CTE.

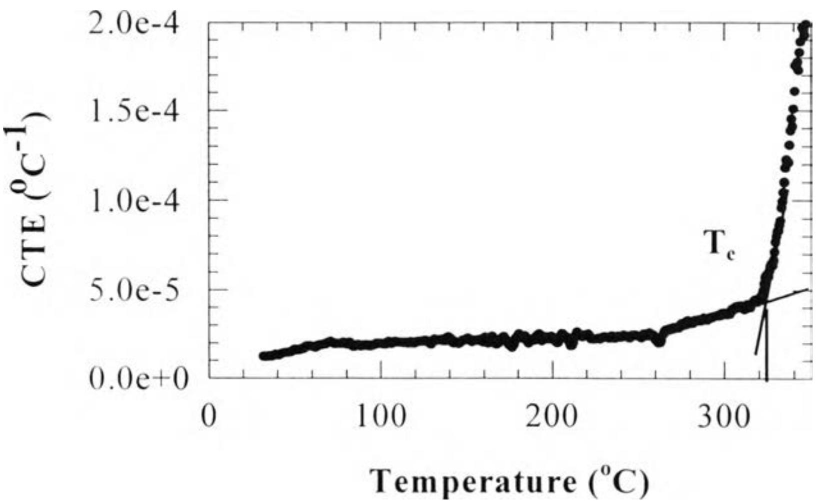

Figure IV.1 The plot of in-plane CTE as a function of temperature of a typical polyimide film.

b) Raw Data

BPDA/PDA (PI2610) (Figure 4.15)

Materials	Clay content (%wt)	T_c (°C)		
		#1	#2	Average
PI2610	0	328	324	326.0±2.8
PI2610-Clay 0.5%	0.50	308	307	307.5±0.7
PI2610-Clay 1 %	1.00	310	311	310.5±0.7
PI2610-Clay 3 %	2.67	312	316	314.0±2.8
PI2610-Clay 6 %	5.96	306	309	307.5±2.1
PI2610-Clay 9 %	8.85	310	318	314.0±5.6

BTDA/ODA-MDA (PI2579) (Figure 4.15)

Materials	Clay content (%wt)	T_c (°C)		
		#1	#2	Average
PI2579	0	305	298	301.5±4.9
PI2579-Clay 1 %	1.04	301	303	302.0±1.4
PI2579-Clay 3 %	3.04	296	294	295.0±1.4
PI2579-Clay 6 %	5.86	298	305	301.5±4.9
PI2579-Clay 9 %	8.79	260	265	262.5±3.5
PI2579-Clay11%	10.95	285	283	284.0±1.4

(3) Yielding Temperature (T_y)

a) Definition

The temperature at which the film starts to permanent deform. It can be found by extrapolating a 0.2 % off-set of the elongation axis to the temperature axis on the curve as shown in Figure IV.2.

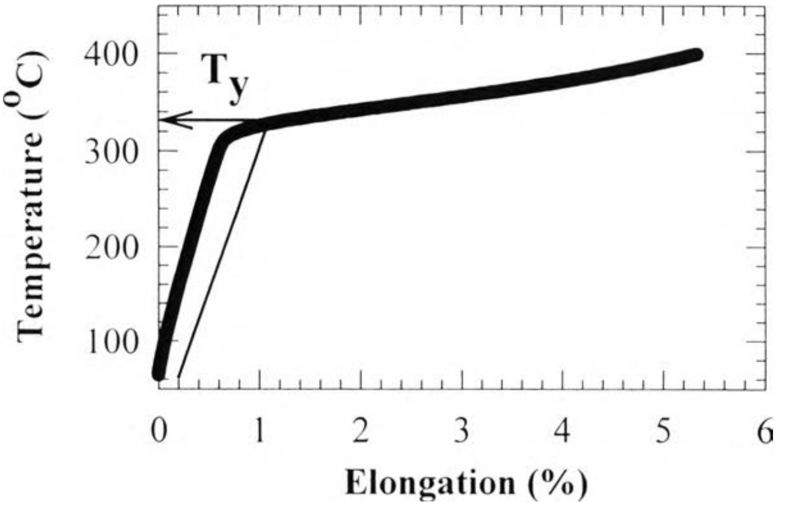

Figure IV.2 The plot of temperature as a function of elongation of a typical polyimide film.

b) Raw Data

BPDA/PDA (PI2610) (Table 4.6)

Materials	Clay content (%wt)	T_y (°C)		
		#1	#2	Average
PI2610	0	370	360	365.0±7.1
PI2610-Clay 0.5%	0.50	325	324	324.5±0.7
PI2610-Clay 1 %	1.00	323	332	327.5±6.4
PI2610-Clay 3 %	2.67	334	350	342.0±11.3
PI2610-Clay 6 %	5.96	-	-	-
PI2610-Clay 9 %	8.85	-	-	-

BTDA/ODA-MDA (PI2579) (Table 4.6)

Materials	Clay content (%wt)	T_y (°C)		
		#1	#2	Average
PI2579	0	316	309	312.5±4.9
PI2579-Clay 1 %	1.04	310	313	311.5±2.1
PI2579-Clay 3 %	3.04	312	312	312.0±0.0
PI2579-Clay 6 %	5.86	320	330	325.0±7.1
PI2579-Clay 9 %	8.79	330	320	325.0±7.1
PI2579-Clay 11 %	10.95	318	320	319.0±1.4

Appendix V : Thermal Cycling Data of BPDA/PDA Polyimide Film and Its Clay Nanocomposites

Testing Conditions : (1) Annealed from 30 to 300 °C with a rate of 10 °C/min

(2) Held for 10 minute

(3) Cooled down to 30 °C with a rate of 5 °C/min

(4) Heated up from 30 to 400 °C with a rate of 5 °C/min and measured the change in length

(5) Cooled down to 30 °C

(6) Repeated step (4) and (5) for a total of 10 cycles

Remark : All steps were performed under a constant force of 30 mN.

(Figure 4.16)

Cycle No.	α_{50-250} (ppm/°C)		
	PI2610	PI2610-Clay 1 %	PI2610-Clay 9 %
1	28.06	19.31	34.31
2	21.78	18.77	41.24
3	21.83	20.76	41.15
4	22.79	22.64	39.35
5	21.98	21.56	34.88
6	24.42	21.25	34.84
7	22.74	24.50	40.35
8	23.36	20.48	42.47
9	22.28	30.58	35.91
10	23.94	27.56	39.24

Appendix VI : Tensile Properties Data of BPDA/PDA Polyimide Film and Its Clay Nanocomposites

(1) Tensile Modulus

(Table 4.7)

Materials	Clay content (%wt)	Tensile modulus* (GPa)		
		#1	#2	Average
PI2610	0	7.00	6.64	6.82±0.25
PI2610-Clay 0.5 %	0.51	7.63	6.41	7.02±0.86
PI2610-Clay 3 %	2.96	8.01	7.45	7.73±0.40
PI2610-Clay 8 %	8.02	8.04	7.79	7.92±0.18

* Initial slope of the stress-strain curve.

(2) Ultimate Strength

(Table 4.7)

Materials	Clay content (%wt)	Tensile strength* (GPa)		
		#1	#2	Average
PI2610	0	5.46	4.52	4.99±0.66
PI2610-Clay 0.5 %	0.51	5.32	4.65	4.99±0.47
PI2610-Clay 3 %	2.96	6.88	6.01	6.44±0.62
PI2610-Clay 8 %	8.02	6.98	6.80	6.89±0.13

* Strength at break.

(3) Ultimate Elongation

(Table 4.7)

Materials	Clay content (%wt)	Ultimate elongation* (%)		
		#1	#2	Average
PI2610	0	2.97	3.07	3.02±0.07
PI2610-Clay 0.5 %	0.51	2.30	2.40	2.35±0.07
PI2610-Clay 3 %	2.96	1.49	1.65	1.57±0.11
PI2610-Clay 8 %	8.02	0.86	1.03	0.94±0.12

* Elongation at break.

Appendix VII : Water Absorption Data of BPDA/PDA Polyimide Film and Its Clay Nanocomposites

(Figure 4.19)

Materials	Clay content (%wt)	Water content* (%wt)			
		#1	#2	#3	Average
PI2610	0	2.20	1.80	1.90	1.97±0.21
PI2610-Clay 1 %	1.17	1.19	1.70	1.80	1.80±0.10
PI2610-Clay 3 %	2.89	1.70	1.60	1.80	1.70±0.10
PI2610-Clay 6 %	6.19	1.60	1.50	1.70	1.60±0.10
PI2610-Clay 9 %	8.87	1.50	1.40	1.30	1.40±0.10
PI2610-Clay 11%	10.86	1.40	1.50	1.70	1.53±0.15

* Water content of the films were measured by using TGA technique.

Appendix VIII : Dielectric Strength Data of BPDA/PDA Polyimide Film and Its Clay Nanocomposites

(1) BPDA/PDA (PI2610) (Figure 4.21)

No.	Thickness (mil)	Dielectric breakdown (V)	Dielectric strength (V/mil)
1	0.80	5300	6625
2	1.04	6400	6154
3	0.76	4500	5921
4	0.92	5400	5870
5	0.64	3400	5312
6	0.92	6200	6739
Average		5200±1115	6104±527

(2) PI2610-Clay 0.96 %wt (Figure 4.21)

No.	Thickness (mil)	Dielectric breakdown (V)	Dielectric strength (V/mil)
1	0.92	6600	7174
2	0.84	6400	7616
3	0.72	5500	7639
4	0.88	6000	6818
5	0.52	4600	8846
6	1.16	7800	6724
Average		6150±1080	7470±776

(3) PI2610-Clay 2.07 %wt (Figure 4.21)

No.	Thickness (mil)	Dielectric breakdown (V)	Dielectric strength (V/mil)
1	0.68	5600	8235
2	1.16	9000	7758
3	0.88	6500	7386
4	0.92	7100	7771
5	0.72	5800	8056
6	0.96	8100	8438
Average		7017±1332	7932±384

(4) PI2610-Clay 6.80 %wt (Figure 4.21)

No.	Thickness (mil)	Dielectric breakdown (V)	Dielectric strength (V/mil)
1	0.72	6100	8472
2	1.12	8000	7143
3	0.56	4800	8571
4	0.92	6000	6521
5	0.84	7000	8333
6	1.20	8800	7330
Average		6783±1457	7728±847

(5) PI2610-Clay 8.85 %wt (Figure 4.21)

No.	Thickness (mil)	Dielectric breakdown (V)	Dielectric strength (V/mil)
1	0.68	5900	8676
2	0.52	3800	7308
3	1.04	8000	7692
4	0.84	6000	7143
5	0.96	7700	8021
6	0.64	3000	4688
Average		5733±2016	7255±1371

(6) PI2610-Clay 10.96 %wt (Figure 4.21)

No.	Thickness (mil)	Dielectric breakdown (V)	Dielectric strength (V/mil)
1	0.44	2500	5682
2	1.12	8600	7679
3	1.20	9500	7916
4	0.72	3000	4167
5	1.08	8600	7963
6	0.76	3000	3947
Average		5867±3344	6226±1882

CURRICULUM VITAE

Name : Mr. Wittaya Lilayuthalert

Birth Date : 25 February 1974

Nationality : Thai

University Education :

1991-1994 Bachelor's Degree of Science in Chemistry,
Second Class Honors, Prince of Songkla University