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APPENDIX A

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

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 HCl as a conditioning solvent prior to increase the volume. A diagram of preparation method is shown in Figure A1

Preparation of Unknown Solution

Sample solution was taken from the supernatant part in the preparation of Organically modified montmorillonite. This solution was diluted into 1000 times and used it as sample solution in AAS.

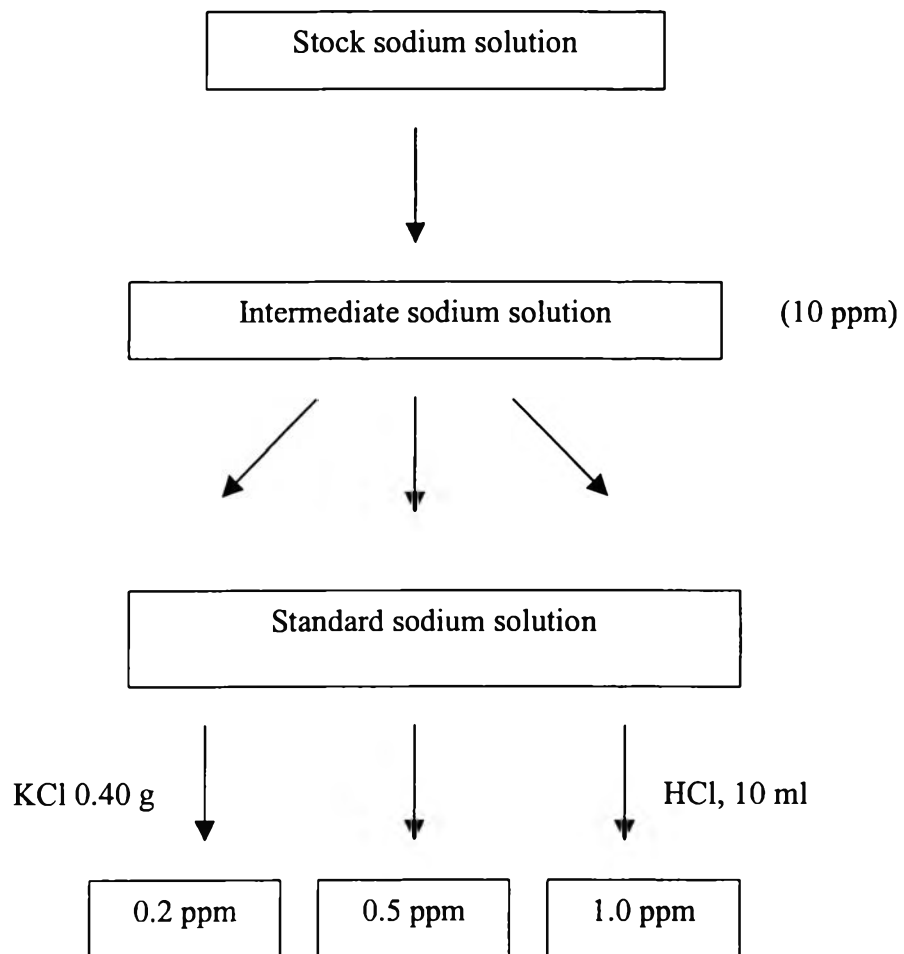


Figure A1 A preparation diagram of standard sodium solution for a calibration curve.

Conditions of Instrument

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Integration
Slit Width (nm)	0.5
Slit Height	Normal
Wavelength (nm)	589.0
Flame	Air-Acetylene
Sample Introduction	Manual
Delay Time	2
Time Constant	0.05
Measurement Time (sec)	1.0
Replicates	3
Background Correction	Off
Air Flow (L/min)	13.5
Acetylene Flow (L/min)	2.00

Table A1 Light wavelengths of sodium lamp and their intensities

Wavelength (nm)	Slit Width (nm)	Conc. For 0.2 absorbance (mg/L)	Relative Lamp Intensity
589.0	0.5	0.15	100
589.6	0.5	0.30	60
330.3	0.5	80.0	2

Table A2 Relationship between concentration and absorbance of standard sodium solution for OH-MMT

Sample	Conc. (ppm)	% RSD	Mean absorbance	Readings		
Blank	0.00		0.001	0.001	0.000	0.001
Blank	0.00		0.000	0.000	0.000	0.000
Blank	0.00		0.000	0.000	0.000	0.000
Standard 1	0.20	1	0.086	0.087	0.085	0.086
Standard 2	0.50	0.5	0.238	0.237	0.239	0.237
Standard 3	1.00	0.5	0.534	0.536	0.535	0.531

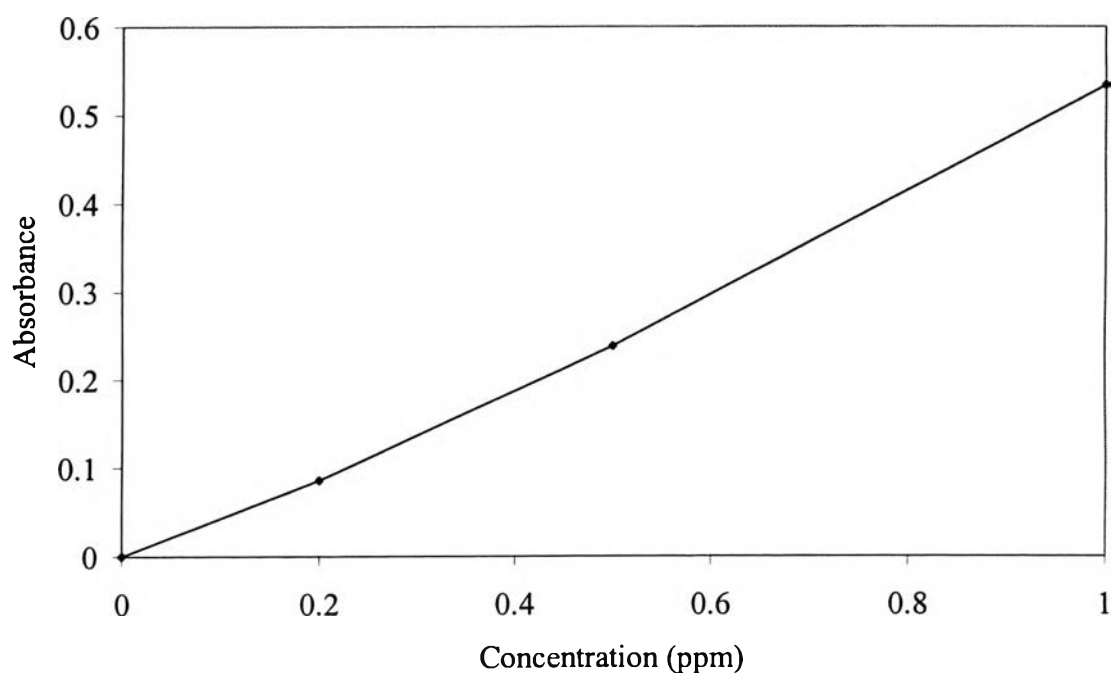


Figure A2 Calibration curve obtained from standard Na⁺ solutions for OH-MMT.

Table A3 Na⁺ concentration of the supernatant of OH-MMT

Sample	Conc. (ppm)	% RSD	Mean absorbance	Readings		
OH 1	0.94	0.8	0.497	0.501	0.494	0.495
OH 2	0.94	0.9	0.503	0.501	0.509	0.500
OH 3	0.94	0.9	0.503	0.498	0.503	0.507

Calculation for Na⁺ content

$$\begin{aligned}
 \text{Na}^+ \text{ concentration from AAS} &= 0.94 \text{ ppm (or } \mu\text{g/ml)} \\
 \text{Dilution factor} &= 200 \\
 \text{Total concentration} &= 0.94 \times 200 \text{ } \mu\text{g/ml} \\
 \text{Amount of supernatant} &= 1.4 \text{ L} \\
 \text{Amount of Na}^+ \text{ in the supernatant} &= 0.94 \times 200 \text{ } \mu\text{g/ml} \times 1400 \text{ ml} \\
 &= 263,200 \text{ } \mu\text{g} \\
 &= 263.2 \text{ mg}
 \end{aligned}$$

Calculation for Na⁺ exchange percentage

$$\begin{aligned}
 \text{Na}^+ \text{ exchange percentage} &= \frac{263.2 \text{ mg}}{273.7 \text{ mg}} \times 100 \\
 &= 96.16 \%
 \end{aligned}$$

APPENDIX B

Kjeldahl Nitrogen Determination Method

The Kjeldahl method is a means of determining the nitrogen content of organic and inorganic substances. Although the technique and apparatus have been altered considerably over the past 100 years, the basic principles introduced by Johan Kjeldahl endure today. Since 1883, the Kjeldahl method has gained wide acceptance and is now used for a variety of applications. Kjeldahl nitrogen determinations are performed on food and beverages, meat, feed, grain, waste water, soil and many other samples. The method has been refined and tested for a wide variety of substances and approved by various scientific associations including:

AOAC International (formerly the Association of Official Analytical Chemists)

Association of American Cereal Chemists

American Oil Chemists Society

Environmental Protection Agency, International Standards Organization

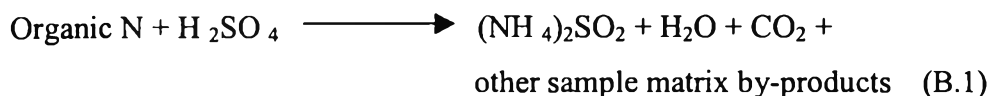
United States Department of Agriculture

The Kjeldahl method may be broken down into three main steps:

The Digestion Process

The decomposition of nitrogen in organic samples utilizing a concentrated acid solution. This is accomplished by boiling a homogeneous sample in concentrated sulfuric acid. The end result is an ammonium sulfate solution.

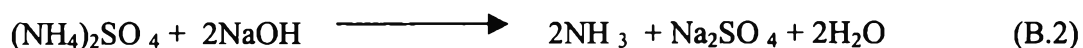
A general equation for the digestion of an organic sample is shown below as one basic example:



A number of interrelated digestion conditions determine the rate of reaction and the completeness of the breakdown of nitrogen to ammonium sulfate. Among these are heat input to the acid digestion mixture, amount of inorganic salt added to elevate the acid boiling temperature, reflux rate of H_2SO_4 in the neck of the digestion flask, length of digestion, and catalyst addition. Adjusting any one of these factors has an influence on the others. Proper digestion conditions for a given sample matrix are achieved through establishing a balance of these factors in a controlled and repeatable fashion. In addition, if the sample contains nitrate or nitrite nitrogen, it is possible to chemically pretreat the digest to include or exclude this nitrogen source from the analysis as desired in a particular situation.

The Distillation Process

This process is done by adding excess base to the acid digestion mixture to convert NH_4^+ to NH_3 , followed by boiling and condensation of the NH_3 gas in a receiving solution. The acid digestion mixture is diluted and made strongly alkaline with NaOH , liberating NH_3 as follows:



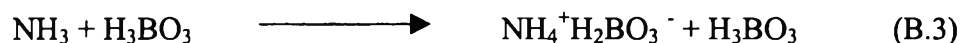
The Kjeldahl flask is attached to a water condenser and is heated to boil off the NH_3 gas from the digest. The tip of the condenser is submerged in a flask of acidic receiving solution, either standard acid or boric acid solution, to again trap the distilled NH_3 in receiving solution.

The Titration Process

The process is to quantify the amount of ammonia in the receiving solution. There are two types of titration: back titration and direct titration. Both methods indicate the ammonia present in the distillate with a color change and allow for calculation of unknown concentrations.

Nitrogen Determination by direct titration

If boric acid is used as the receiving solution instead of a standardized mineral acid, the chemical reaction is:



The boric acid captures the ammonia gas, forming an ammonium-borate complex. As the ammonia collects, the color of the receiving solution changes.



The addition of sulfuric acid exactly neutralizes the ammonium borate complex, and a reverse color change is produced. The boric acid method has two advantages: only one standard solution is necessary for the determination and the solution has a long shelf life.

Calculations

The calculations for % nitrogen or % protein must take into account which type of receiving solution was used and any dilution factors used during the distillation process. In the equations below, “N” represents normality. “ml blank” refers to the milliliters of base needed to back titrate a reagent blank if standard acid is the receiving solution, or refers to milliliters of standard acid needed to titrate a reagent blank if boric acid is the receiving solution. When boric acid is used as the receiving solution the equation is:

$$\% \text{ Nitrogen} = \frac{(\text{ml standard acid} - \text{ml blank}) \times \text{N of acid} \times 1.4007}{\text{weight of sample in grams}} \quad (\text{B.5})$$

If it is desired to determine % protein instead of % nitrogen, the calculated % N is multiplied by a factor, the magnitude of the factor depending on the sample matrix.

APPENDIX C

TGA Results of PPV, Protein and Their Nanocomposites.

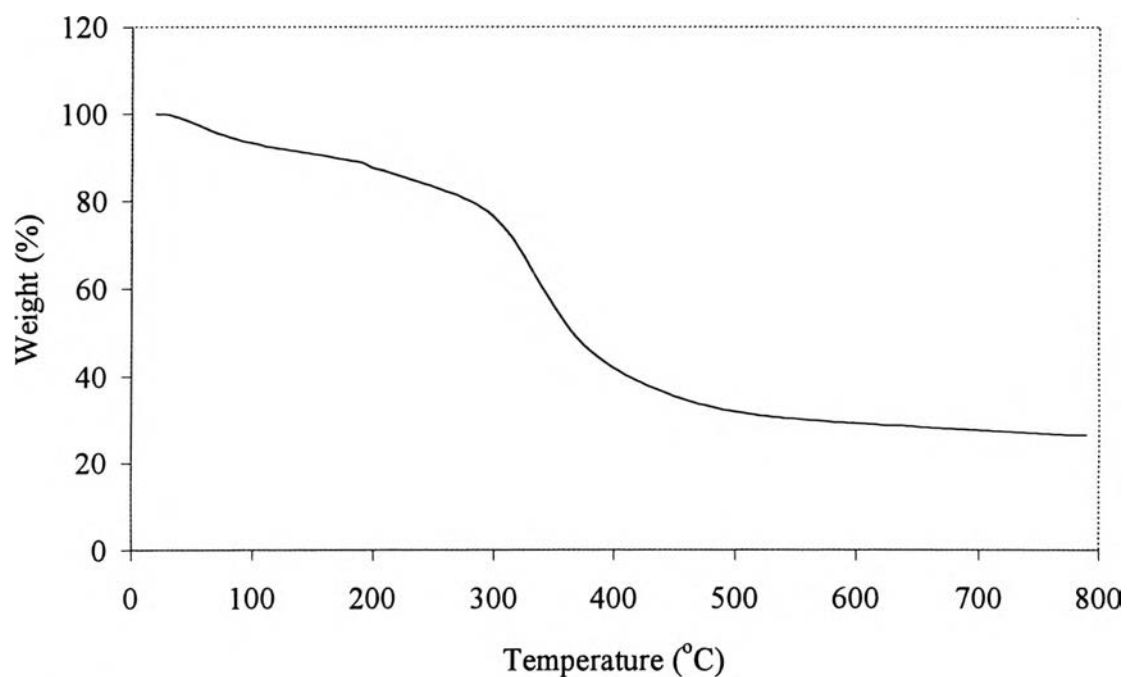


Figure C1 TGA thermogram of protein/OH-MMT 30 wt %.

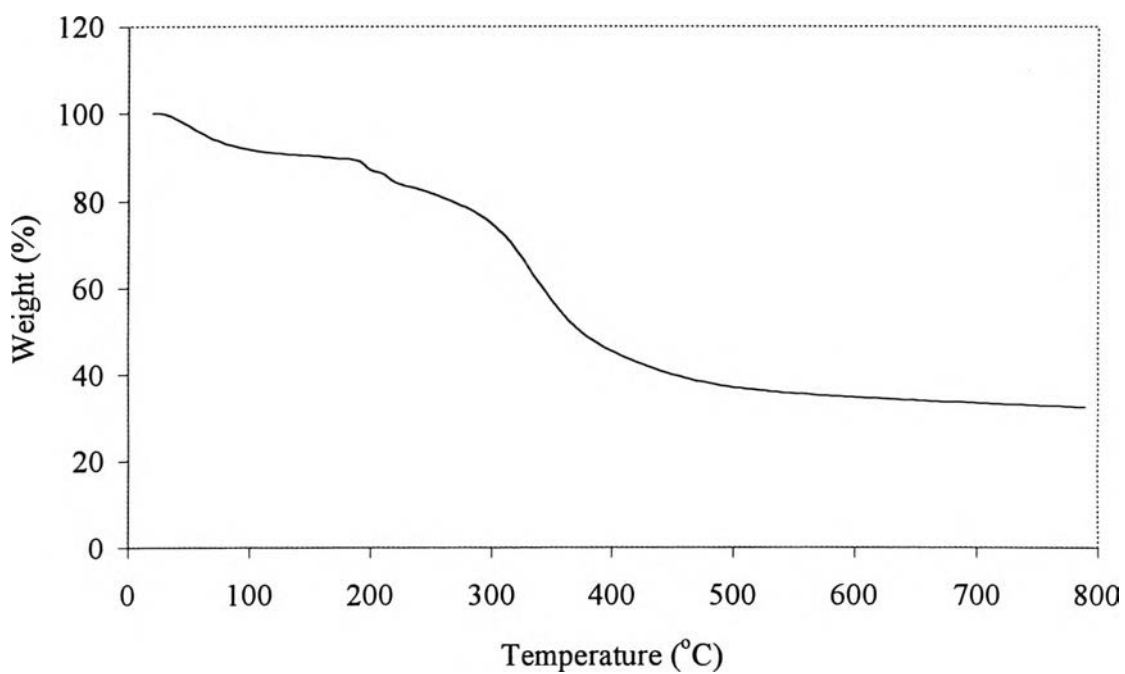


Figure C2 TGA thermogram of protein/OH-MMT 40 wt %.

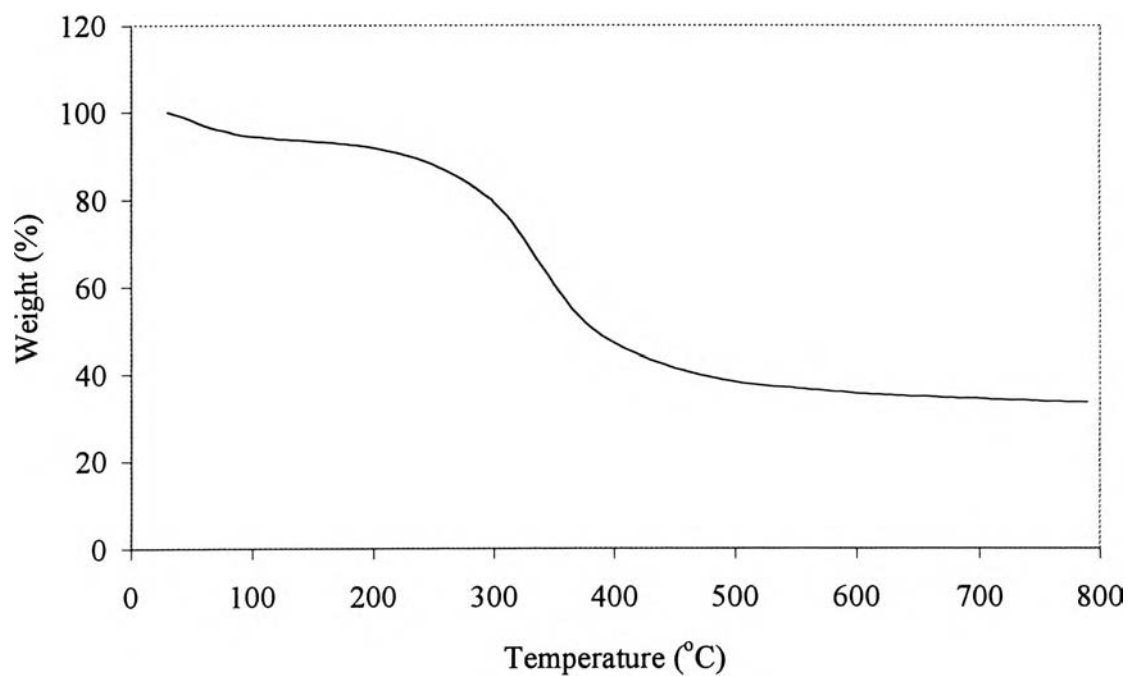


Figure C3 TGA thermogram of protein/OH-MMT 50 wt %.

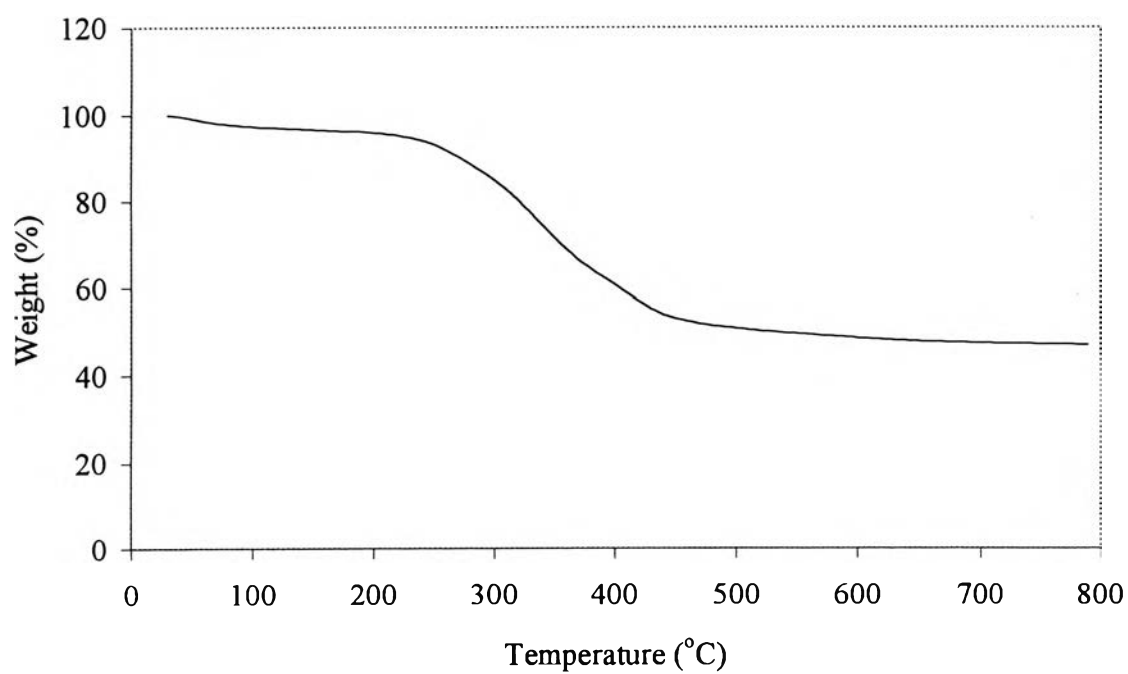


Figure C4 TGA thermogram of protein/OH-MMT 60 wt %.

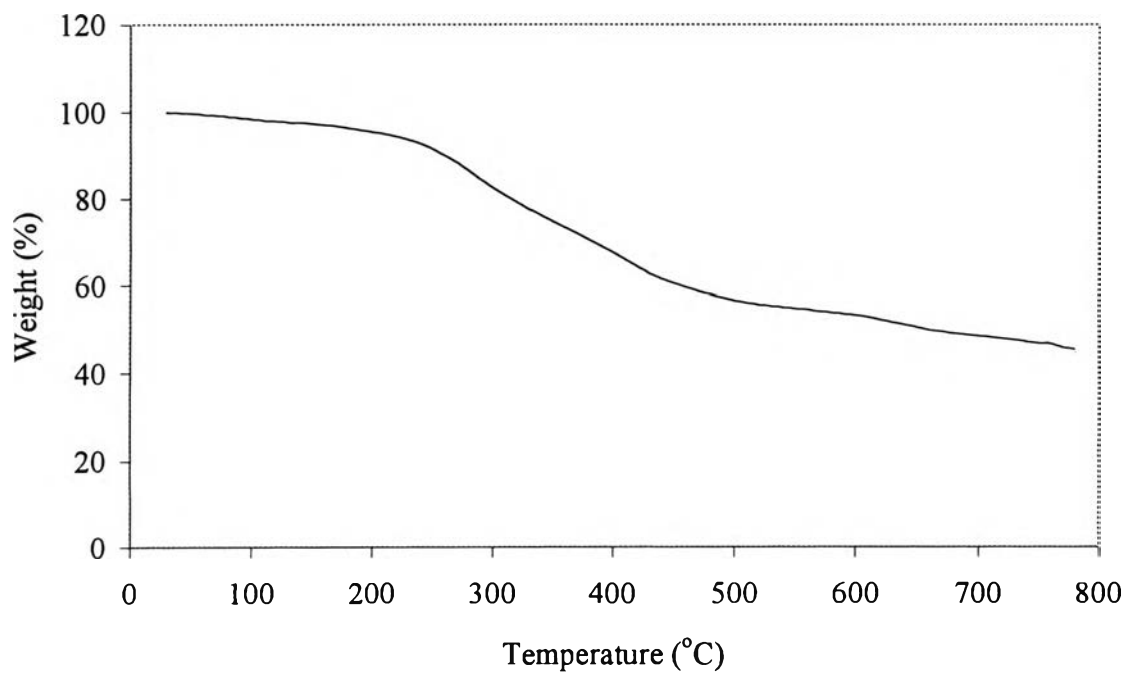


Figure C5 TGA thermogram of PPV/OH-MMT 30 wt %.

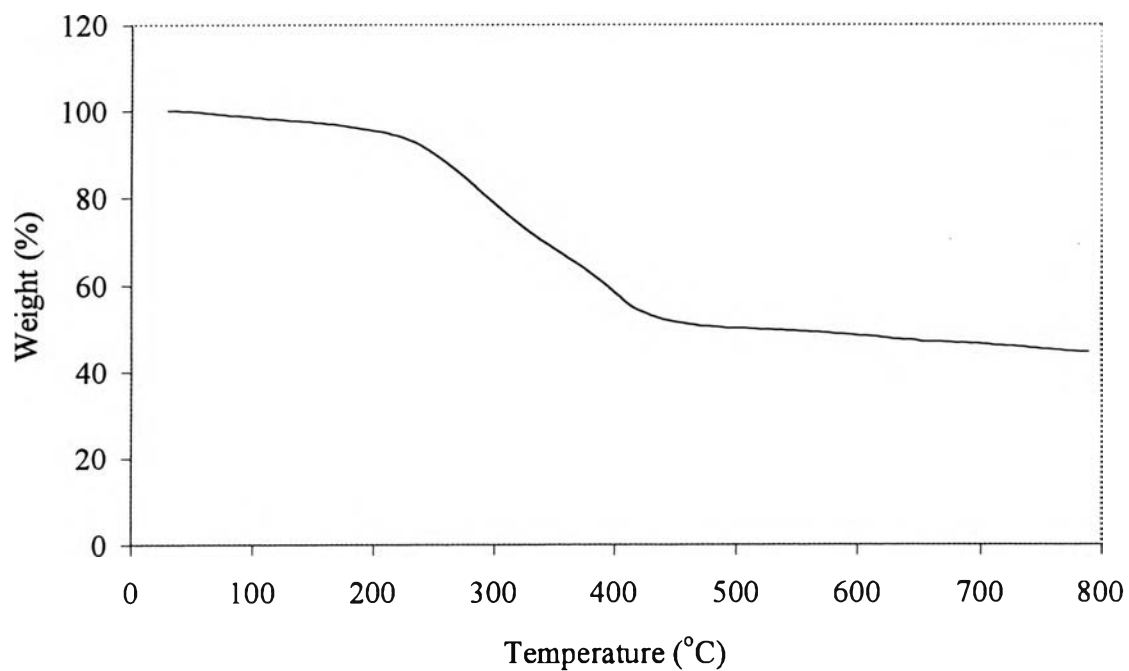


Figure C6 TGA thermogram of PPV/OH-MMT 40 wt %.

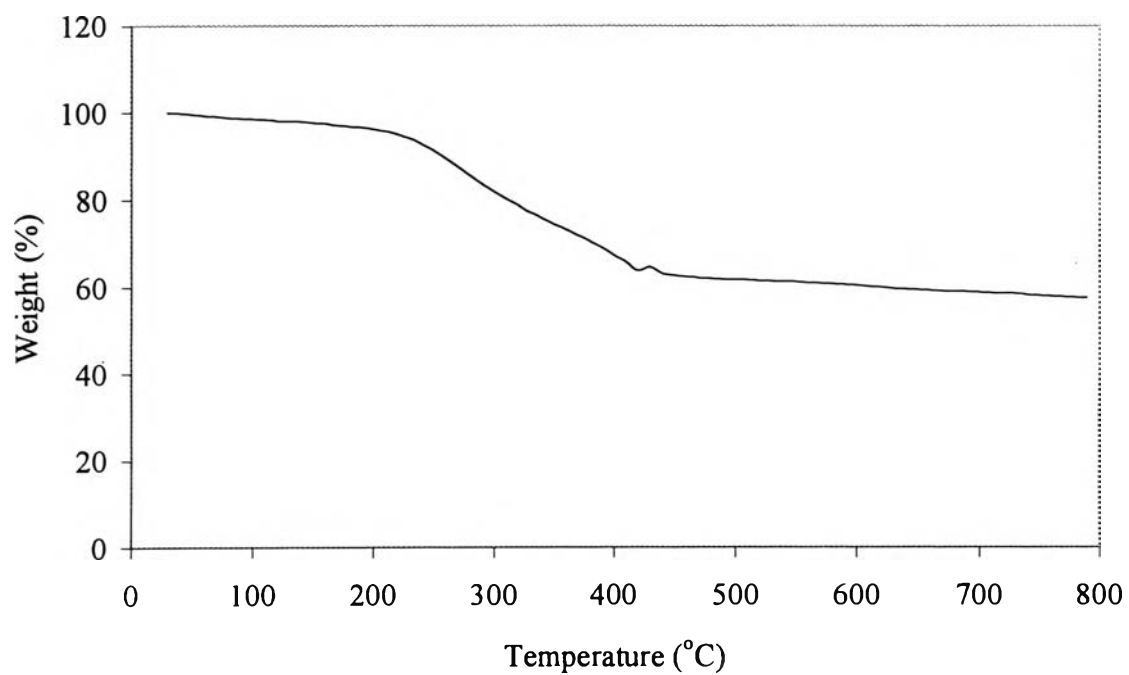


Figure C7 TGA thermogram of PPV/OH-MMT 50 wt %.

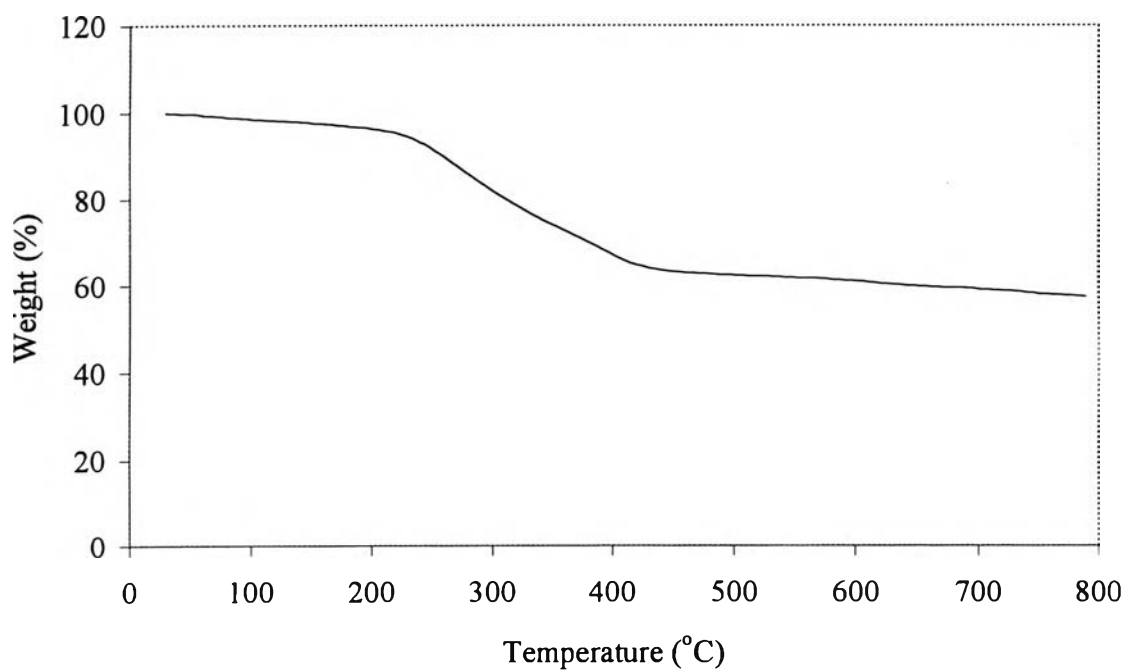


Figure C8 TGA thermogram of PPV/OH-MMT 60 wt %.

APPENDIX D

Water Absorption Data of Polymer/Layered Silicate Nanocomposites

Table D1 The change of weight loss of PPV/OH-MMT

OH-MMT content (wt %)	Water content (wt %)			
	#1	#2	#3	Average
0	1.29	1.94	1.93	1.72
30	1.34	1.83	1.87	1.68
40	1.21	1.76	1.80	1.59
50	1.20	1.72	1.76	1.56
60	1.15	1.58	1.65	1.46
100	1.08	1.27	1.43	1.26

Table D2 The change of weight loss of protein/OH-MMT

OH-MMT Content (wt %)	Water content (wt %)			
	#1	#2	#3	Average
0	8.23	7.24	6.58	7.35
30	7.65	6.73	5.90	6.76
40	6.91	6.02	5.82	6.25
50	5.39	5.53	5.79	5.57
60	3.99	2.95	1.28	2.74
100	1.08	1.27	1.43	1.26

APPENDIX E

Environmental Stability Test Results as a Function of Time

Table E1 The change of PL intensity of PPV

Time (min)	Intensity (cps)	Relative intensity
0	558	1
5	201	0.3602
10	193	0.3459
15	184	0.3297
20	176	0.3154
25	177	0.3172
30	174	0.3118

Table E2 The change of PL intensity of PPV-clay 30 wt %

Time (min)	Intensity (cps)	Relative intensity
0	2106	1
5	1010	0.4796
10	853	0.4050
15	823	0.3908
20	821	0.3898
25	758	0.3599
30	746	0.3542

Table E3 The change of PL intensity of PPV-clay 40 wt %

Time (min)	Intensity (cps)	Relative intensity
0	2054	1
5	1100	0.5355
10	938	0.4567
15	865	0.4211
20	800	0.3895
25	757	0.3685
30	720	0.3505

Table E4 The change of PL intensity of PPV-clay 50 wt %

Time (min)	Intensity (cps)	Relative intensity
0	2212	1
5	1482	0.6700
10	1380	0.6239
15	1210	0.5470
20	1097	0.4959
25	974	0.4403
30	941	0.4254

Table E5 The change of PL intensity of PPV-clay 60 wt %

Time (min)	Intensity (cps)	Relative intensity
0	3109	1
5	2850	0.9167
10	2715	0.8733
15	2568	0.8260
20	2451	0.7884
25	2350	0.7559
30	2296	0.7385

Table E6 The change of PL intensity of protein extracted from the scales of seabass

Time (min)	Intensity (cps)	Relative intensity
0	918	1
5	578	0.6296
10	413	0.4499
15	397	0.4325
20	369	0.4020
25	370	0.4031
30	363	0.3954

Table E7 The change of PL intensity of protein-clay 30 wt %

Time (min)	Intensity (cps)	Relative intensity
0	1085	1
5	706	0.6507
10	589	0.5429
15	524	0.4829
20	482	0.4442
25	456	0.4203
30	450	0.4147

Table E8 The change of PL intensity of protein-clay 40 wt %

Time (min)	Intensity (cps)	Relative intensity
0	2218	1
5	1620	0.7304
10	1384	0.6240
15	1243	0.5604
20	1190	0.5365
25	1100	0.4959
30	1081	0.4874

Table E9 The change of PL intensity of protein-clay 50 wt %

Time (min)	Intensity (cps)	Relative intensity
0	1675	1
5	1271	0.7588
10	1150	0.6866
15	1050	0.6269
20	1080	0.6448
25	1023	0.6107
30	996	0.5946

Table E10 The change of PL intensity of protein-clay 60 wt %

Time (min)	Intensity (cps)	Relative intensity
0	2862	1
5	2337	0.8166
10	2272	0.7939
15	2217	0.7746
20	2181	0.7621
25	2130	0.7442
30	2116	0.7393

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