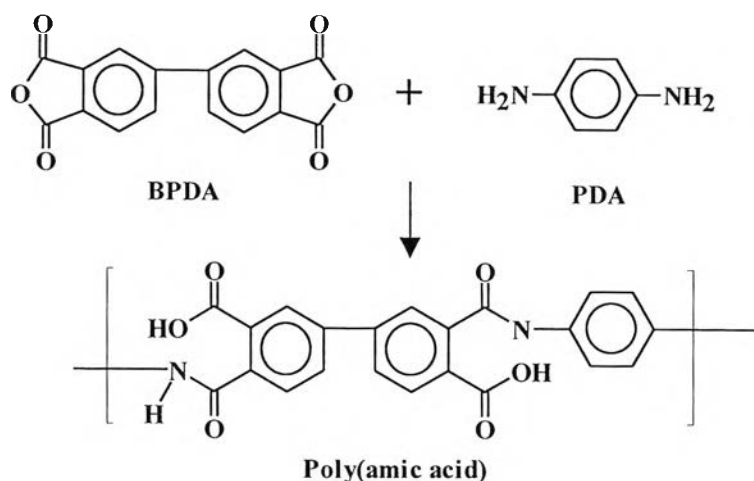# CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Poly(amic acid) : PI2610 (BPDA-PDA)


Poly(amic acid)

The Pyralin® BPDA-PDA poly(amic acid) in N-methyl-2-pyrrolidone (NMP) solution was provided by DuPont Co. BPDA-PDA is a rigid rod-like type of polyimide. The solution viscosity at 25 °C is equal to 27.5 poise and solid content is 10.5%. PI2610-Series polyimide solutions are highly viscous due to their high molecular weight. The solution should be refrigerated or frozen for 1 year shelf life.

3.1.2 N-methyl-2-pyrrolidone (NMP)
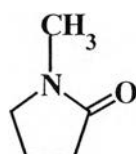
NMP, used as a solvent, was purchased from Merck. Its boiling point is about 205 °C.

3.1.3 Dodecylamine
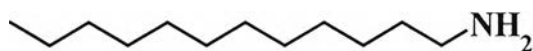
Dodecylamine of purum grade of Fluka was used as a modifying agent. The melting point is 27-29 °C.

3.1.4 Sodium montmorillonite : $Na_{0.6}[(Mg_{0.6}Al_{3.4})Si_8O_{20}(OH)_4]$

Sodium montmorillonite (Kunipia-F) with cation exchange capacity (CEC) of 119 meg/100 g was supplied by Kunimine Industrail Co., Ltd., Japan.

3.1.5 Hydrochloric acid (HCl)

HCl (36 %wt) of Univar was used without further purification.

3.1.6 Adhesion Promoter (VM-651)

VM-651, an aminosilane base adhesion promoter, is a product of HD Microsystems, an enterprise of Hitachi Chemical and DuPont Electronics. VM-651 is an organosilane (γ-amino propyltriethoxysilane (γ-APS)) which is used to improve the adhesion of all types of Pyralin polyimide coatings to substrates such as silicon dioxide or silicon nitride coated wafer. This product is easy to apply and effective at very low organosilane concentrations.

3.2 Equipment

3.2.1 Wide Angle X-ray Diffractometer (WAXD)

The WAXD is a technique commonly used to determine the basal spacing in nanocomposite materials. WAXD was performed at room temperature by a Rigaku Model D/MAX 2000 diffractometer. The CuKα radiation source was operated at 40 kV and 30 mA Patterns were recorded by monitoring the diffraction appeared in the 2θ range from 2° to 30° with scan speed 5 degrees/minute and scan step 0.02 degree.

3.2.2 Thermogravimetric Analyzer (TGA)

Using a DuPont 2950 thermogravimetric analyzer, characterizations of the nanocomposite were performed by heating 10 mg of each sample up to 750 °C at the heating rate 10 °C/min under the nitrogen atmosphere. The mass change with increasing temperature was monitored and recorded.

3.2.3 Atomic Absorption Spectroscopy (AAS)

An atomic absorption spectrometer Varian SpectrAA-300 was used to determine % sodium ion exchanged from clay. Acetylene was used as fuel and air was used as supported gas. Sodium cathode lamp was used as the hollow cathode lamp for sodium ion with 5 mA lamp current. To determine the absorbance of sodium ion, the wavelength at 589.0 nm was used.

3.2.4 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded on a VECTER 3.0 BRUKER spectrometer in the wavenumber range 4000-400 cm^{-1} using a deuteriated

triglycinesulfate detector (DTGS) with a specific detectivity, D, of 1×10^{9} $\mathrm{cm.Hz}^{0.5}.\mathrm{w}^{-1}$.

3.2.5 Gas Permeability Tester

Brugger gas permeability tester, as showed in Figure 3.1, was used for the estimation of the steady state rate of transmission of gas through plastics in the form of film, sheeting, and laminates following ASTM D1434-82. Samples, 110 mm diameter circular shape, to be tested must have at least one smooth side which can be well sealed and this side must always face the lower part of the permeation cell.
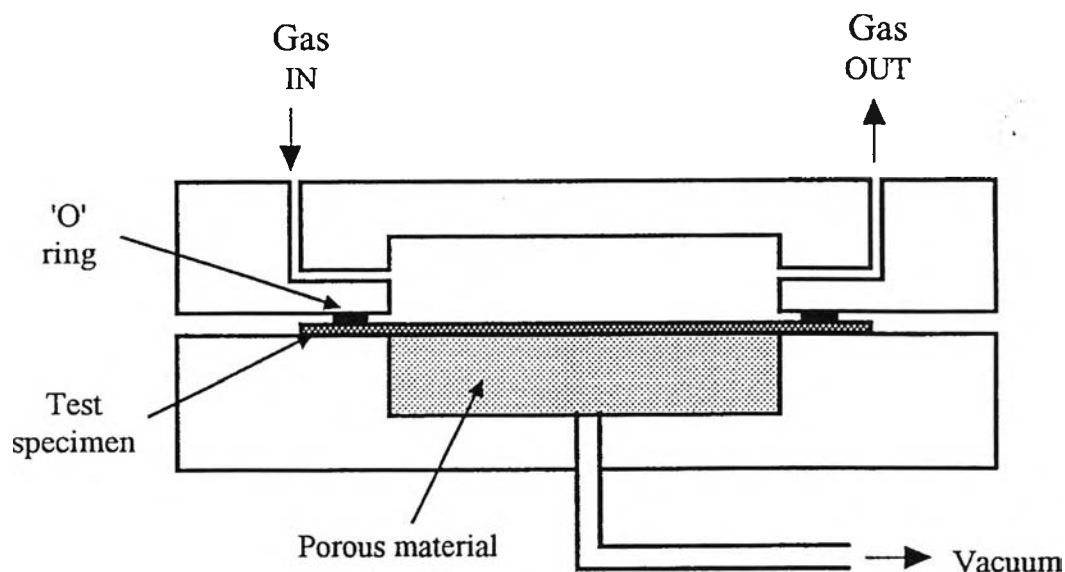

Figure 3.1 The brugger gas permeability cell.

This appliance consumes 220 volts alternating current and 30 watts power. The measuring range is about 1-300 $\mathrm{cm}^{3}/(\mathrm{m}^{2}.\mathrm{day}.\mathrm{bar})$. Measuring gas was fed into tester cell with 100 $\mathrm{cm}^{3}/\mathrm{min}$ flow rate at 25 °C

3.2.6 Electrical Resistivity Measurement Unit

The electrical resistivity of films at different temperatures varied from 50 °C to 350 °C was measured by using the unit demonstrated in Figure 3.2. Electrical voltage of 10.00 volts direct current was charged to a sample. The sample was placed also in contact with heater surface for temperature increment by the step of 50 °C. After leaving at a certain temperature for about 60 minutes to reach the constant value, the current indicated by PicoAmpmeter was recorded.

Power supply
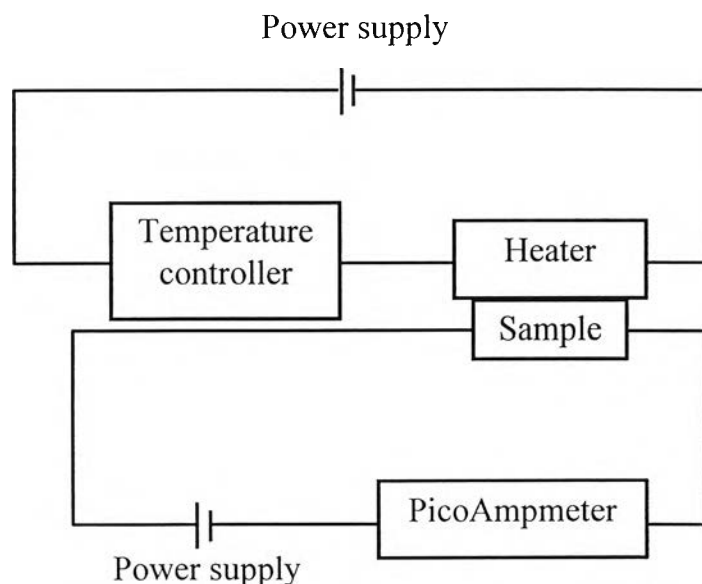
Figure 3.2 A diagram of electrical resistivity measurement unit.

3.2.7 Universal Testing Machine

Instron Universal Testing Machine model 4206 was used to determine shear strength of interface between polyimide and polyimide-clay nanocomposite thin film and silicon wafer. The machine was set at gauge length (initial grip separation) 50 mm and applied 5 kN load cell.
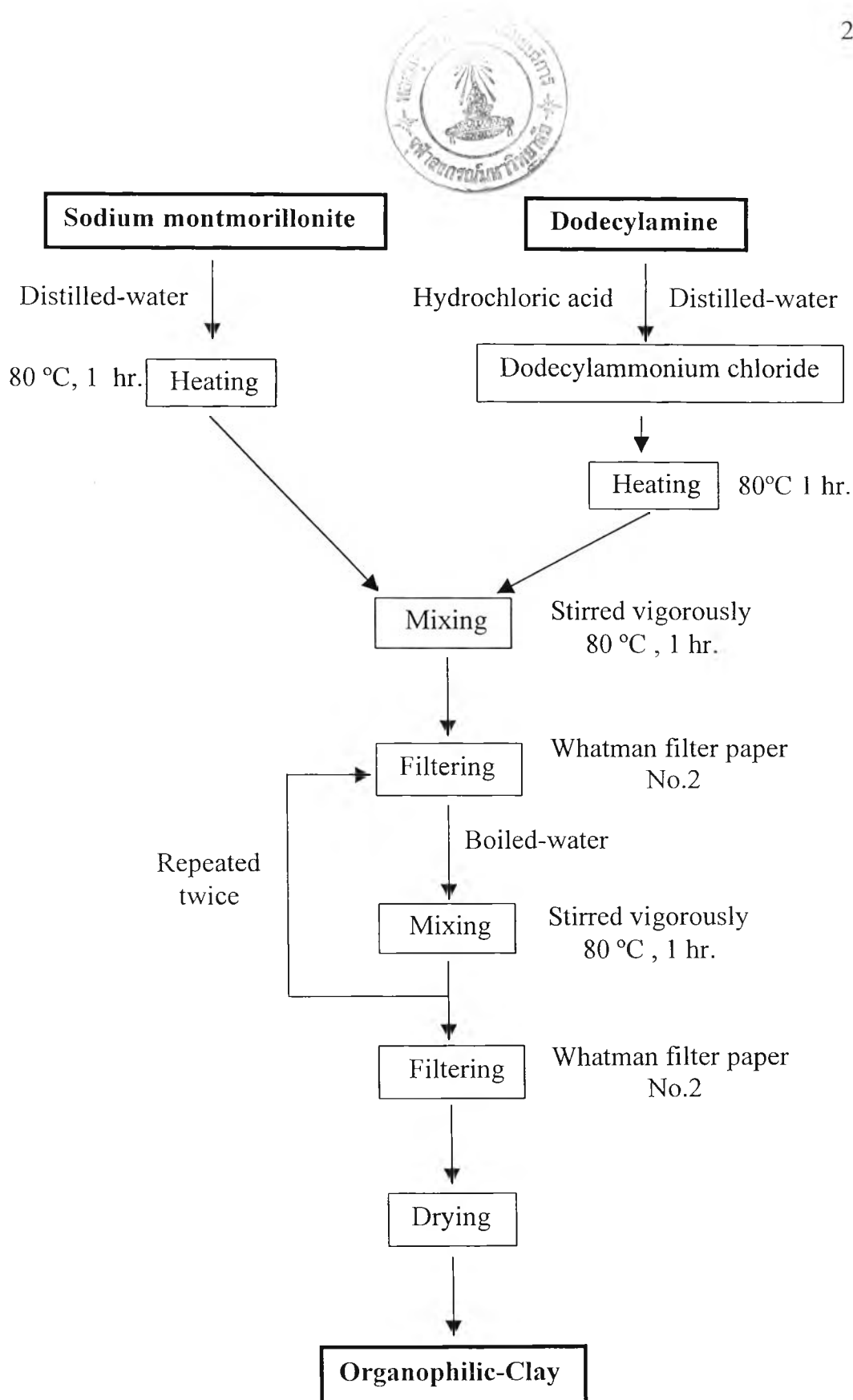
3.2.8 Optical Microscope (OM)

The optical microscope (Leoca, model DMRXE), connecting with 12 V 100 W transmitted light lamp, was used to investigate the surface of adhesion specimens after failure. This work used only 40 times lens and 10 times eye lens.

3.3 Methodology

3.3.1 Preparation of Organophilic-Clay Filler

In a 500 mL beaker, 4.41 g of dodecylamine, 2.4 mL of concentrated hydrochloric acid, and 100 mL of distilled water were placed. This solution was heated to 80 °C. In 200 mL of water, 10 g of clay was dispersed at 80 °C for 1 hour. The dispersion of montmorillonite was added to the solution of ammonium salt of dodecylamine, and this mixture was stirred vigorously at 80 °C for 1 hour (see stoichiometry calculation of organophillic-clay in Appendix I). A white precipitate was isolated by filtration, placed in a 500 mL breaker with 200 mL of hot water, and stirred for 1 hour. This process was repeated twice to remove the residue of ammonium salt of dodecylamine. The organophilic-clay was then collected and dried. Figure 3.3 shows a flow chart of preparation method.

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┌─────────────────────────┐                    ┌─────────────────────┐
│ Sodium montmorillonite  │                    │    Dodecylamine     │
└─────────────────────────┘                    └─────────────────────┘
            │                                             │
   Distilled-water                    Hydrochloric acid │ Distilled-water
            │                                             │
            ▼                          ┌──────────────────────────────┐
80 °C, 1  hr. │ Heating │              │  Dodecylammonium chloride     │
            └──────────┘              └──────────────────────────────┘
                                                      │
                                                      ▼
                                            │ Heating │  80°C 1 hr.
                                            └─────────┘
            
                  ▼              ◄
              ┌──────────┐        Stirred vigorously
              │  Mixing  │        80 °C , 1 hr.
              └──────────┘
                   │
                   ▼
              ┌──────────┐        Whatman filter paper
   ────────►  │ Filtering│        No.2
              └──────────┘
   Repeated         │
   twice       Boiled-water
   │               │
   │               ▼
   │          ┌──────────┐        Stirred vigorously
   └──────    │  Mixing  │        80 °C , 1 hr.
              └──────────┘
                   │
                   ▼
              ┌──────────┐        Whatman filter paper
              │ Filtering│        No.2
              └──────────┘
                   │
                   ▼
              ┌──────────┐
              │  Drying  │
              └──────────┘
                   │
                   ▼
          ┌────────────────────┐
          │  Organophilic-Clay │
          └────────────────────┘
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Figure 3.3 A diagram of preparation method of organophilic-clay filler.

3.3.2 Characterization of Organophilic-Clay Filler

The organophilic-clay filler prepared from sodium montmorillonite and dodecylamine was characterized to verify the structure and composition by using these following techniques (as showed in Figure 3.4):

- **FTIR**: The infrared spectra were used to investigate the characteristic group frequencies of dodecylamine, sodium montmorillonite, and dodecylamine montmorillonite. In this experiment, characteristics of the organophilic-clay were obtained using a transmission mode of FTIR with KBr disc.

- **WAXD**: This technique was used to identify the structure of crystalline materials on an atomic level, e.g. the degree of crystallinity and orientation of the crystalline in both clay and modified-clay. The basal spacing of samples were calculated from the powder diffraction patterns.

- **TGA**: Thermogravimetric analysis technique was used to determine thermal stability of dodecylamine, sodium montmorillonite, and dodecylamine montmorillonite by putting dried powder in a small disc inside the heater chamber.

- **AAS**: The % ion exchange was determined by using this technique. The calibration curve was first plot from the absorption of standard sodium solution. Then % sodium exchanged from clay was achieved from the interception of calibration curve.
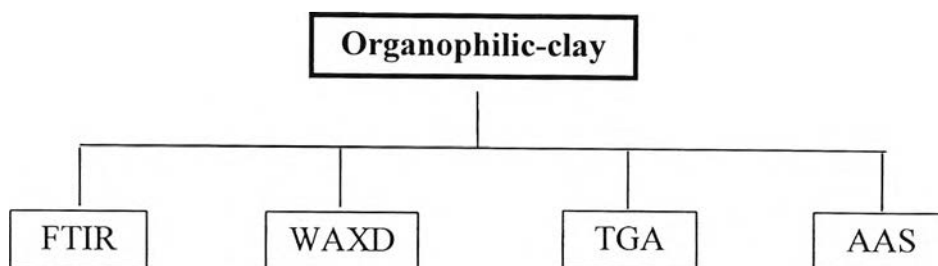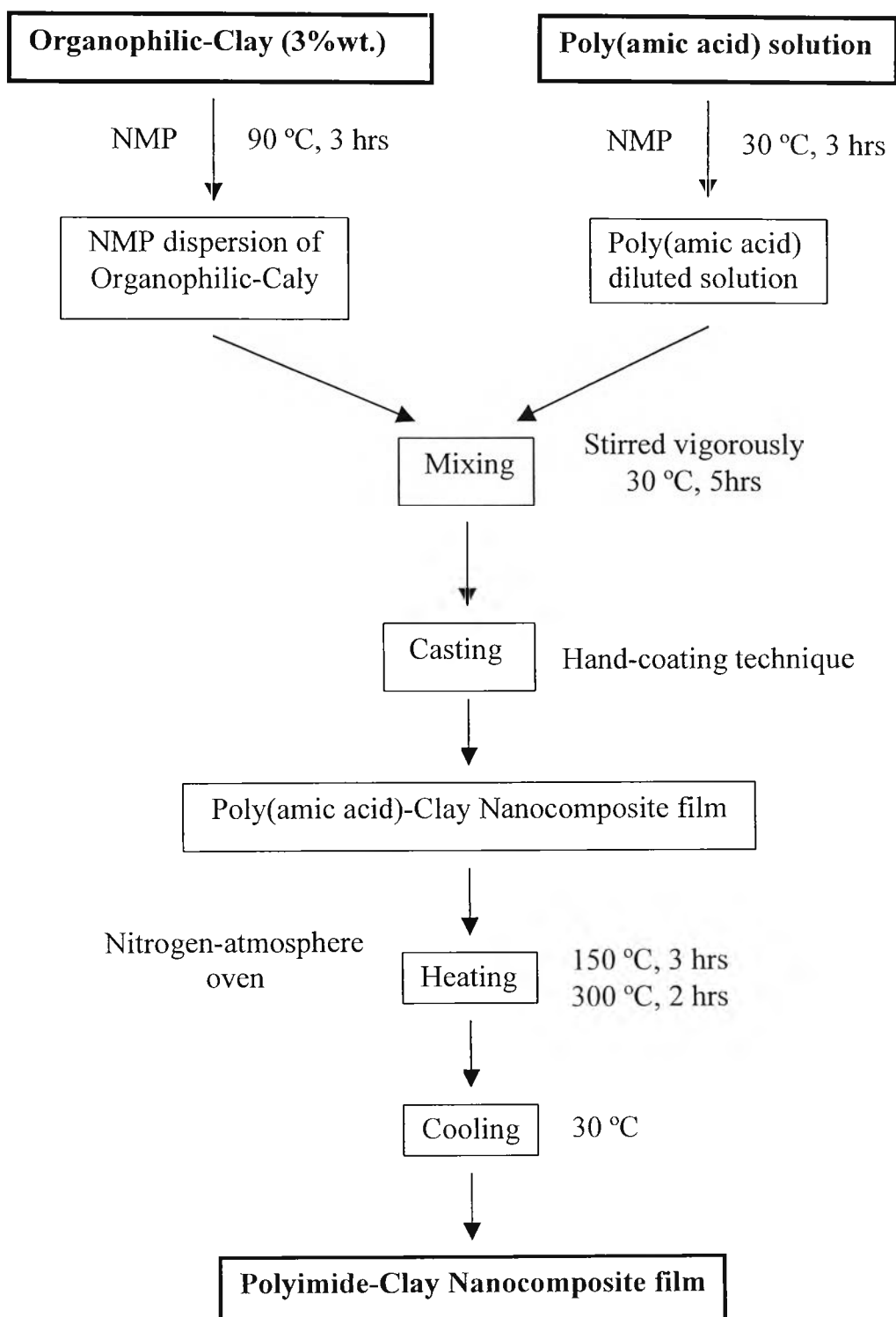
Figure 3.4 A diagram of characterization of organophilic-clay filler.

3.3.3 Preparation of Polyimide-Clay Nanocomposites Thin Film

A mixture of 0.15 g of organophilic-clay and 5 g of NMP solvent was stirred vigorously at 90 °C for 3 hours, yielding a 3.5 wt% of clay in NMP solvent. The Pyralin® BPDA-PDA poly(amic acid) solution was diluted with NMP solvent and then was mixed with the stock solution of clay dispersed in NMP and stirred vigorously at 30 °C for 3 hours, yielding poly(amic acid)-clay mixture solution.

A puddle of ordinary poly(amic acid) and poly(amic acid)-clay solution was cast on a glass substrate (onto silicon wafer for adhesion test) by hand coating technique. The wet film was dried at 150 °C for 3 hours and finally imidized at 300 °C for 2 hours with heating rate of 2 °C/min in nitrogen atmosphere oven. Then, the film was cooled down to 30 °C in the rate of 5 °C/min. A diagram of the preparation method is showed in Figure 3.5.
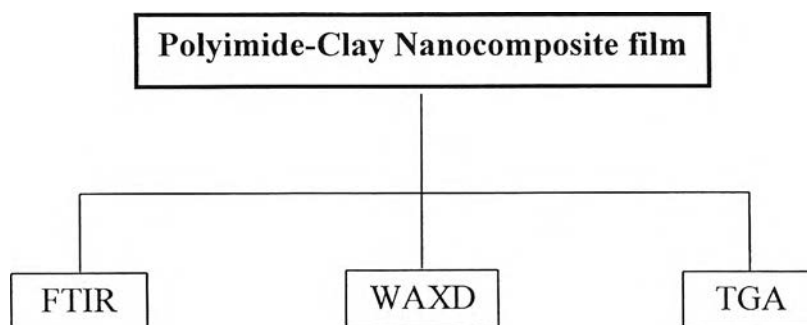
28

Organophilic-Clay (3%wt.)   Poly(amic acid) solution

NMP | 90 °C, 3 hrs   NMP | 30 °C, 3 hrs

NMP dispersion of   Poly(amic acid)
Organophilic-Caly   diluted solution

Mixing   Stirred vigorously
          30 °C, 5hrs

Casting   Hand-coating technique

Poly(amic acid)-Clay Nanocomposite film

Nitrogen-atmosphere
oven   Heating   150 °C, 3 hrs
                             300 °C, 2 hrs

Cooling   30 °C

Polyimide-Clay Nanocomposite film

Figure 3.5 A diagram of preparation method of polyimide-clay nanocomposite film.

3.3.4 Characterization of Polyimide-Clay Nanocomposite Film

The films were characterized to inspect the composition and characteristic by using these following techniques (as showed in Figure 3.6):

- **FTIR**: The thin films of PI and PI-clay nanocomposite were characterized by transmission mode of FTIR to examine the characteristic group.

- **WAXD**: This technique was used to determine d-spacing of the 40 μm thin films of PI and PI-clay nanocomposite which were prepared by solution casting on the glass substrate.

- **TGA**: Small pieces of films were cut and put into a small disc inside the heater chamber and then heated up from 30 °C to 750 °C. Determination of thermal stability was available by observation of % mass loss.

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         ┌──────────────────────────────────────┐
         │  Polyimide-Clay Nanocomposite film   │
         └──────────────────────────────────────┘
                           │
         ┌─────────────────┼─────────────────┐
      ┌──────┐         ┌────────┐         ┌──────┐
      │ FTIR │         │  WAXD  │         │ TGA  │
      └──────┘         └────────┘         └──────┘
```

Figure 3.6 A diagram of characterization of polyimide-clay nanocomposite film.

3.3.5 Property Measurement

The properties of polyimide and polyimide-clay nanocomposite films were considered whether they met the requirement of protective coating or not. A diagram of property measurement is showed in Figure 3.7.
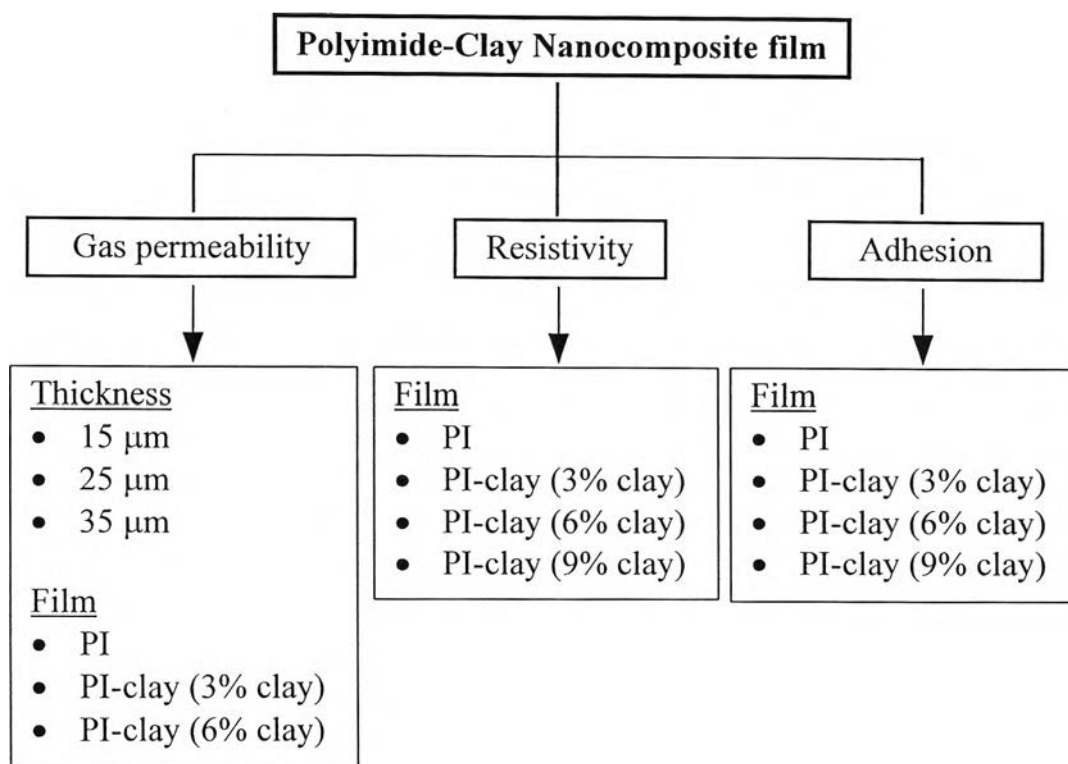
Figure 3.7 A diagram of property measurement.

3.3.5.1 Gas permeability

The test specimen (PI or PI-clay nanocomposite film) was placed, wrinkle-free, on top of the porous material and the two halves of the permeability cell were clamped together. The 'O' ring ensures an air-tight seal between the two cell halves. The test gas (O_2 gas) with flow rate 100 cm^3/min was circulated through the top half of the permeation cell and the vacuum applied below the specimen until all the air was removed from the specimen. Vacuum was then turned off and the rate of gas permeation through the specimen (monitored by the change in vacuum pressure) was recorded with time.

Under steady conditions, a plot of log gas pressure (mm Hg) versus time (s) should give a straight line, the slope (N) of which is used to calculate the gas permeability (using an appropriate equation incorporating

an appliance factor). The gas permeability, G, in units of $cm^3/(m^2.day.bar)$, is calculated from,

$$G = \frac{7.76 \times 10^{10} \times V}{78.5K \times 29N} \qquad cm^3/(m^2.day.bar) \qquad (3.1)$$

where:

V = volume of the evacuation chamber

K = absolute temperature (degrees Kelvin)

N = slope of the graph.

If the evacuation chamber volume, V, is $0.4370\ cm^3$ then this expression simplifies to,

$$G = \frac{1.49 \times 10^7}{KN} \qquad cm^3/(m^2.day.bar) \qquad (3.2)$$

3.3.5.2 Electrical resistivity

In insulator application of polyimide, the electrical resistivity is a functional significance. More often electrical resistivity measurements are useful in investigating the fundamental characteristics of polymer materials and determining the presence of impurities or fillers. The unit resistance, electrical resistivity, was calculated from the measure value of electrical current using the measurement unit shown in Figure 3.2. Polyimide or polyimide-clay film was coated onto an electrode as shown in Figure 3.8.
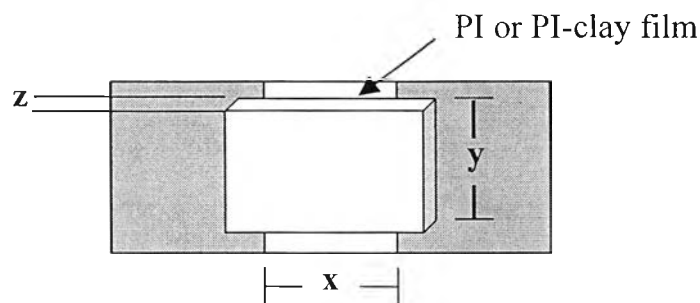
Figure 3.8 A sample for electrical resistivity measurement.

Finally, the electrical resistivity can be calculated by using equation 3.3 ,

$$\rho \; = \; \frac{V \cdot y \cdot z}{I \cdot x} \qquad (\Omega.cm) \qquad (3.3)$$

where ρ is electrical resistivity, V is voltage, I is current, x is length of sample, y is width of sample, and z is thickness of sample.

3.3.5.3 Adhesion

The standard test method for evaluating the shear strength of adhesive bonds is described in ASTM D1002 lap shear test. This test method is one of the most common study test methods for the evaluation of adhesive bonds. Test specimens were conformed to the form and dimensions in Figure 3.9 and then placed in the grips of the testing machine. Then the loading was applied immediately to pull the specimen at crosshead speed of 50 mm/min. The load at failure was recorded and expressed in shear strength in the unit of N/mm^2 (MPa), using the equation 3.4,

$$\text{Shear strength} \; = \; \frac{F}{A} \qquad (N/mm^2) \qquad (3.4)$$

where F is applied load at failure and A is adhesion area.
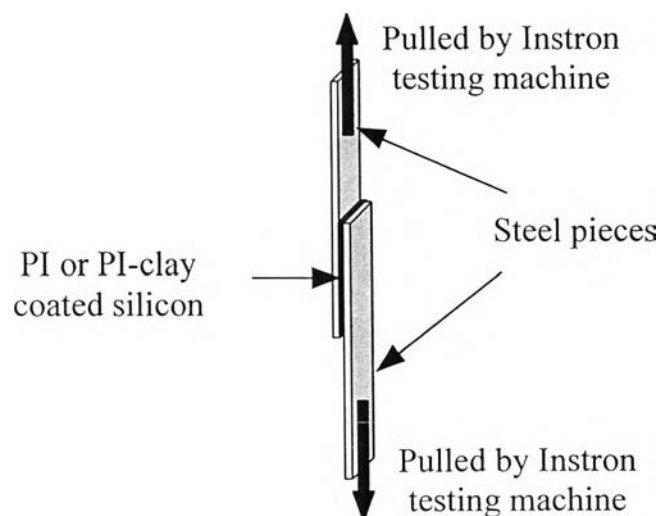
Figure 3.9 A sample for adhesion test.