

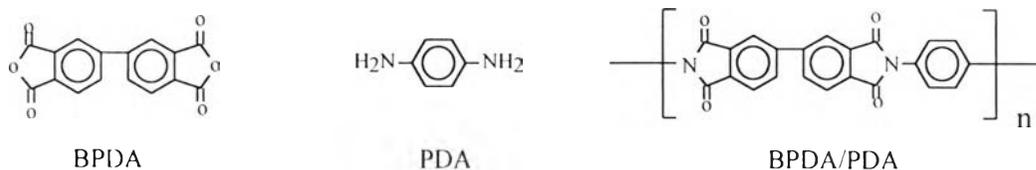


CHAPTER III EXPERIMENTAL SECTION

3.1 Materials

The BPDA-PDA and BTDA/ODA-MDA (see abbreviations in section 3.5) poly(amic acid) in N-methyl-2-pyrrolidone (NMP) solution were kindly supplied by Du Pont Singapore Pte Ltd.. The chemical structure, some characteristics of poly(amic acid) precursors, and the resulting polyimide films (after subjected to programmed thermal treatment under nitrogen-atmosphere) are shown in Figure 3.1.

- PI2610 (BPDA/PDA)** - Viscosity @ 25 °C : 27.5 poise
(Rigid rod-like) - Solid content : 10.5 %wt



- PI2579 (BTDA/ODA-MDA)** - Viscosity @ 25 °C : 0.11 poise
(flexible) - Solid content : 9.5 %wt

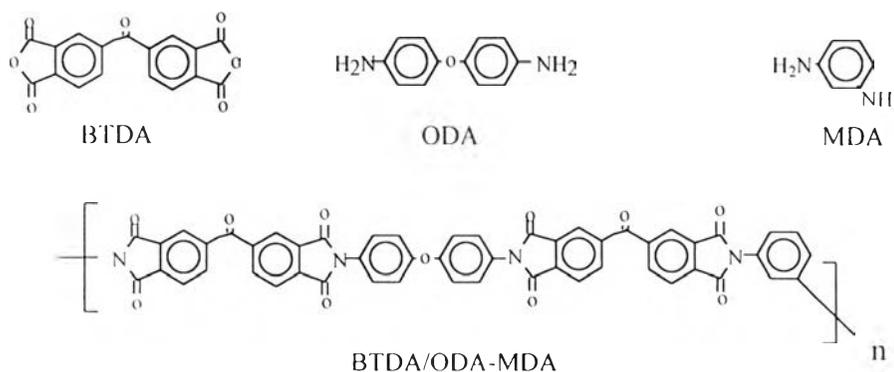


Figure 3.1 Chemical structure, some characteristics of poly(amic acid) precursors, and the resulting polyimide films.

Sodium-montmorillonite with cation exchange capacity of 119 meq/100 g was supplied by Kunimine Industrial Co.,Ltd., *Japan*. N-methyl-2-pyrrolidone (NMP) was purchased from Fluka. Dodecylamine and hydrochloric acid were supplied by Merck.

3.2 Methods

3.2.1 Preparation of Organophilic-Clay Filler

A mixture of 4.42 g of dodecylamine, 2.4 ml of concentrated hydrochloric acid and 250 ml of distilled-water was stirred at 80 °C for 1 hour, yielding a dodecylammonium chloride solution . The swelling solution of clay in water was prepared by dispersing 10 g of sodium-montmorillonite powder in 200 ml of distilled-water and stirred at 80 °C for 1 hour (see stoichiometric calculation of organophilic-clay in appendix I). The organophilic- clay was obtained by mixing a hot solution of dodecylammonium chloride with a hot solution of sodium-montmorillonite in water and stirred vigorously at 80 °C for 1 hour. A white precipitate was isolated by filtering, washing with 200 ml of boiled-water and stirred for 1 hour. This process was repeated twice to remove the unreacted dodecylamine from the mixture solution. The product was obtained after filtering and drying in vacuum-desiccator for 1 week. A diagram of preparation method is shown in Figure 3.2.

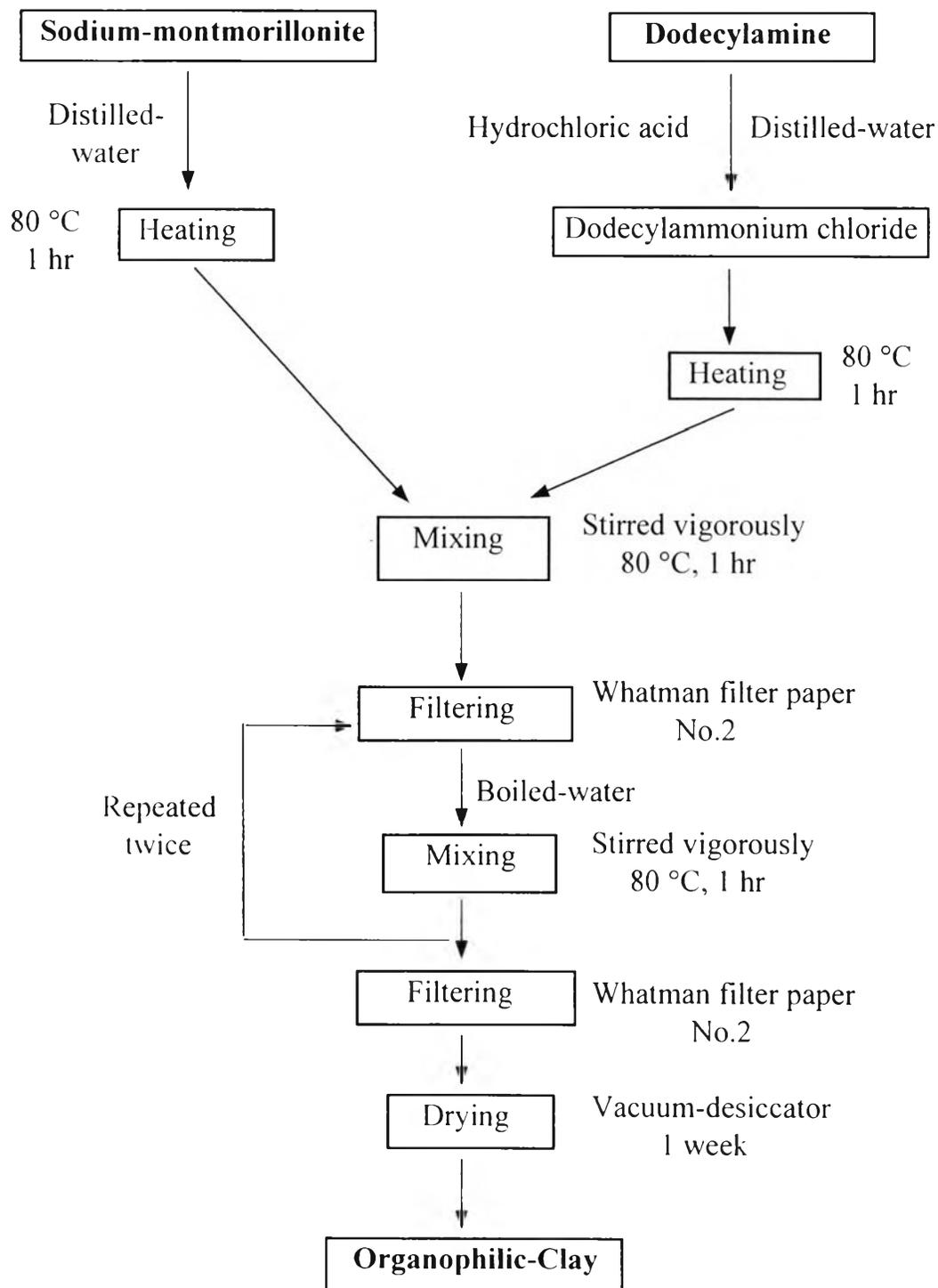


Figure 3.2 A diagram of preparation method of organophilic-clay filler.

3.2.2 Preparation of Polyimide-Clay Nanocomposites Thin Film

The Pyralin[®] BPDA-PDA poly(amic acid) solution (solid content = 10.5 % wt) was diluted with NMP solvent (ratio 1:1) for smooth surface film. The Pyralin[®] BTDA/ODA-MDA poly(amic acid) solution (solid content = 9.5 % wt) was used as received.

The stock solution of clay dispersed in NMP was prepared by mixing 0.70 g of organophilic-clay with 20 g of NMP solvent at 90 °C for 3 hours, yielding a 3.5 % weight of clay in NMP solvent.

The poly(amic acid) solution and various contents of clay dispersed in NMP solvent were mixed together in a glass container and stirred vigorously at 30 °C for 3 hours, yielding the variety of poly(amic acid)-clay mixture solution.

A puddle of ordinary poly(amic acid) or poly(amic acid)-clay solution was cast onto a glass substrate with the size of 2.5 x 8.0 cm² by hand-coating technique and using glass slide as a blade. The wet film was dried at 100 °C for 1 hour, at 200°C for 2 hours and finally imidized at 300 °C for 2 hours, respectively, in a nitrogen-atmosphere oven. Then, the film was cooled down to 30 °C, the poly(amic acid) precursor was again applied on the top of the polyimide layer, dried and re-cured to obtained the multi-layers of polyimide film with roughly 20-25 μm total thickness. Assuming the effect of thickness is negligible, so the short-range differ in thickness is considered to be no significant affect. A diagram of the preparation method is shown in Figure 3.3.

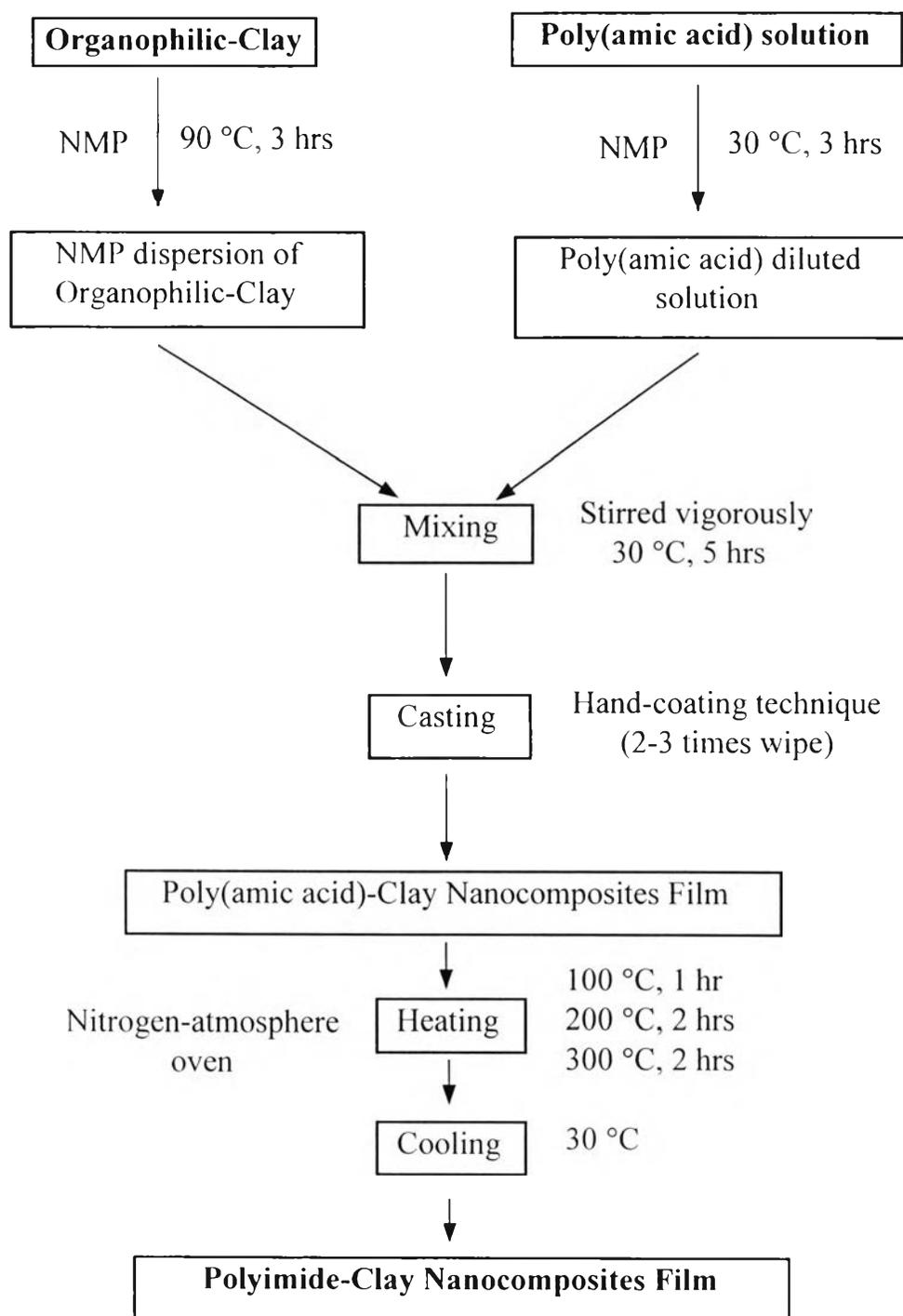


Figure 3.3 A diagram of preparation method of polyimide-clay nanocomposites thin film.

3.3 Characterization Techniques

3.3.1 Transmission Electron Microscopy (TEM)

Transmission Electron Microscope is a particular instrument used to provide information on the fine morphology and structure of polymeric materials. In addition, this technique can provide the pattern of Selected Area Electron Diffraction (SAED) which relates to orientation and atomic spacing of the material as suggested by Sawyer and Grubb (1996). The pattern is regularly used to identify crystal structure in a polycrystalline material.

In this experiment, a thin section of TEM specimen was prepared by cutting with a diamond knife of an LKB Bromma 2088 Ultratome[®] V. The knife in water trough was used for collecting a 100 nm thick slice of material and the sample was moved up and down with a small advance for each cut. The sections were picked up from the water surface on a copper supporting grid and stained with saturated vapor of 0.2 g of ruthenium chloride in 5 %wt of aqueous sodium hypochlorite for 1 hour to enhance the phase contrast of the images. The micrographs and SAED patterns were produced using a JEOL-200 CX Electron Microscope with an acceleration voltage of 100 kV. The magnification of all images was adjusted in the range of 1000 to 50,000 X.

3.3.2 Fourier-Transform Infrared Spectroscopy (FTIR)

In polymer composite applications, the infrared spectra are usually used to investigate the characteristic group frequencies of both mineral fillers and polymer-filler composites. In this experiment, characteristics of the organophilic-clay were obtained using a transmission mode of FTIR with KBr disc. The evidence of polyimide nanocomposites with various dodecylamine-clay contents were obtained using a specular reflectance mode of FTIR. All

specimens were prepared by solution-casting 2 times onto the aluminium substrate with roughly 20-25 μm total thickness.

The FTIR spectra of both transmission and specular reflectance mode were obtained using the Biorad FTS45A Fourier Transform Infrared Spectrophotometer with a resolution of 4 cm^{-1} , 16 numbers of scan per sample, and the angle of incidence IR beam in reflected mode was set at 45 degree.

3.3.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis technique was used to determine thermal stability of both ordinary polyimides and their clay nanocomposites. The dried films were scraped off from the substrate and cut to small pieces. Each thermogram was measured using the NETZSCH TG 209 Thermogravimetric Analyzer. The chamber inside the analyzer was exposed to a continuous flow of nitrogen as a protective gas at flow rate of 10 ml/min and a purge gas at flow rate of 20 ml/min. The specimen was heated up from 30 $^{\circ}\text{C}$ to 950 $^{\circ}\text{C}$ with a rate of 10 $^{\circ}\text{C}/\text{min}$, followed by cooling down to 30 $^{\circ}\text{C}$ with a rate of 10 $^{\circ}\text{C}/\text{min}$. The mass changes during temperature increase were monitored and recorded using the NETZSCH TG controller software.

3.3.4 Wide-Angle X-ray Scattering (WAXS)

The Wide-Angle X-ray Scattering is a technique commonly 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 pure clay minerals and the corresponding clay nanocomposite materials. For WAXS measurements, all specimens were prepared by solution-casting 4 times onto the glass substrate. Then, multi-layers of film were obtained with roughly a total thickness of 60 μm to ensure that the X-ray incident beam cannot

penetrate the film. The powder diffraction patterns of clay minerals and WAXS patterns of polyimide-clay nanocomposites were obtained from the Philips Analytical X-ray Diffractometer using $\text{CuK}\alpha$ radiation. A copper tube anode with a generator tension of 40 kV and a current of 30 mA were used.

3.4 Properties Measurements

3.4.1 Thermal Expansion Coefficient (CTE)

Thermal Expansion Coefficient (CTE) is a material property indicating dimensional stability of the protective material when temperature changes. The thermal mismatch between a coating material and a substrate can cause a development of thermally induced stresses which lead to unwanted structural bending, cracking, warping and delamination as reported by Jou et al. (1991) and Pottiger et al. (1994). The definition of CTE is given by

$$\alpha = 1/L_0(dL/dT) , \quad (3.1)$$

where α is thermal expansion coefficient, L_0 is initial length between grips, L is length, and T is temperature.

For CTE measurements, each film was cut into a rectangular shape consisting of 3 mm in width, 10 mm in length, and roughly 20-25 μm total thickness. The CTE of the film was measured using the Perkin-Elmer DMA-7e Dynamic Thermomechanical Analyzer with an extension quartz probe in the temperature scan mode. The dimensional changes during temperature increase were recorded using the Perkin-Elmer Thermal Analysis controller software. The specimen was annealed at first to 300 $^{\circ}\text{C}$ with a rate of 10 $^{\circ}\text{C}/\text{min}$ under a constant force of 30 mN in order to remove absorbed

water or any residual stresses and followed by cooling down with a rate of 5 °C/min to 30 °C and held for 1 hour. After annealing, the changes in length of a film were measured by heating up to 400 °C with a rate of 5 °C/min to obtain the CTE of material and then cooling down to room temperature again. Since the CTE was temperature dependent, the average value from 2 measurements was reported.

3.4.2 Thermal Cycling CTE

The thermal expansion coefficient of protective coating materials under several cycles of thermal operation was measured using the Perkin-Elmer DMA-7e Dynamic Thermomechanical Analyzer with an extension quartz probe in the temperature scan mode under a constant force of 30 mN. The dimensional changes during temperature increase were recorded using the Perkin-Elmer Thermal Analysis controller software. Each specimen was annealed to 300 °C at first, held for 10 minutes, followed by cooling down to 30 °C with a cooling rate of 5 °C/min. In the first cycle, the changes in length of the film was monitored by heating the film with a rate of 5 °C/min to 400 °C, held for 10 minutes and cooling down to 30 °C with a cooling rate of 5 °C/min. Similarly, the further cycles were done for a total of 10 cycles for each specimen. The dimension of each specimen in this experiment was performed as well as the conventional CTE experiment.

3.4.3 Ductile-Brittle Characteristics

The ductile-brittle characteristics of polymeric material can be investigated by comparing the stress-strain curve. Generally, the brittle materials usually have a high elastic modulus but a lower percent elongation at break. In contrast, the ductile materials usually have a low elastic modulus but a higher percent elongation at break.

In this experiment, specimens with roughly 40 μm in total thickness were kept in a desiccator at 25 ± 2 °C and 40 ± 5 % relative humidity for 96 hours prior to the test in order to remove absorbed water. The tensile experiment was performed using the CEAST testing machine model DY-30 in the extension mode. Each specimen was cut into a rectangular shape consisting of 1 cm in width and 12 cm in length. The testing temperature was set at 23 ± 2 °C. All tests were performed using a cross-head speed of 12.5 mm/min with a 100 N load cell.

3.4.4 Water Absorption

Water absorption in the protective coating material is generally important, since it can damage the electrical insulating performance, dimensional stability and mechanical properties of the material. The extent of water absorption in the films under excess condition was determined by measuring percent mass loss of the material between 80 and 150 °C. The polymer films were dried at 200 °C for 2 hours prior to the test in order to remove absorbed water. Then, the specimens were immersed in distilled water at 25 ± 3 °C for 48 hours. The content of water absorption in the films were measured using the NETZSCH TG209 Thermogravimetric Analyzer with a heating rate of 10 °C/min. The chamber inside the instrument was exposed to nitrogen as a protective gas at flow rate of 10 ml/min and as a purge gas at flow rate of 20 ml/min. The mass changes during temperature increase were monitored and recorded using the NETZSCH TG controller software.

3.4.5 Dielectric Strength

The dielectric strength measurement is one of many parameters useful for evaluation of the insulating performance of the protective coating material. In order to obtain more reliable results, all specimens were kept in

desiccator at a temperature of 25 ± 3 °C and 24 ± 5 % of relative humidity for 96 hours prior to the test in order to remove absorbed water. The short-time breakdown experiment was performed using the Yasuda Seiki electrical puncture tester with the electrode system as shown in Figure 3.4. The compressive force between the electrodes was approximate 500 g.

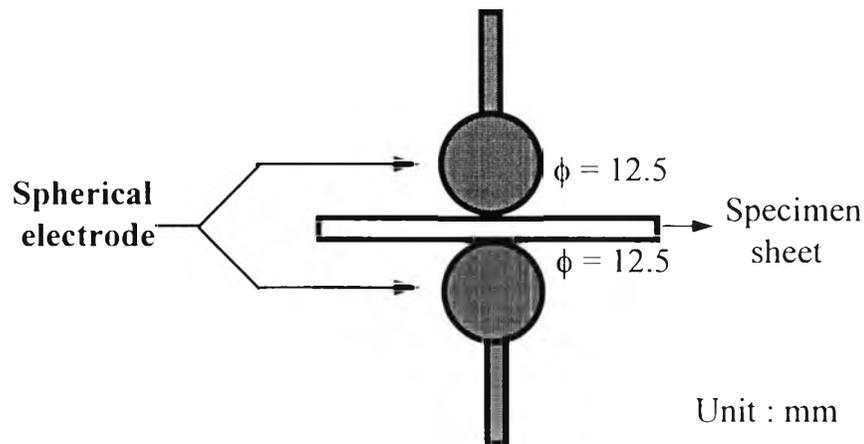


Figure 3.4 The electrode system for electrical puncture tester.

The testing temperature was set at 25 ± 3 °C, with a relative humidity of 75 ± 5 %. The 50 Hz of power frequency was applied to the specimens and the dial was adjusted to 0.5 on the current relay. The applied voltage was slowly raised from zero with a uniform rate until the breakdown occurred within 10 to 20 seconds.

3.5 Abbreviations

BPDA = 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl] propane dianhydride

PDA = *p*-phenylenediamine

BTDA = 3,3',4,4'-benzophenone tetracarboxylic dianhydride

ODA = 4,4'-oxydianiline

MDA = *m*-phenylenediamine

meq = milliequivalent