CHAPTER III

EXPERIMENTAL

3.1 Materials

All reagents and solvents were of analytical grade quality obtained from Fluka and Aldrich. Methylene chloride (CH_2Cl_2) was refluxed over calcium hydride (CaH_2) and distilled immediately before use Zinc (II) acetate dehydrate, nickel (II) acetate tetrahydrate, salicylaldehyde, triethylenetetramine, tolylene 2,4-diisocyanate terminated poly (propylene glycol) prepolymers with molecular weight of 1000 and 2300 (PP1000 and PP2300), tolylene 2,4-diisocyanate terminated poly (1,4-butanediol) prepolymers with molecular weight of 900 and 1600 (PB900 and PB1600), dimethyl sulfoxide (DMSO) and dibutyltin dilaurate (DBTDL) were used without further purification.

Commercial Bentonite H (BNH) was supported by Ceramic "R" us (Bangkok, Thailand). The organoclay used in this study was the commercial bentonite H (131 mequiv/ 100 g of clay) which was modified by tallowtrimethyl ammonium chloride (TTM), oleylmethylbis(2-hydroxyethyl)ammonium chloride (OMH) and octadecylmethyl[ethoxylate(15)] ammonium chloride (ODMH). The organoclay was obtained from Metallurgy and Materials Science Research Institute, Chulalongkorn University.

3.2 Equipment

Fourier Transform Infrared Spectrophotometer (FTIR)

IR spectra was obtained by a Nicolet Impact 410 FTIR spectrophotometer at room temperature by potassium bromide (KBr) disc method. The sample was compressed as a disc by hydraulic press. The sample was scanned from 4000-500

cm^{-1} at a resolution of 16.0 cm^{-1} and the number of scans was 32. The measurement was controlled by Omnic software.

X-ray Diffractometer (XRD)

X-ray diffractometer used in this study was Bruker model D8 ADVANCE with CuKα radiation (1.5406 Å). The Voltage and the current of X-ray tubes were 40 kV and 30 mA, respectively. The measurement was scanned with 2θ intervals from 1.0 to 30.0° with scan speed 10.0 second/step and step size 0.02°. The measurements were operated by EVA program.

Transmission Electron Microscope (TEM)

The microscopic investigation of the composites structure was performed by JEOL JEM 2010 TEM at an acceleration voltage of 200 keV. The sample were prepared with Leica EMFCS cryogenic ultramicrotome system by a glass knife into 80-100 nm thick slices at $-10^{\circ}C$. A carbon layer of 3 nm thickness was deposited on these slices after mounding on 200 mesh copper grids for TEM observation. The samples were dried in oven at $50^{\circ}C$ for 48 hours.

Thermogravimetric Analyzer (TGA)

Thermogravimetric analysis was examined using a Netzsch STA 409C thermogravimetric analyzer in 1:1 air/nitrogen atmosphere at the heating rate of $20^{\circ}C/min$ from temperature range $20^{\circ}C$ to $1000^{\circ}C$. The result of thermal stability was reported in percentages weight loss of polymers.

Limiting Oxygen Index (LOI)

LOI was performed on an apparatus following ASTM D2863-70 using a modified procedure as described in the literature [39].

3.3 Methodology

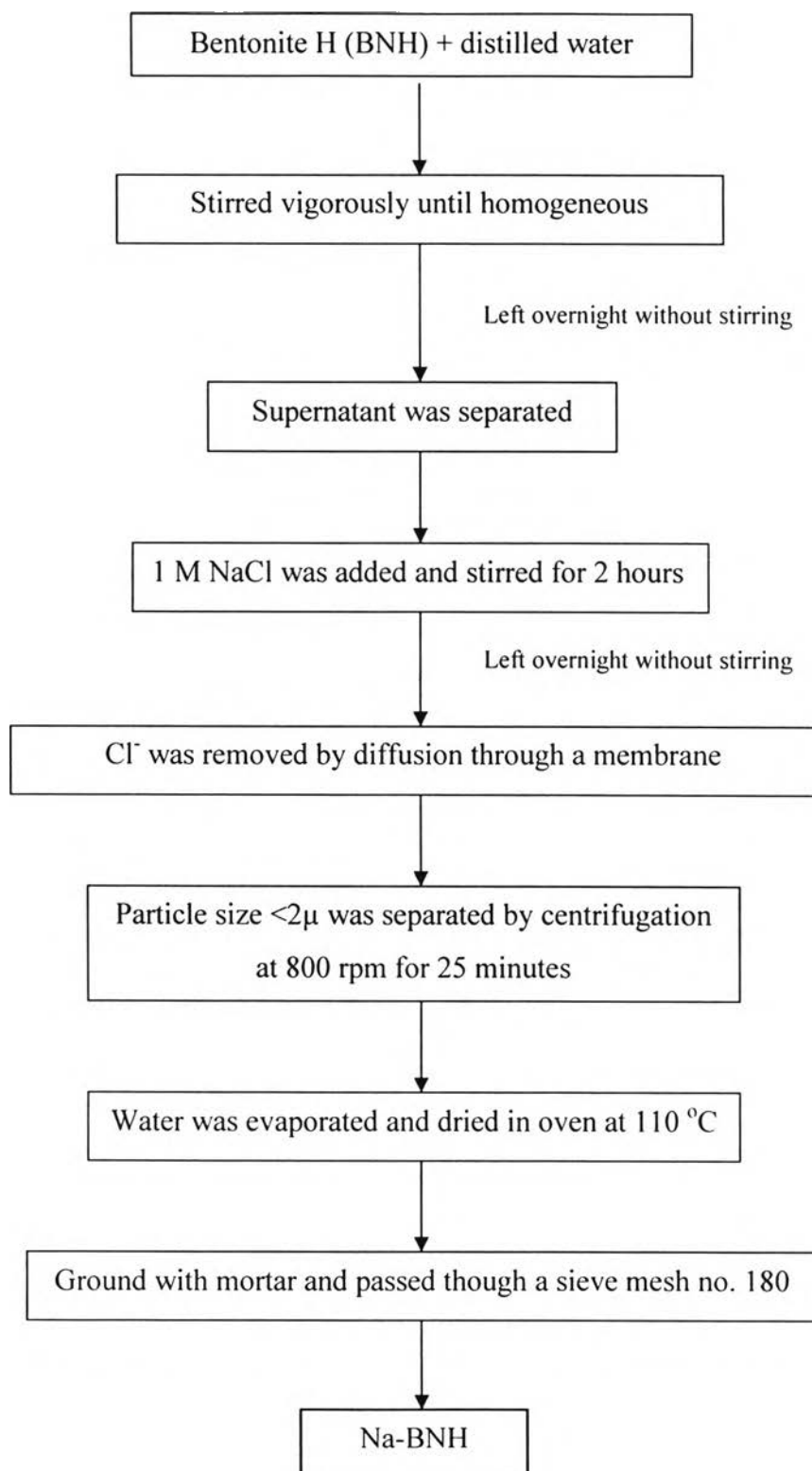### 3.3.1 Preparation of Organoclay

3.3.1.1 Preparation of Na-Bentonite (Na-BNH)

The preparation of Na-BNH was performed according to the method reported in the literature [37]. Bentonite H was stirred vigorously in water until homogeneous and left overnight without stirring. The supernatant was separated and 1 M of sodium chloride (NaCl) was added. The solution was stirred overnight at room temperature to ensure a complete exchange reaction. Excess sodium ion was removed by centrifugation at 2500 rpm for 10 minutes. Chloride ion was removed from the clay suspension by diffusion through a semipermeable membrane until no appeared white precipitate of silver chloride (AgCl) was detected with silver nitrate (AgNO$_3$) solution. The particle size separation, for particle size smaller than 2 µm, was carried out at the spinning speed of 800 rpm for 15 minutes at room temperature. Water was evaporated by a rotary evaporator at 60 °C at 100 mbar clay powder. Na-BNH was dried in a vacuum oven at 110°C for 3 days, ground with mortar, and then passed through a sieve mesh no.180. IR (KBr, cm^{-1}); 3628 (O-H stretching); 3434 (O-OH stretching); 1037 (Si-O stretching); 522 (Al-O stretching) and 468 (Si-O bending). XRD (concentration of surfactant 1.5 mmol); d-spacing 14.01 Å.

3.3.1.2 Preparation of Organoclay

The organoclay was prepared by Mrs.Sarintorn Limpanart at the Metallurgy and Materials Science Research Institute, Chulalongkorn University according to the method reported in the literature [37]. Na-BNH was dispersed in distilled water at a concentration of 1 wt%. Surfactant used in modified clay were tallowtrimethyl ammonium chloride (TTM), oleylmethylbis(2-hydroxyethyl)ammonium chloride (OMH) and octadecylmethyl [ethoxylate(15)] ammonium chloride (ODMH). The surfactants were dispersed in distilled water at various concentrations of 0.5, 1.0 and 1.5 mmol. Both solutions were heated to 70°C

for 20 minutes. The intercalation was achieved by pouring the surfactant solution into the clay dispersion. The reaction was stirred at 70°C for another 2 hours. Then, the stirring was stopped and the mixture was left overnight to reach an equilibrium stage. The solution was filtered and chloride ion was washed from organoclay. The organoclay was dried under vacuum at 75°C, ground with mortar and then passed through a sieve mesh no.325. For TTM: IR (KBr, cm^{-1}); 3632 (O-H stretching); 3442 (O-OH stretching); 2929, 2854 (C-H stretching of methyl and methylene group); 1479 (CH$_3$ deformation); 1041 (Si-O stretching); 523 (Al-O stretching) and 465 (Si-bending): XRD (concentration of surfactant 0.5, 1.0, 1.5 mmol); d-spacing 14.66, 19.37, 20.03 Å, respectively. For OMH: IR (KBr, cm^{-1}); 3629 (O-H stretching); 3422 (O-OH stretching); 2929, 2857 (C-H stretching of methyl and methylene group); 1469 (CH$_3$ deformation); 1042 (Si-O stretching); 523 (Al-O stretching) and 465 (Si-bending): XRD (con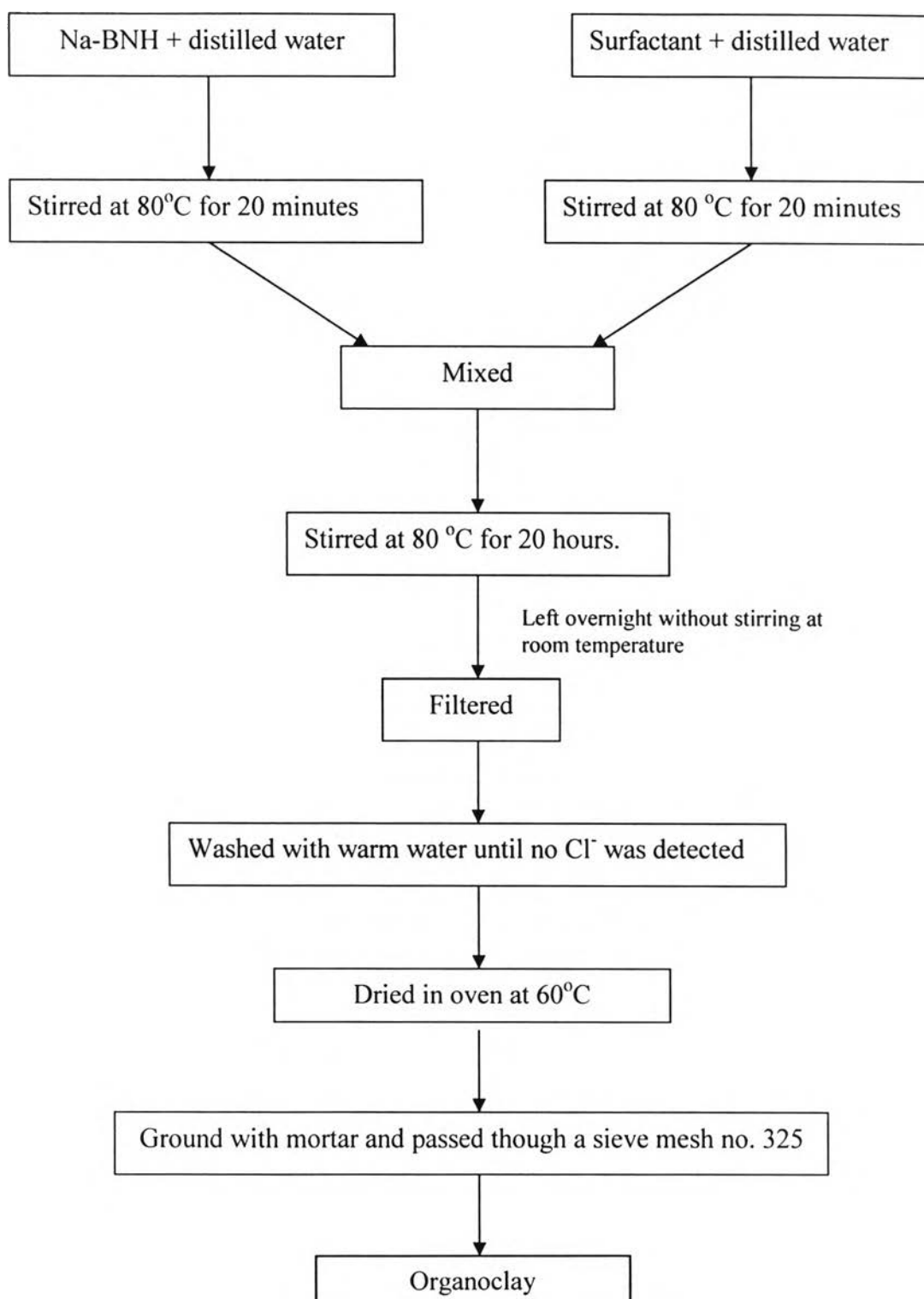centration of surfactant 0.5, 1.0, 1.5 mmol); d-spacing 14.18, 21.07, 21.15 Å, respectively. For ODMH: IR (KBr, cm^{-1}); 3628 (O-H stretching); 3431 (O-OH stretching); 2926, 2860 (C-H stretching of methyl and methylene group); 1468 (CH$_3$ deformation); 1038 (Si-O stretching); 523 (Al-O stretching) and 463 (Si-bending): XRD (concentration of surfactant 0.5, 1.0, 1.5 mmol); d-spacing 32.48, 33.89, 33.61 Å, respectively.

Scheme 3.1 The diagram of process for Na-BNH preparation

```
┌─────────────────────────────┐          ┌─────────────────────────────┐
│  Na-BNH + distilled water   │          │ Surfactant + distilled water│
└─────────────────────────────┘          └─────────────────────────────┘
              │                                        │
              ▼                                        ▼
┌─────────────────────────────┐          ┌─────────────────────────────┐
│ Stirred at 80°C for 20 minutes│        │ Stirred at 80 °C for 20 minutes│
└─────────────────────────────┘          └─────────────────────────────┘
              │                                        │
               ╲                                      ╱
                ╲                                    ╱
                 ▼                                  ▼
                    ┌──────────────────┐
                    │      Mixed       │
                    └──────────────────┘
                             │
                             ▼
                  ┌────────────────────────┐
                  │ Stirred at 80 °C for 20 hours. │
                  └────────────────────────┘
                             │
                             │     Left overnight without stirring at
                             │     room temperature
                             ▼
                       ┌──────────┐
                       │ Filtered │
                       └──────────┘
                             │
                             ▼
        ┌──────────────────────────────────────────┐
        │ Washed with warm water until no Cl⁻ was detected │
        └──────────────────────────────────────────┘
                             │
                             ▼
                ┌────────────────────────┐
                │   Dried in oven at 60°C │
                └────────────────────────┘
                             │
                             ▼
   ┌──────────────────────────────────────────────────┐
   │ Ground with mortar and passed though a sieve mesh no. 325 │
   └──────────────────────────────────────────────────┘
                             │
                             ▼
                    ┌──────────────────┐
                    │    Organoclay    │
                    └──────────────────┘
```

Scheme 3.2 The diagram of process for organoclay preparation

3.3.2 Preparation of Polyurethane

3.3.2.1 Preparation of Metal Complexes

3.3.2.1.1 Preparation of Hexadentate Schiff Base Zinc Complex (ZnSal₂trien)

The preparation of ZnSal$_2$trien was performed according to the method reported in the literature [38]. A cool (0-10°C) solution of triethylenetetramine (1 mL, 6.70 mmol) in methanol (10 mL) was added dropwise to a cool solution of salicylaldehyde (1.18 g, 9.66 mmol) and zinc (II) acetate dihydrate (1.05 g, 4.84 mmol) in the methanol (15 mL). The mixture was stirred for 15 minutes then neutralized by a 2 M sodium hydroxide solution (5 mL, 10 mmol) and stirred for 1 hour. The yellow crystals of ZnSal$_2$trien precipitated from the solution upon standing at room temperature for 12 hours. The yellow crystals were isolated by filtration and dried *in vacuo* for at least 24 hours (1.86 g, 93%). IR (KBr, cm^{-1}); 3646, 3300, 3000, 2800, 1634, 1600, 1448, 1200, 930, 870.

3.3.2.1.2 Preparation of Hexadentate Schiff Base Nickel Complex (NiSal₂trien)

The preparation of NiSal$_2$trien was performed according to the method reported in the literature [38]. A cool (0-10°C) solution of triethylenetetramine (1 mL, 6.70 mmol) in methanol (10 mL) was added dropwise to a cool solution of salicylaldehyde (1.18 g, 9.66 mmol) and nickel (II) acetate tetrahydrate (1.03 g, 4.84 mmol) in methanol (20 mL). The mixture was neutralized by a 2M sodium hydroxide solution (5 mL, 10 mmol) and stirred for 1 hour. The brown crystal of NiSal$_2$trien was precipitated from the solution upon standing at room temperature for 12 hours. NiSal$_2$trien crystals were isolated by filtration and dried *in vacuo* (0.532 g, 97%). IR (KBr, cm^{-1}); 3634, 3448, 3278, 2900, 2866, 1642, 1596, 1456, 1223, 953, 850.

3.3.2.2 Preparation of Metal-Containing Polyurethanes

The preparation of metal-containing polyurethanes from MSal$_2$trien (M = Zn^{2+} and Ni^{2+}) and prepolymers (PB900, PB1600, PP1000, PP2300) was performed according to the method reported in the literature [39]. MSal$_2$trien were dissolved in dried methylene chloride (10 mL). The solution of MSal$_2$trien was added to a solution of prepolymer in dried methylene chloride (10 mL). The composition of starting materials in the preparation of metal-containing polyurethanes is shown in Tables 3.1 and 3.2. Then, dibutyltin dilaurate (2-3 drops) was added to the reaction mixture as a catalyst. After refluxing under nitrogen for 8 hours at 40°C, the solvent was removed from the mixture by rotary evaporator. The precipitated polymer was filtered and dried *in vacuo*. The metal-containing polyurethanes were obtained as yellow powder and brown elastomer for zinc-containing polyurethane and nickel-containing polyurethane, respectively.

PB900Zn; IR (KBr, cm^{-1}); 3400, 2924, 2858, 1720, 1635, 1536, 1456, 1230, 1113, 763.

PB1600Zn; IR (KBr, cm^{-1}); 3288, 2924, 2852, 1720, 1635, 1597, 1536, 1447, 1367, 1230, 1113, 814, 758.

PP1000Zn; IR (KBr, cm^{-1}); 3293, 2970, 2924, 2863, 1729, 1635, 1536, 1449, 1378, 1291, 1224, 1106, 927, 763.

PP2300Zn; IR (KBr, cm^{-1}); 3288, 2965, 1724, 1630, 1536, 1455, 1369, 1224, 922, 866, 763.

PB900Ni; IR (KBr, cm^{-1}); 3298, 2924, 2853, 1720, 1640, 1598, 1536, 1342, 1230, 1113, 758.

PB1600Ni; IR (KBr, cm^{-1}); 3297, 2931, 2856, 1720, 1640, 1597, 1536, 1451, 1367, 1225, 1113, 885, 815, 756.

PP1000Ni; IR (KBr, cm^{-1}); 3293, 2970, 2924, 2858, 1720, 1635, 1598, 1541, 1455, 1373, 1291, 1230, 1112, 932, 820, 758.

PP2300Ni; IR (KBr, cm^{-1}); 3297, 2922, 2865, 1724, 1635, 1597, 1536, 1451, 1376, 1343, 1296, 1230, 1108, 929, 864, 819, 758.

Table 3.1 Composition of starting materials in the preparation of zinc-containing polyurethanes

Polymer Codes	Wt.% of ZnSal₂ trien in polymer	Wt. of ZnSal₂ trien (g)	Wt. of prepolymer (g)	Total wt. (g)	Yield (%)
PB900Zn	30	0.1750	0.3780	0.5530	61
PB1600Zn	20	0.1500	0.5749	0.7249	50
PP1000Zn	30	0.1500	0.3590	0.5090	66
PP2300Zn	20	0.1500	0.8264	0.9764	53

Table 3.2 Composition of starting materials in the preparation of nickel-containing polyurethanes

Polymer Codes	Wt. % of NiSal₂ trien in polymer	Wt. of NiSal₂ trien (g)	Wt. of prepolymer (g)	Total wt. (g)	Yield (%)
PB900Ni	30	0.1500	0.3282	0.4782	98
PB1600Ni	20	0.1500	0.5835	0.7335	96
PP1000Ni	30	0.1500	0.3647	0.5147	97
PP2300Ni	20	0.1500	0.8388	0.9888	90

3.3.3 Preparation of Metal-Containing Polyurethane/Clay Nanocomposites

The metal-containing polyurethane/clay nanocomposites were prepared by use of solvent method. Different amounts of organoclay (1, 3, 5 wt%, based on polymer nanocomposites) was mixed with 2.0 mL of DMSO and stirred vigorously at room temperature for 30 minutes by a vortex mixer. The metal-containing polyurethane (2.0 g) was dissolved with DMSO (6.0 mL) and stirred until homogeneous with magnetic stirrer at 90 °C for 30 minutes, yielding a 30 wt% of polymer in solution. The metal-containing polyurethane solution was cooled to room temperature and mixed with the solution of organoclay dispersed in DMSO and stirred until homogeneous by a vortex mixer for 1 hour, yielding metal-containing polyurethane/clay mixture in DMSO. The metal-containing polyurethane/clay mixture was immediately cast onto a petri dishes. The nanocomposite films were dried in a vacuum oven at 50°C for 24 hours. A diagram of the preparation method is shown in Scheme 3.3.

```
┌─────────────────────────┐        ┌─────────────────────────┐
│  Organoclay 1, 3, 5 wt%.│        │ Metal-containing        │
│      (based on          │        │ Polyurethane            │
│ polyurethane/clay       │        │       2.0 g             │
│ nanocomposites)         │        │                         │
└───────────┬─────────────┘        └───────────┬─────────────┘
            │                                   │
            ▼                                   ▼
┌─────────────────────────┐        ┌─────────────────────────┐
│  Dissolved in DMSO      │        │ Dissolved in DMSO (6.0 mL)│
│     (2 mL)              │        │ at 90°C for 30 minutes  │
└───────────┬─────────────┘        └───────────┬─────────────┘
            │                                   │ cooled down to
            │                                   │ room temperature
            ▼                                   ▼
┌─────────────────────────┐        ┌─────────────────────────┐
│  DMSO dispersion of     │        │ Metal-containing        │
│     organoclay          │        │ polyurethane            │
│                         │        │ solution (30 wt%)       │
└───────────┬─────────────┘        └───────────┬─────────────┘
            │                                   │
            └────────────┐         ┌────────────┘
                         ▼         ▼
              ┌─────────────────────────┐
              │   Stirred vigorously    │
              │      (1 hour)           │
              └───────────┬─────────────┘
                          │
                          ▼
              ┌─────────────────────────┐
              │  Casting on a petri     │
              │       dishes            │
              └───────────┬─────────────┘
                          │ dried in a vacuum oven
                          ▼
              ┌─────────────────────────┐
              │ Metal-containing        │
              │ polyurethane            │
              │ nanocomposite films     │
              └─────────────────────────┘
```

Scheme 3.3 A diagram of preparation method for metal-containing polyurethane/clay nanocomposites

3.3.4 Characterization of Metal-Containing Polyurethane Nanocomposite Films.

The film were characterized to inspect the composition and characteristic by using the techniques, as follows:

FTIR: The thin films of metal-containing PU/clay nanocomposites were characterized by transmission mode of FTIR to examine the characteristic functional groups.

XRD: This technique was used to determine the interlayer spacing of pure organoclay and the corresponding clay nanocomposite materials which were prepared by solution casting on a glass slide.

TEM: This technique was used to characterize the morphology of nanocomposites.

3.3.5 Thermal Property

Thermal stability of nanocomposite materials was studied by TGA. The weight loss due to the formation of volatile products after degradation at high temperature was monitored as a function of temperature.

3.3.6 Flame Retardant Property

The LOI is one of the methods for studying the fire retardant properties. The result of LOI was reported in the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that would just support flaming combustion of a material initially at room temperature.