การสังเคราะห์และวิเคราะห์คุณลักษณะของพอลิอิไมด์/พอสนาโนคอมโพสิทโดยการสังเคราะห์เอมีนพอส

นางสาวอนัตตา อินโอสถ

SYNTHESIS AND CHARACTERIZATION OF POLYIMIDE/POSS NANOCOMPOSITE

VIA AMINE POSS

Miss Anatta Inosot

A Thesis Submitted in Partial Fulfillment of the Requirements

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Field of study   Chemical Engineering

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อนัตตา อินโอสถ: การสังเคราะห์และวิเคราะห์คุณลักษณะของพอลิอิไมด์/พอสนาโนคอม
โพสิทโดยการสังเคราะห์เอมีนพอส (SYNTHESIS AND CHARACTERIZATION OF
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ดร. มล. ศุภกนก ทองใหญ่, 73 หน้า

งานวิจัยนี้ มุ่งเน้นที่จะศึกษาถึง การสังเคราะห์และวิเคราะห์คุณลักษณะของพอลิอิไมด์/
พอสนาโนคอมโพสิทโดยการสังเคราะห์เอมีนพอส ซึ่งจุดประสงค์ของงานวิจัยนี้เพื่อปรับปรุง
คุณสมบัติด้านต่างๆ ของแผ่นฟิล์มพอลิอิไมด์ โดยเฉพาะค่าคงที่ไดอิเล็กทริค (k) ที่ต้องการให้มีค่าที่
ต่ำลง และมีคุณสมบัติทางกลที่สูงขึ้น เพื่อให้เหมาะสมต่อการนำไปประยุกต์ใช้งานด้าน
อิเล็กทรอนิก ดังนั้นในงานวิจัยนี้จึงเลือกใช้เอมีนพอส (OAPS) เพื่อปรับปรุงคุณสมบัติด้านต่างๆ
ของแผ่นฟิล์มพอลิอิไมด์ให้ดีขึ้น โดยทำการเปลี่ยนแปลงหมู่ของเอมีน(NH$_2$) ใน OAPS เป็น 4 10
และ 18 หมู่ นอกจากนี้ยังทำการเปลี่ยนแปลงปริมาณของการใส่ OAPS เป็น 50% 75% 100%
125% และ 150% จากน้ำหนัก OAPS 0.00588 กรัม โดยคำนวณปริมาณสารในการเตรียมพอลิอิไมด์
จากปริมาณสารสัมพันธ์ การไตเตรทหาจำนวนของหมู่เอมีนใน freshly OAPS ได้เท่ากับ 18 หมู่ ต่อ
OAPS 1 โมเลกุล ส่วนการลดหมู่เอมีนเป็น 4 และ 10 จะเตรียมจากการทำปฏิกิริยากาของ fresh
OAPS กับ Phthalic anhydride การพอลิอิไมด์/พอสนาโนคอมโพสิทถูกเตรียมโดยวิธี 2 step
polymerization จากการทดลองนี้สามารถตรวจสอบโครงสร้างของเอมีนพอส และพอลิอิไมด์/
พอสนาโนคอมโพสิทได้จาก FTIR ส่วนค่าคงที่ไดอิเล็กทริคและความหนาแน่นของคอมโพสิทมี
ค่าลดลง เมื่อเพิ่มปริมาณพอสและลดหมู่ของเอมีนลง จากผลการทดลองพบว่าปริมาณ OAPS ที่
เหมาะสมที่สุดในการสังเคราะห์แผ่นฟิล์มคือที่ 100% ซึ่งมีค่าคงที่ไดอิเล็กทริคเป็น 2.83 3.09 และ
3.19 ที่หมู่เอมีนต่อ OAPS 1 โมเลกุลเป็น 4 10 และ 18 ตามลำดับ นอกจากนี้พอลิอิไมด์/พอสที่เติม
OAPS 100% ยังแสดงคุณสมบัติทางความร้อนและทางกลที่ดี จากการวิเคราะห์ด้วย TGA พบว่ามี
อุณหภูมิการสลายตัว (T$_{d,5\%}$) อยู่ระหว่าง 449-460 องศาเซลเซียส และ tensile strength ของฟิล์มอยู่
ในช่วง 72.1-94.4 เมกะปาสคาล

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่ออาจารย์ที่ปรึกษา	
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KEY WORD: POLYIMDE, POLYIMIDE/POSS, LOW DIELECTRIC CONSTANT OCTA(AMINOPHENYL)SILSESQUIOXANE

      ANATTA INOSOT: SYSNTHESIS AND CHARACTERIZATION OF POLYIMIDE/POSS NANOCOMPOSITE VIA AMINE POSS. THESIS ADVISOR: ASSOC. PROF. ML. SUPAKANOK THONGYAI, Ph.D., 73 pp.

      The ease of processing, the high mechanical and the low dielectric properties were required for the polyimide composite. In this research, the properties of the synthesized polyimide with various amount of OAPS (Octa(Amino Phenyl) Silsesquioxane) that have well defined amine functional group were investigated. The OAPS having 4, 10 and 18 amine group with various amount of loading OAPS (50%, 75%, 100%, 125% and 150% of 0.00588 g OAPS) were added to the stoichiometric balance polyimides. The titration amount of amine in the fresh OAPS was 18 groups per OAPS and the amine groups of 10 and 4 were prepared by reactions of fresh OAPS with controlled amount of Phthalic anhydride. The PI/OAPS nanocomposites were prepared by two step method and the cooperation was confirmed by FTIR. The dielectric constants and densities of the nanocoposites were decreased as OAPS loading increase and as the amine groups per one OAPS decreased. It can be see that the best OAPS loading for the synthesized PI/OAPS films were at 100% and the dielectric constant of the films are 2.83, 3.09 and 3.19 with 4,10 and 18 amine groups per OAPS respectively. The PI/OAPS films at 100% OAPS loading showed the optimum thermal and mechanical properties. The thermal degradation temperatures ($T_{d,5\%}$) of the films were between 449- 460 ℃ and the tensile strengths of the films were in the range of 72.1-94.4 MPa.

Department   Chemical Engineering   Student's signature ....

Field of study   Chemical Engineering   Advisor's signature ....

Academic Year .... 2006 ....

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CHAPTER I

INTRODUCTION

Polyimides are a very interesting group of incredibly strong and astoundingly heat and chemical resistant polymers. Their strength and heat and chemical resistance are so great that these materials often replace glass and metals, such as steel, in many demanding industrial applications. Polyimides are even used in many everyday applications. Who knows, you may even have a few in your house. They are used for the struts and chassis in some cars as well as some parts under-the-hood because they can withstand the intense heat and corrosive lubricants, fuels, and coolants that cars required. Do you have polyimides in your kitchen? They are also used in the construction of many appliances as well as microwave cookware and food packaging because of their thermal stability, resistance to oils, greases, and fats, and their transparency to microwave radiation.

Polyimides have found applications in a host of technologies as inter-metal dielectric, high-temperature adhesive, photoresist, nonlinear optical material, membrane, and Langmuir-Blodgett (L-B) film. The applications of polyimides range from aerospace to microelectronics to optoelectronics to composites to fiber optics [1].

Polyimides (PIs) are widely used in microelectronic industries because of their outstanding characteristics, such as excellent tensile strength and modulus, good thermal stability and dielectric property, and good resistance to organic solvents [2–7]. With the miniaturization of IC, applications such as circuit-printing films and semiconductor coatings however require the PIs to possess lower coefficient of thermal expansion (CTE), higher glass transition temperature and better thermal mechanical strength to avoid debonding between PIs and inorganic substrate and flaws in the PI interlayer. Incorporation of inorganic materials such as ceramics, silsesquioxane, and silica nanoparticles has been proved very effective in providing enhancements in thermal mechanical property of PIs [8].

Polyhedral oligomeric silsesquioxanes (POSS) combining unique inorganic-organic chemical compositions with nano-sized cage structures have long been important and interesting class of materials. The incorporation of POSS cages into polymeric materials often results in reinforced improvements in polymer nanocomposites properties such as increases in use temperature and oxidation resistance, in improved mechanical properties, as well as reductions in flammability and heat evolution. Such exceptional material properties make POSS nanocomposites a likely involvement in many applications [9].

In this research, reported synthesis and characterization novel polyimide nanocomposites by introducing the nanoporous functional POSS into polyimide matrices. Both dielectric properties and thermomechanical properties of the novel polyimides were significantly improved. Introducing POSS to improve dielectric properties of the polyimide, the networks based on the covalent bonds between POSS and polyimide improved thermomechanical properties of the polyimide.

1.1 The Objective of This Thesis

To synthesize novel polyimides nanocomposite with families of POSS amine and to improve thermomechanical and dielectric constant properties of the nanocomposites.

1.2 The Scope of This Thesis

1.2.1   To synthesize octa(aminophenyl)silsesquioxane (OAPS).

1.2.2   To vary the number of functional group of amine group in OAPS by reaction with phathalic anhydride.

1.2.3   To synthesize and characterize polyimide nanocomposite with families of POSS amine.

CHAPTER II
THEORY

The basic theories concerned in this work were mentioned such as polyimide, synthetic method, thermal curing and POSS.

2.1 Polyimide

Polyimides are high temperature engineering polymers originally developed by the DuPont Company. When compared to most other organic or polymeric materials, polyimides exhibit an exceptional combination of thermal stability (>500°C), mechanical toughness and chemical resistance. In addition, they have excellent dielectric properties. Because of their high degree of ductility and inherently low CTE, polyimides can be readily implemented into a variety of microelectronic applications. Multilayer thin and thick film applications on large silicon or ceramic substrates can be readily achieved

There are two general types of polyimides. The first type, so called linear polyimides, is made by combining imides bonds into long chains (Figure 2.1(a)). Aromatic heterocyclic polyimides is the another type (Figure 2.1(b)), where R′ and R″ are two carbon atoms of an aromatic ring.

(a)   (b)
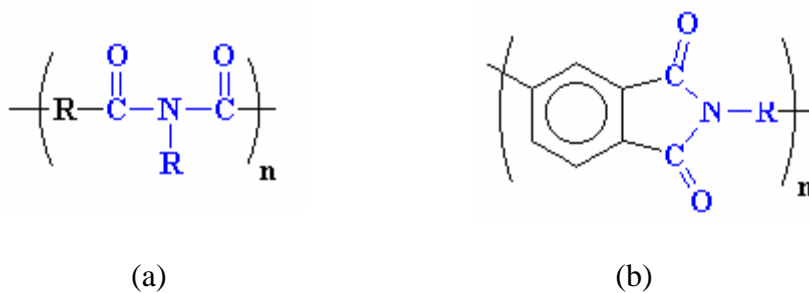
Figure 2.1 a)linear polyimde b) Aromatic heterocyclic polyimides [1].

Aromatic heterocyclic polyimides are typical of most commercial polyimides, such as G.E.'s Ultem and DuPont's Kapton. Therefore these polyimides will be explained in details. These polymers have such incredible mechanical and thermal

properties that they are used in place of metals and glass in many high performance applications in the electronics, automotive, and even the aerospace industries. These properties come from strong intermolecular forces between the polyimide chains.

2.2 Synthetic Methods

2.2.1 Two-step method via poly(amic acids)

The majorities of polyimides possess extended rigid planar aromatic and heteroaromatic structures and are infusible and insoluble. The earlier pioneers at Dupont Co. coped with this common problems of intractability generally associated with high-temperature polymers by synthesizing the soluble polymer precursor, namely "poly(amic acid)" and converting it to the final polyimide [10]. Figure 2.2 presents an example of the synthesis of Kapton polyimide. This highly elegant process made it possible to bring the first significant commercial polyimide products into the market namely Du Pont's Kapton[TM] and it is still the method of choice in majority of applications.
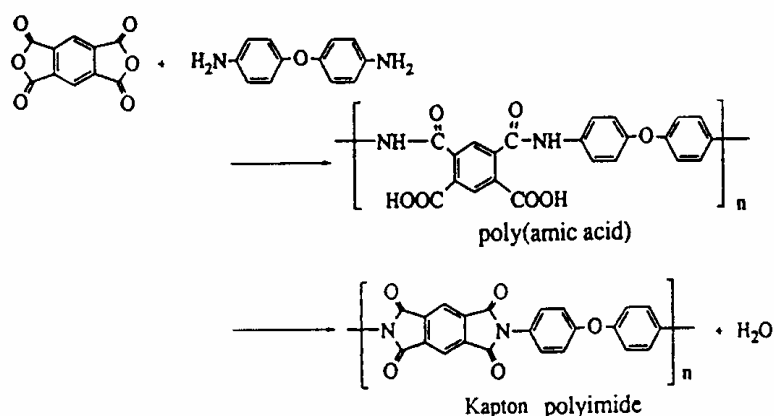
Figure 2.2 Preparation of Kapton polyimide [1].

The two-step poly(amic acid) process is the most commonly practiced procedure of making polyimides. In this process, a dianhydride and a diamine react at ambient temperature in a dipolar aprotic solvent such as N-methyl- 2-pyrrolidinone (NMP) or N,Ndimethylacetamide (DMAc) to form a poly(amic acid), which is then cyclized into the polyimide product. The reaction of 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) and 4,4'-diaminodiphdiphenylether (ODA) proceed rapidly at

room temperature to form a viscous solution of poly(amic acid), which is an ortho-carboxylated aromatic polyamide.

Poly(amic acid)s are shaped into articles such as films and fibers by removal of solvent. The shaped poly(amic acid) films, for example, are thermally or chemically converted to the final polyimide products. The conversion produces water as a by-product. Because water must be removed during this in-situ imidization, the process is generally suitable only for the preparation of thin object such as films. The arrows in poly(amic acid) structure denote isomerism (Figure 2.3), indicating that the main chain is composed of mixture of 1,3 and 1,4-phenylenebisamide linkages.

2.2.1.1 Formation of poly(amic acid)

When a diamine and a dianhydride are added into a dipolar aprotic solvent such as N,N-dimethylacetamide, poly(amic acid) is rapidly formed at ambient temperatures. The reaction mechanism involves the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group, followed by the opening of the anhydride ring to form amic acid group as illustrated in Figure 2.3

The most important aspect of this process is that it is an equilibrium reaction [11-17]. Often it appears to be an irreversible reaction because a high-molecular-weight poly (amic acid) is readily formed in most cases as long as pure reagents are used. This is because the forward reaction is much faster than the reverse reaction, often by several orders of magnitude. If the large reaction rate difference is not met, the high-molecular-weight poly(amic acid) is not formed. Therefore, it is important to examine the driving forces that favor the forward reaction over the reverse reaction. It should also be noted that the acylation reaction of amines is an exothermic reaction and that the equilibrium is favored at lower temperatures. The forward reaction in dipolar solvents is a second-order-reaction and the reverse reaction is a first-order reaction. Therefore, the equilibrium is favored at high monomer concentrations to form higher molecular-weight poly (amic acids).
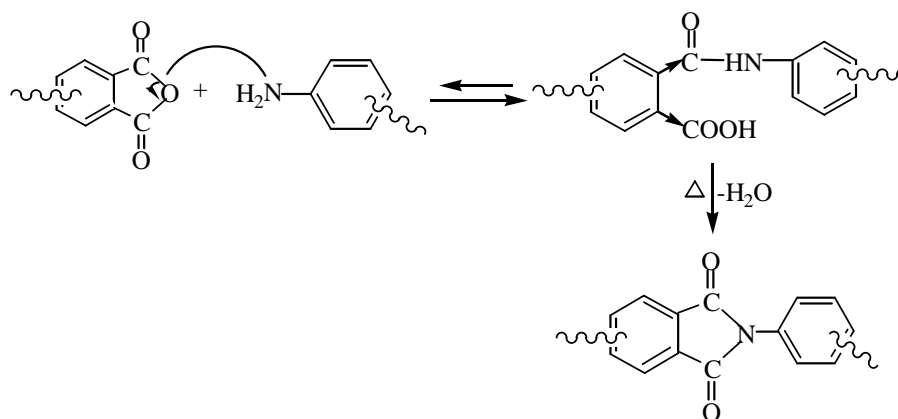
Figure 2.3 Reaction mechanism of imide formation [1].

2.2.1.2   Thermal Imidization of Poly (amic acid)

Conversion of poly(amic acid)s to the corresponding polyimides is most commonly performed thermally in "solid state". This method is suitable for preparation of thin objects such as films, coatings, fibers, and powders in order to allow the diffusion of by-product and solvent without forming brittles and voids in the final polyimide products. The cast films are dried and heated gradually up to 250-350°C, depending upon the stability and glass transition temperature (T_g) of the polymer. Too rapid a heating may cause the formation of bubbles in the sample. When a DMAc solution of poly(amic acid) is cast and "dried" at ambient temperature to a nontacky state, the resulting film still contains a substantial amount of the solvent (typically up to 25% by weight, depending on the drying conditions). In the subsequent heating, imidization reaction takes place not in a true solid state but rather in a very concentrated viscous solution, at least during the initial and the intermediate stages of thermal imidization. The presence of residual solvent plays an important role in the film forming behaviars. The imidization proceeds with faster rate in the presence of dipolar amide solvents. The observation is attributed to the specific solvation to allow the favorable conformation of amic acid group to cyclize [18]. It may also be explained by the plasticizing effect of the solvent to increase the mobility of the reacting functional groups. The favorable property of amide solvent also suggests that its basicity to accept protons may be responsible for the specific effect. The proton of the carboxylic group is strongly hydrogen-bonded to the carbonyl group of the amide solvent. The cyclization of o-carboxyaminde group results in dehydrogen bonding and release of the solvent molecule along with water of condensation. The

thermal imidization process of poly(amic acid)s is complex. It is normally unlikely to describe the thermal imidization reaction by simple kinetic expression as the process typically involves several interrelated elementary reactions.

2.2.1.3   Mechanism of Chemical Imidization

The kinetic study of model compounds revealed that isoimides and imides are formed via a mixed-anhydride intermediate (7), which is formed by acylation of the carboxylic group of amic acid (6), as illustrated in Figure 2.4
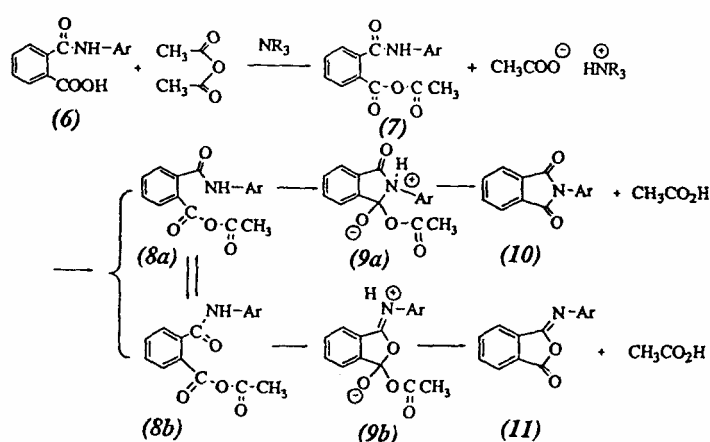
Figure 2.4 Mechanism involved in chemical dehydration of amic acid (R, ethyl; Ar; phenyl) [1].

The presence of the intermediate mixed-anhydnide was detected by IR as well as proton nuclear magnetic resonance (NMR). Convincing evidence was also presented when di- functional acid chloride such as sebacoyl chloride was used instead of acetyl chloride for cyclization of poly(amic acid). The solution viscosity temporarily increased during the reaction because of the interchain mixed-anhydnide formation. The viscosity gradually decreased back to the normal level as the cyclization proceeded. Imides are formed by intramolecular nucleophilic substitution at the anhydride carbonyl by the amide nitrogen atom *(8a-9a)*, while isoimides are formed as a result of substitution by the amide oxygen *(8b-9b)*. The cyclization of N-phenylphthalamic acids with acetic anhydride proceeds smoothly at room temperature in DMAc in the presence of a tertiary amine. The amine acts as a catalyst as well as an acid acceptor. Use of a less than stoichiometric amount of amine still leads to

completion of the reaction, only at a slower rate. Use of triethylarnine (pk$_a$ 10.6) as a catalyst produced exclusively normal imides. However, a mixture of imide and isoimide was formed when less basic pyridine (pk$_a$ 5.2) was used as a catalyst [19].

2.3 Thermal Curing in Polyimide Films and Coatings

2.3.1. Process for Making Films and Coatings

The synthesis of aromatic polyimides from dianhydrides and diamines can be carried out in either a one-step or two-step method. In the classic (two-step) method, a tetracarboxylic dianhydride (or functional derivative) is added to a solution of a diamine in a polar apotic solvent, such as N-methylpyrrolidone (NMP), at 15-75°C to form a soluble poly(amic acid). The poly(amic acid) is cyclodehydrated (imidized) to the corresponding insoluble polyimide by either heating at temperatures in excess of 300°C (thermal imidization) or through the addition of chemical dehydrating agents (chemical imidization) as shown in Figure 2.5 Since the polyimide is insoluble, films or coatings are generally prepared from the poly(amic acid). Polyimides that are soluble in organic solvents can be prepared using a one-step method in which the dianhydride and diamine are stirred at 180-220°C in a high-boiling-point organic solvent [20]. The synthesis of the poly(amic acid) precursor and its imidization to the polyimide occur spontaneously. Low-molecular-weight soluble polyimide oligomers terminated by reactive end groups can also be prepared. These "addition" polyimides are then polymerized in situ by heating. This discussion will focus only on polyimides prepared using the two-step method using a thermal (as opposed to chemical) imidization process.
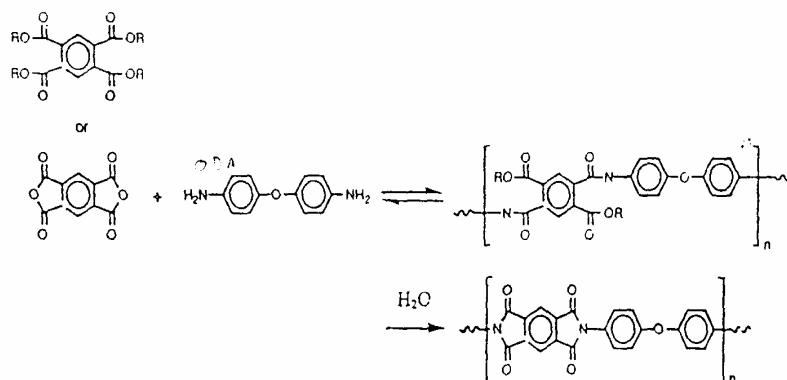
Figure 2.5 General two-step imidizatmon reaction scheme [1].

A tetracarboxylic dianhydride (or functional derivative) is added to a solution of a diamine in a polar aprotic solvent, such as N-methylpyrrolidone (NMP), to form a soluble poly(amic acid). The poly(amic acid) is cyclodehydrated to the corresponding insoluble polyimide by either heating at temperatures in excess of 300°C, or through the addition of chemical dehydrating agents.

The six steps in the preparation of coatings by thermal cure are :
1. Substrate preparation
2. Application of the adhesion promoter
3. Deposition of the precursor solution onto the substrate
4. Drying the coating to remove solvent and allow the substrate to be handled
5. Patterning the coating
6. Curing the coating to remove any remaining solvents and to complete the conversion of the precursor to the polyimide

2.3.1.1   Substrate Preparation.

Proper substrate preparation is necessary for defect-free coatings and for good interfacial adhesion between the coating and the substrate. Any contaminants (organic or inorganic) or particles on the surface of the substrate will be trapped by the coating. Therefore, substrates should be thoroughly cleaned and completely dried prior to use. A dehydration bake at 200°C or higher may be necessary to remove adsorbed moisture.

2.3.1.2   Adhesion Promoters.

The role of the adhesion promoter is to prime the surface to promote good interfacial adhesion by acting as a coupling agent between the polyimide precursor and the substrate. The adhesion promoter is either incorporated into the precursor solution (i.e. a "built-in" adhesion promoter) or added as a separate processing step. "Built-in" adhesion promoters generally fall into one of two categories: coupling agents that are mixed into the precursor solution, or silicon-containing moieties that are part of the polymer backbone. Adhesion promoters should not be used if the coating is to be removed from the substrate after cure to obtain a free-standing film. To investigate the effect of the adhesion promoters on either the curing process or the properties of cured films or coatings, a substrate, such as aluminum, that can be

removed from the cured coating without damaging or altering the morphology of the coating, must be used.

2.3.1.3. *Solution Deposition.*

- *Spin Coating.* Spin coating is the most widely used technique for depositing polyimide precursor solutions onto silicon wafers. The spin coating process consists of dispensing a predetermined amount of the precursor solution onto the substrate held on a vacuum chuck, accelerating to a desired spin speed, and then spinning at a constant spin speed for a set period of time. The precursor solution can be applied to the substrate by either flooding the surface of the substrate with solution prior to spinning (static or puddle dispense) or by slowly rotating the substrate while depositing a small quantity of the solution into the center of the substrate (dynamic dispense). Most of the original solution dispensed onto the substrate is spun off during the process. The solution remaining on the substrate is dried through solvent evaporation.

- *Applicator Blade Coating (Casting).* A technique often used to prepare samples in the laboratory is applicator blade coating (see ASTM D 823 [21]). A uniform coat is produced by an applicator blade pushed across the substrate at a constant speed either by hand or by a motor-driven device. The blade applicator can have either fixed or adjustable clearances. The parameters that control the thickness, uniformity, and morphology of the coating include the solvent composition, polymer composition, molecular weight, solution concentration (viscosity), applicator blade clearance, and the environmental conditions. For a given precursor system with constant composition, molecular weight, and concentration, the coating thickness depends only on the clearance of the applicator blade. A motor-driven blade applicator is preferred over hand-held draw-down applicators for the preparation of coatings of uniform thickness.

2.3.1.4. *Drying.*

The next step in the process is the drying step, also referred to as the soft-bake, prebake or B-stage step. The objectives of the drying step are to remove residual solvents from the coating so that the substrate can be handled during subsequent processing without altering the coating, and to increase adhesion of the coating to the substrate. Excess solvent in the coating can adversely affect both the exposure and

subsequent developing steps in the patterning process. Overdrying can also lead to problems in patterning the coating and may result in cracking and/or delamination. For conventional (nonphotosensitive) polyimides, the drying step must provide sufficient chemical resistance and adhesion so that the coating will not be attacked by the deposition of the photoresist. For photosensitive polyimides, the surface of the coating must be tack free so that the coating will not stick to the exposure mask in contact mode. In addition, since the development of the photosensitive coating is a function of the solubility difference between the exposed and unexposed regions, the correct solvent level must be maintained in the coating.

The parameters that must be considered to ensure correct drying include the solvent composition, vapor pressure and boiling point ; the polymer composition and molecular weight; the solution concentration (viscosity); the glass transition temperature of the polymer/solvent mixture (i.e., the point at which the gel can sustain a load); the temperature at which the precursor begins to imidize; the thermal stability of the components of the precursor system; the time, temperature, and drying rate; and the environmental conditions (e.g., relative humidity, exhaust flow rate, etc.). For a given precursor system with constant molecular weight and composition, the variables that control the drying process are time, temperature, and the drying rate.

2.3.1.5 Curing.

The last step in the coating process is the cure, also referred to as the postbake. The cure conditions play a critical role in controlling the morphology of the cured coating, which in turn dictates the final properties. The objectives of the cure step are the removal of any residual solvents and to complete the conversion of the precursor into the polyimide, and, in the case of photosensitive polyimides, to complete the removal of the photoinitiator system. An excellent discussion of the mechanism and kinetics of thermal cure is provided by Harris [22].

The parameters that must be controlled to ensure proper curing of the polyimide include the polymer composition and molecular weight; the glass transition temperature of the polyimide; the temperature at which the precursor begins to imidize; the thermal stability of the polyimide; the time, temperature, and heating rate; and the environmental conditions (e.g., atmosphere, relative humidity, exhaust flow rate, etc.).

2.3.1.6   Film Preparation.

As mentioned earlier, films can be prepared by remove the coatings from the substrate anytime after the drying, patterning, or curing steps. An effective technique for preparing films by spin coating is to deposit the precursor solution without any adhesion promoter onto a silicon wafer, containing 100-150 nm thermally grown oxide layer. After cure, the coatings can be removed from the wafers by cutting around the edge of the wafer with a sharp blade and then dissolving the oxide in dilute (6:1) aqueous hydrofluoric acid (HF) for 15 min or less, allowing the films to float off the substrate. Experience has shown that the properties of the film are not altered if the coating remains in the HF bath for 15 min or less.

2.4   Polyhedral oligomeric silsesquioxanes (POSS)

In an attempt to meet the US Air Force's demand for a new generation of lighter weight, higher performance polymeric materials, the US Air Force Office of Scientific Research and the US Airforce Research Laboratory have, for the past decade, pursued the development of new chemical feedstock technologies based on Polyhedral Oligomeric Silsesquioxanes (POSS).

(a)   (b)
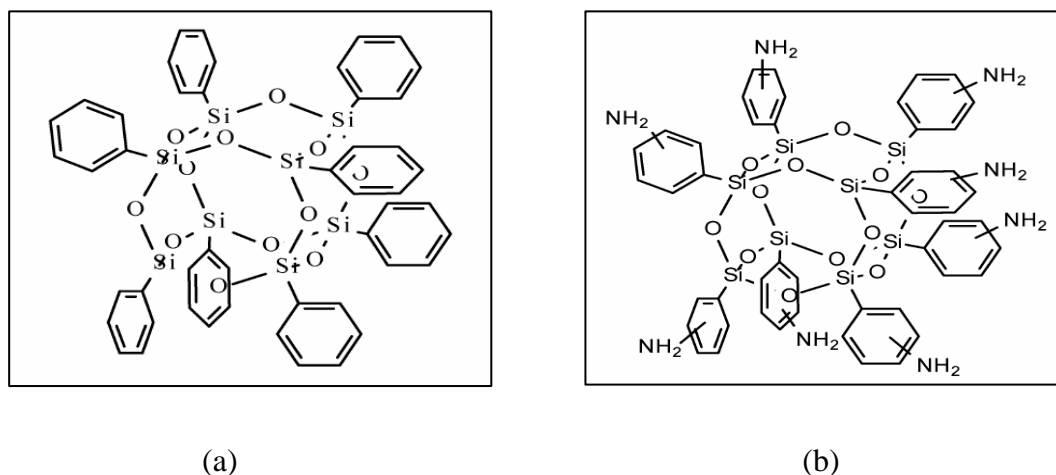
Figure 2.6 Structure of POSS (a) Octa(phenyl)silsesquioxane (OPS)   (b) Octa
(aminophenyl)silsesquioxane (OAPS or POSS amine) [30].

Within six years this investment has paid off with the development and large-scale production of the first new polymer feedstocks in the past forty years. POSS technology is also the only hybrid and nanostructured chemical feedstock technology

developed to date. Because of its chemical nature, POSS technology is easily incorporated into common plastics via copolymerization or blending and hence requires little or no alteration to existing manufacturing processes. POSS additives radically upgrade the thermal and physical properties of most plastics.

Combining unique inorganic-organic chemical compositions with nano-sized cage structures have long been important and interesting class of materials. Cages like hybrid molecules of silicon and oxygen with similarities to both silica and silicone. The incorporation of POSS cages into polymeric materials often results in reinforced improvements in polymer nanocomposites properties such as increases in use temperature and oxidation resistance, in improved mechanical properties, as well as reductions in flammability and heat evolution. Such exceptional material properties make POSS nanocomposites a likely involvement in many applications. This work therefore focuses on the novel properties of POSS nanocomposites *i.e.* mechanical, thermal stability and fire retardant, viscoelastic and dielectric properties in a broader perspective.

2.4.1. Properties Enchancements with POSS

Polymer nanocomposites are polymers filled with particles having at least one dimension in the nanometer range and have attracted tremendous attention from researchers in the field of polymer science during the recent years. Compared to neat polymers, nanocomposites can exhibit substantially improved:

- Increased T_{dec}
- Increased T_g
- Reduced Flammability
- Reduced Heat Evolution
- Lower Density
- Disposal as Silica
- Extended Temperature Range
- Increased Oxygen Permeability
- Lower Thermal Conductivity
- Thermoplastic or Curable

- Enhanced Blend Miscibility

- Oxidation Resistance

- Altered Mechanicals

- Reduced Viscosity

.

2.4.2 POSS Technology

POSS Technology is derived from a continually evolving class of compounds closely related to silicones through both composition and a shared system of nomenclature. POSS chemical technology has two unique features (1) the chemical composition is a hybrid, intermediate ($RSiO_{1.5}$) between that of silica (SiO_2) and silicone (R_2SiO). (2) POSS molecules are physically large with respect to polymer dimensions and nearly equivalent in size to most polymer segments and coils.
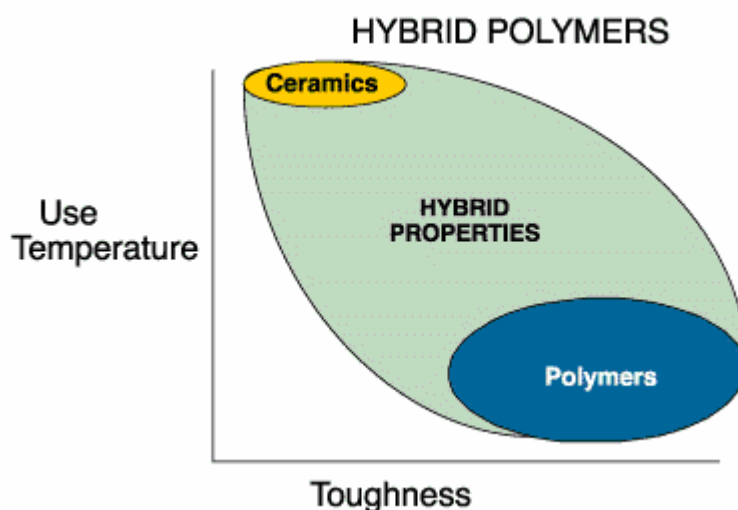
Figure 2.7 Polymer with oxidation resistance, toughness and processability.

2.4.3 POSS Polymer Systems

POSS molecules can be thought of as the smallest particles of silica possible. However unlike silica or modified clays, each POSS molecule contains covalently bonded reactive functionalities suitable for polymerization or grafting POSS monomers to polymer chains. Each POSS molecule contains nonreactive organic functionalities for solubility and compatibility of the POSS segments with the various polymer systems.
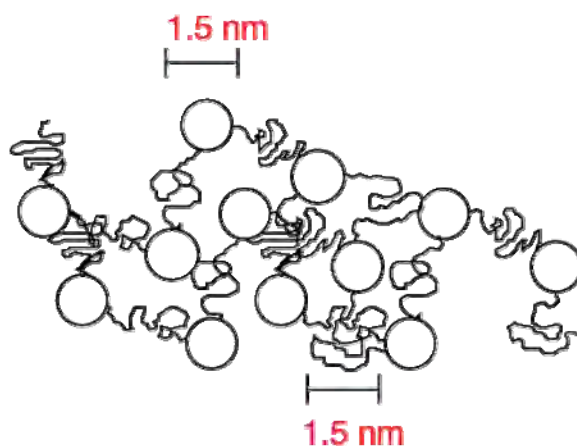
Figure 2.8 Grafting of POSS monomer to polymer chains.
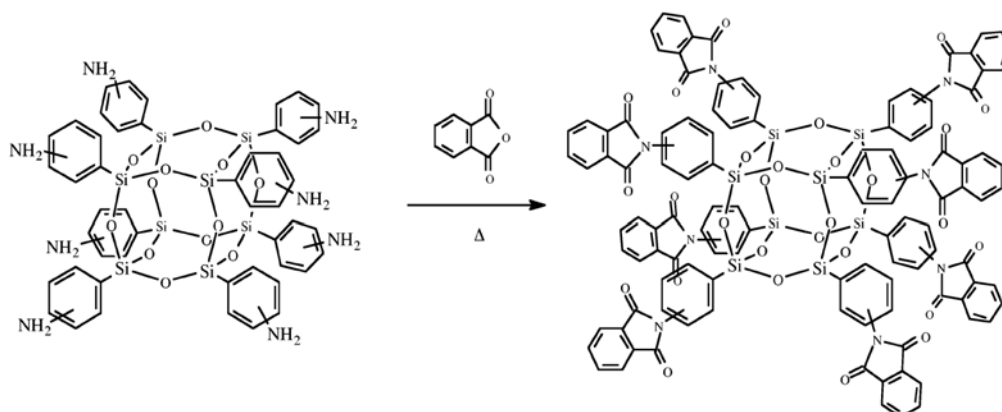
Figure 2.9 Reaction of OAPS with Phthalic anhydride.

The chemical diversity of POSS technology is very broad and a large number of POSS monomers and polymers are currently available or undergoing development. POSS chemical technology is easy to use with monomers available in both liquid and solid form and they are soluble in most common solvents. Hence, POSS technology can be used in the same manner as common organics, in either monomer or polymeric (resin) form. POSS chemical feedstocks can be added to nearly all polymer types (glassy, elastomeric, rubbery, semicrystalline and crystalline) and compositions.

2.5 Determine quantitative of amine group [37]

Titration is a laboratory technique by which we can determine the concentration of an unknown reagent using a standard concentration of another reagent that chemically reacts with the unknown. This standard solution is referred to as the "titrant". We have to have some way to determine when the reaction is complete that we are using. This is referred to as the "end point" or more technically the equivalence point. At that point all the unknown has been reacted with the standard titrant and some kind of chemical indicator must let us know when that point has been arrived at.

At the equivalence point:

Number of equivalent weights of titrant = Number of equivalent weights of unknown

or

(Normality of the titrant)(Volume of titrant required to reach end point) = (Normality of unknown) (Volume of unknown)

Generally we know the Normality of the titrant since it is a standard solution. We also pre-measure the volume of the unknown. We then titrate with the standard from a buret into the container with the measured unknown and the chemical indicator until the indicator either turns color or a precipitate indicates that the end point or the equivalence point has been reached. Having the initial and final readings of the titrant buret gives us the volume of the titrant used. The only unknown in the above equation is the Normality of the unknown.

2.5.1   Titrations in non-aqueous solvents

The Bronsted-Lowry theory of acids and bases can be applied equally well to reactions occurring during acid-base titrations in non-aqueous Solvents. This is because their approach considers an acid as any substance which will tend to donate a proton, and a base as any substance which will accept a proton. Substances which give poor end points due to being weak acids or bases in aqueous solution will frequently give far more satisfactory end points when titrations are carried out in non-

aqueous media. An additional advantage is that many substances which are insoluble in water are sufficiently soluble in organic solvents to permit their titration in these non-aqueous media.

In the Bronsted-Lowry theory, any acid (HB) is considered to dissociate in solution to give a proton (H$^+$) and a conjugate base (B$^-$); whereas any base (B) will combine with a proton to produce a conjugate acid (HB$^+$):

$$HB \rightleftharpoons H^+ + B^-$$
$$B + H^+ \rightleftharpoons HB^+$$
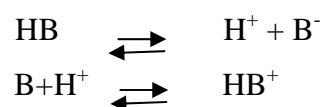
2.5.2   Solvent for non-aqueous solvents

A very large number of inorganic and organic solvents have been used for non-aqueous determinations, but a few have been used more frequently than most. Some of the most widely applied solvent systems are discussed below. In all instances pure, dry analytical reagent quality solvents should be used to assist in obtaining sharp end points.

Glacial ethanoic acid: Glacial ethanoic acid is by far the most frequently used non aqueous solvent. Before it is used it is advisable to check the water content, which may be between 0.1% and 1.0%. and to add just sufficient ethanoic (acetic) anhydride to convert any water to the acid. The acid may be used by itself or in conjunction with other solvents, e.g. ethanoic anhydride, acetonitrile and nitromethane.

Acetonitrile: Acetonitrile (methyl cyanide, cyanomethane) is frequently used with other solvents such as chloroform and phenol, and especially with ethanoic acid. It enables very sharp end points to be obtained in the titration of metal ethanoates when titrated with perchloric acid.

Alcohols: Salts of organic acids, especially of soaps, are best determined in mixtures of glycols and alcohols or mixtures of glycols and hydrocarbons. The most common combinations are ethylene glycol (dihydroxyethane) with propan-2-ol or

butan-l-ol. The combinations provide admirable solvent power for both the polar and non-polar ends of the molecule.

Dioxan: Dioxan is another popular solvent which is often used in place of glacial ethanoic acid when mixtures of substances are to be quantified. Unlike ethanoic acid, dioxan is not a levelling solvent and separate end points are normally possible, corresponding to the individual components in the mixtures.

Dimethylformamide: Dimethylformamide (DMF) is a protophilic solvent which is frequently employed for titrations between, for instance, benzoic acid and amides, although end points may sometimes be difficult to obtain.

2.5.3   Indicators for non-aqueous solvents

The interconversion relationships between ionised and unionised indicator, or the different resonant forms, apply equally well to indicators used for non-aqueous titrations. But their colour changes at the end point vary from titration to titration, as they depend on the nature of the titrand. The colour corresponding to the correct end point may be established by carrying out a potentiometric titration while simultaneously observing the colour change of the indicator. The appropriate colour corresponds to the inflexion point of the titration curve. The majority of non-aqueous titrations are carried out using a fairly limited range of indicators. Here are some typical examples.

Crystal violet: Used as a 0.5% w/v solution in glacial ethanoic acid. Its colour change is from violet through blue, followed by green, then to greenish yellow, in reactions in which bases such as pyridine are titrated with perchloric acid.

Methyl red: Used as a 0.2% w/v solution in dioxan with a yellow to red colour change

1-Naphthol benzein: Gives a yellow to green colour change when employed as a 0.2% w/v solution in ethanoic acid. It gives sharp end points in nitromethane containing ethanoic anhydride for titrations of weak bases against perchloric acid

Quinaldine red: Used as an indicator for drug determinations in dimethylformamide solution. A 0.1% w/v solution in ethanol gives a colour change from purple red to pale green.

Thymol blue: Used extensively as an indicator for titrations of substances acting as acids in dimethylformamide solution. A 0.2% w/v solution in methanol gives a sharp colour change from yellow to blue at the end point.

2.5.4   Amine using a non-aqueous titration

Conventional acid-base titrations are seldom suitable for determining weak bases, but various non-aqueous titrations have proven admirable. If a weak base is to be determined, use an acid as strong as possible in a non-basic solvent. Perchloric acid dissolved in either glacial ethanoic (acetic) acid or dioxan are suitable for this purpose, though the glacial ethanoic acid is preferable for the titration of very weak bases.

Enhancements in the physical properties of polymers incorporating POSS segments result from POSS's ability to control the motions of the chains while still maintaining the processability and mechanical properties of the base resin. This is a direct result of POSS's nanoscopic size and its relationship to polymer dimensions.

CHAPTER III
LITERATURE REVIEWS

This chapter presents the literature reviews of the previous works related to this research. The work can be roughly divided into two parts. The first part concern the polyimide-POSS synthesis (no POSS on the main chain) while the later part concern the polyimide with OAPS (amine POSS) monomer (POSS on the main chain). Both polyimide-POSS synthesis part and polyimide-OAPS synthesis part are shown as below.

3.1 To Synthesize Polyimide with Polyhedral oligomeric silsesquioxanes (POSS).

Chyi-Ming Leu *et al.* [23] studied Low-dielectric-constant nanoporous films (dielectric constant, $k = 2.4$) with thermal integrity and controllable mechanical strength. The films have been prepared by covalently tethering nanoporous polyhedral oligomeric silsesquioxane (POSS) molecules, 1-nm size, to the side chains of polyimide. The tethered POSS molecules in the amorphous polyimide retain nanoporous crystal structure, but form an additional ordered architecture due to microphase separation. With this approach, the dielectric constant of the film can be tuned by the amount of POSS molecules introduced in the nanocomposite film; the polyimide molecules offer additional advantages of maintaining certain thermal and mechanical strengths.

Chyi-Ming Leu *et al.* [24] synthesized polyimide-tethered polyhedral oligomeric silsesquioxane, $(R_7R'Si_8O_{12})$ (POSS), nanocomposites with well-defined architectures by the copolymerization reaction of a new type of diamine monomer: POSS-diamine, 4,4'-oxydianiline (ODA), and pyromellitic dianhydride (PMDA). This type of polyimide-side-chain-tethered POSS nanocomposite presents self-assembly characteristics when the amount of POSS exceeds 10 mol %, as evidenced by transmission electron microscopy. Furthermore, POSS/polyimide nanocomposites have both lower and tunable dielectric constants, with the lowest value of 2.3, and controllable mechanical properties, as compared to that of pure polyimide.

Yiwang Chen *et al.* [25] studied the low dielectric constant nanocomposites of polyimides with grafted methacrylate side chains containing polyhedral oligomeric silsesquioxane (POSS) that were successfully synthesized by thermally initiated free-radical graft copolymerization of methacrylcyclopentyl-POSS (MA-POSS) with the ozone-preactivated poly(amic acid), followed by thermal imidization. The dielectric constant of the film can be tuned by varying the molar ratio of the grafted MA-POSS side chains in the copolymer with dielectric constants approaching 2.2 could be achieved in the PI-g-PMA-POSS film containing 23.5 mol% MA-POSS.

Ding-Ru Yei *et al.* [26] investigated prepared polystyrene/clay nanocomposites using an emulsion polymerization technique. The nanocomposites were exfoliated at up to a 3 wt% content of pristine clay relative to the amount of polystyrene (PS). We used two different surfactants for the montmorillonite: the aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS) and the ammonium salt of cetylpyridinium chloride (CPC). IR spectroscopic analysis further confirms the intercalation of POSS within the clay layers. They used X-ray diffraction (XRD) and transmission electron microscopy (TEM) to characterize the structures of the nanocomposites. The nanocomposite prepared from the clay treated with the POSS containing surfactant is exfoliated, while intercalated clay was obtained from the CPC treated surfactant. The molecular weights of polystyrene (PS) obtained from the nanocomposite is slightly lower than the virgin PS formed under similar polymerization conditions. The value of Tg of the PS component in the nanocomposite is 8°C higher than the virgin PS and its thermal decomposition temperature (21°C) is also higher significantly. The presence of the POSS unit in the MMT enhances the thermal stability of the polystyrene.

Yuan-Jyh Lee *et al.* [27] synthesised novel polyimide (PI) hybrid nanocomposite containing polyhedral oligomeric silsesquioxane (POSS) with well defined architecture has been prepared by copolymerization of octakis(glycidyldimethylsiloxy)octasilsesquioxane (Epoxy–POSS), 4,4'-oxydianiline diamine (ODA), and 4,4'-carbonyldiphthalic anhydride (BTDA). The resultant PI–POSS nanocomposites give variable thermal and mechanical properties. More importantly, they intend to explore the possibility of incorporating POSS moiety through the Epoxy–POSS into the polyimide network to achieve the polyimide hybrid

with lower dielectric constant (low-k) and thermal expansion. The lowest dielectric constant achieved of the POSS/PI material (PI-10P) is 2.65 by incorporating 10 wt% Epoxy–POSS (pure PI, k=3.22). In addition, when contents of the POSS in the hybrids are 0, 3, 10 wt% (PI-0P, PI-3P, PI-10P), and the resultant thermal expansion coefficients (TEC) are 66.23, 63.28, and 58.25 ppm/°C, respectively. The reduction in the dielectric constants and the resultant thermal expansion coefficients of the PI–POSS hybrids can be explained in terms of creating silsesquioxane cores of the POSS and the free volume increase by the presence of the POSS–tethers network resulting in a loose PI structure.

Yuan-Jyh Lee *et al.* [28] investigated dielectric insulator materials that have low dielectric constants (k=2.5) are required as inter-level dielectrics to replace silicon dioxide (SiO_2) in future semiconductor devices. In this paper, they described a novel method for preparing nanoporous polyimide films through the use of a hybrid PEO–POSS template and generated these nanoporous foams are generated by blending polyimide as the major phase with a minor phase consisting of the thermally labile PEO–POSS nanoparticles. The labile PEO–POSS nanoparticles would undergoes oxidative thermolysis to releases small molecules as byproducts that diffuse out of the matrix to leave voids into the polymer matrix. They achieved significant reductions in dielectric constant (from k=3.25 to 2.25) for the porous PI hybrid films, which had pore sizes in the range of 10-40 nm.

Junchao Huang *et al.* [29] investigated novel organic–inorganic nanocomposites were prepared by in situ curing of poly(amic acid) macromolecules with POSS epoxide, octa(ethylcyclohexylepoxidedimethylsiloxy)silsesquioxane (OC). Solid-state ^{29}Si NMR data show that properties of the interphases can be varied systemically by adjusting the nano-tether structure of the POSS molecules. DMA studies conclude that the cross-linking densities of the nanocomposites increase significantly so that some of these nancomposites are found to lose glass transition temperature; the nanocomposite networks were predominantly formed by the linkage between the terminal amine groups of the polyimide molecules and the epoxide groups of the POSS molecules. Furthermore, in the nanocomposites two factors, the soft interphase around OC molecules and the increasing cross-linking density,

compete with each other, and their influences on morphologies, coefficient of thermal expansion, mechanical strength and hardness of these nanocomposites.

3.2 To Synthesize Polyimide with Octa(aminophenyl)silsesquioxane (OAPS, POSS amine).

Richard M. Laine *et al.* [30] syntyhesised variety of octafunctional cubes (Scheme 1) with polymerizable moieties that offer access to highly cross-linked (thermoset) nanocomposites having: (1) controlled porosities with high surface areas, (2) novel mechanical properties, and (3) high thermal stabilities. In a complementary fashion, POSS materials offer access to robust thermoplastics with good to excellent properties including resistance to atomic oxygen.
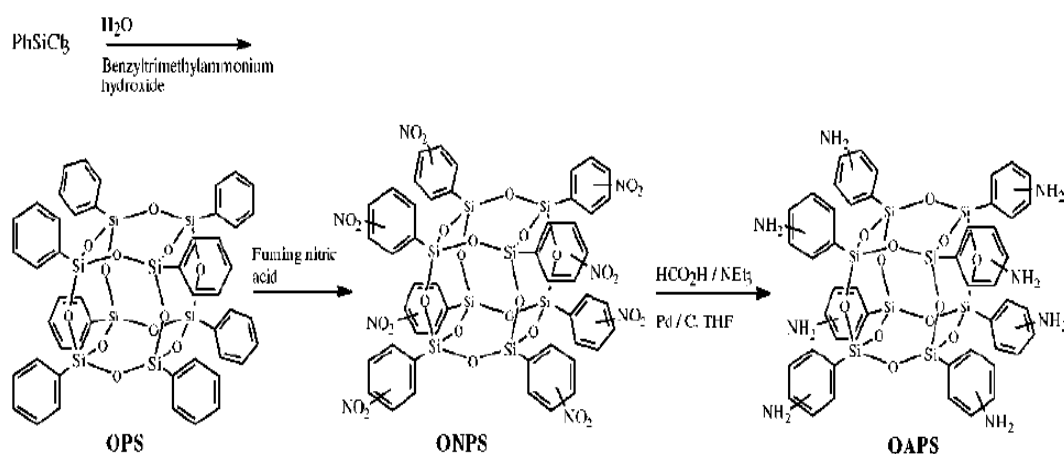
Figure 3.1 Synthesis of Octa(aminophenyl)silsesquioxane.

Chyi-Ming Leu *et al.* [31] synthesized nanoporous polyhedral oligomeric silsesquioxanes (POSS) containing amine groups (NH_2-POSS) were reacted with poly(amic acid) having anhydride end groups to form porous POSS/polyimide nanocomposites. The van der Waals interaction between tethered POSS molecules is incompatible with the polar-polar interaction of imide segments, resulting in a self-assembled system of zigzag shaped cylinders or lamellas about 60 nm long and 5 nm wide, as determined by transmission electron microscopy. The incorporation of 2.5 mol % nanoporous POSS results in a reduction of the dielectric constant of the

polyimide nanocomposite from 3.40 for the pure polyimide to 3.09 without any degradation in mechanical strength.

Ryo Tamaki *et al.* [32] synthesised octaaminophenylsilsesquioxane (OAPS) that can be served as a nanosized building block for the construction of materials with nanometer control of the periodicity of the organic and inorganic components and bonding between components. They described the synthesis of a prototypical three-dimensional polyimide by reaction of OAPS with pyromellitic dianhydride (PMDA). Model studies with phthalic anhydride provided useful cure conditions. Thus, stoichiometrically correct OAPS/PMDA nanocomposites were obtained following curing of NMP and DMF reaction solutions at lower temperatures and then to >350 °C/N_2 under vacuum. The resulting materials offer thermal stabilities in air and N2 of >500 °C (5% mass loss temperature) and char yields/N2 >75%. X-ray powder patterns indicate that the resulting materials are completely amorphous, as might be expected from the extreme rigidity of the organic tethers linking cube vertexes that will prevent long-range ordering from occurring during curing. These materials hold promise for high compressive strength applications.

Jiwon Choi *et al*. [33] studied on structure-processing-property relationships in cubic silsesquioxane (cube) nanocomposites. They focused on imide nanocomposites prepared from octaaminophenylsilsesquioxane (OAPS) as a model nanobuilding block for rigid, high-temperature hybrid nanocomposite materials. OAPS units are linked NH_2 vertex to NH_2 vertex by reaction with various dianhydrides to form three-dimensional nanocomposites. The architecture of the organic tethers between vertices can be manipulated to optimize processability, rigidity, and thermomechanical properties. Studies were initiated using an extreme tether structure with zero flexibility prepared by solvent casting and then curing mixtures of OAPS with pyromellitic dianhydride (PMDA) at 330 °C. The resulting materials are extremely brittle, making thermomechanical property measurements quite difficult. Tether rigidity, length, and cross-link densities were then modified using reactions of OAPS with oxydiphthalic anhydride (ODPA) and diluting with oxydianiline (ODA) to adjust nanocomposite stiffness. FTIR and DMA of the OAPS/ODPA/ODA nanocomposites suggest that cure temperatures of >500 °C are necessary for optimal imidization. However, increasing the cross-link density alone by increasing OAPS loading without

curing at high temperatures also significantly improves thermomechanical stabilities. DMA, TGA, and nanoindentation measurements show that macroscopic relaxation is eliminated completely at OAPS loadings of >60 mol % providing 5% mass loss at temperatures >570 °C and compressive moduli of 3.8 GPa.

Junchao Huang *et al*. [34] synthesised series of functional polyhedral oligomer silsesquioxnae (POSS)/polyimide (PI) nanocomposites were prepared using a two-step, first, the octa(aminophenyl)silsesquioxane (OAPS)/NMP solution was mixed with poly(amic acid) (PAA) solution prepared by reacting 4,4'-diaminodiphenylmethane and 3,3',4,4'-benzophenonetetracarboxylic dianhydride in NMP, and second, the polycondensation solution was treated by thermal imidization. The well-defined 'hard particles' (POSS) and the strong covalent bonds between the PI and the 'hard particles' lead to a significant improvement in the thermal mechanical properties of the resulting nanocomposites. The glass transition temperature dramatically increases while the coefficient of thermal expansion (CTE) decreases, owing to the significant increase of the crosslinking density in the PI–POSS nanocomposites. The thermal stability and mechanical property of the nanocomposites were also improved.

Jiwon Choi *et al.* [35] studied Selected epoxy-functionalized cube nanocomposites were prepared from octa(aminophenyl)silsesquioxane (OAPS), poly(aminophenyl)silsesquioxane (PAPS), octa(dimethylsiloxypropylglycidyl ether)silsesquioxane (OG), diglycidyl ether of bisphenol A (DGEBA) and diaminodiphenylmethane (DDM). A systematic comparison of properties was conducted using GPC, FTIR, ^{29}Si NMR, TGA, and DMA. In these studies, they found that (1) tethers with aromatic components increase char yields and decomposition temperatures, (2) cube loadings are important in thermal stabilities, (3) aromatic tether structure, short lengths and high cross-link densities reduce tether segmental relaxation motions which in turn stiffen the network and minimize macroscopic glass transitions. Finally, nanocomposites prepared from OAPS and PAPS exhibit nearly identical thermomechanical properties with PAPS offering a low cost alternative to OAPS.

Junchao Huang *et al.* [36] synthesised two series of nanoporous polyimide nanocomposites with well-defined tether architecture have been prepared from octa(aminophenyl)silsesquioxane. Transmission electron microscopy, solid-state ^{29}Si nuclear magnetic resonance, model reaction, and density measurement show that the nanostructures of the polyimide nanocomposites are well defined and can be adjusted accordingly. The polyimide nanocomposites exhibit tunable dielectric constant with a lowest value of 2.29. The thermomechanical properties of the polyimide have been improved significantly with the addition of octa(aminophenyl)silsesquioxane; for instance, glass transition temperature increases by 80°C and storage modulus by 46%, as compared to the neat polyimide. Moreover, thermal stability, coefficient of thermal expansion, hardness, and moisture absorption of the polyimide nanocomposites are also improved significantly.

From these works, they can commonly find thermomechanical and dielectric properties of polyimide nanocomposite were improved with POSS. Furthermore, in this research, polyimide nanocomposite was prepared by families POSS amine via two step polymerization. The major differences from previous works were the absolute measurement of amine in OAPS and the cooperated different arms of OAPS onto the properties of the nanocomposites.

CHAPTER IV
EXPERIMENT

In this chapter, the experimental procedures in this study divided into six parts as below,

    (i)   Chemicals and Equipments

    (ii)   Preparation of octa(nitrophenyl)silsesquioxane (ONPS)

    (iii)   Preparation of octa(aminophenyl)silsesquioxane (OAPS)

    (iv)   Titration of OAPS to determine quantitative of amine group in OAPS

    (v)   Preparation of polyimide films

    (vi)   Characterization of polyimide films

The details of each part were described as follows.

4.1 Chemicals and Equipments

4.1.1 Chemicals

The chemicals used in these experiments were analytical grade, but only critical materials were specified as followed:

1. Octaphenyl-POSS (OPS) was purchased from Hybrid plastic company.

2. Fuming nitric acid (HNO_3) was purchased from Merck KGaA Germany.

3. Iron (particle size 10 μm) was purchased from Merck KGaA Germany.

4. *N,N*-dimethylacetamide (DMAc) was purchased from Merck KGaA Germany.

5. Ethanol (CH_3OH, 99.9%) was purchased from Merck KGaA Germany.

6. Hydrochloric acid (HCl, 36.5-38.0%) was purchased from J.T. Buker.

7. Ammonium hydroxide solution (NH_4OH, 28 wt%) was purchased from APS Ajax Finechem.

8. 1,4-dioxan ($C_4H_8O_2$, 99.0%) was purchased from Merck KGaA Germany.

9. Acetic acid (glacial, 100%) was purchased from Merck KGaA Germany.

10. Perchloric acid ($HClO_4$, 70-72%) was purchased from Merck KGaA

Germany.

11. Potassium hydrogen phthalate ($C_8H_5KO_4$) was purchased from Merck KGaA Germany.

12. Crystal violet was purchase from TSL Chem.

13. Pyrromellitic dianhydride (PMDA) was purchased from Aldrich chemical Company, Inc .

14. 3,4′-Oxydianiline (ODA) was purchased from Aldrich chemical Company, Inc.

15. Phthalic anhydride (PA) was purchased from Merck KGaA Germany.

16. N-Methyl-2-pyrrolidinone (NMP, 99.5%) was purchased from Merck KGaA Germany.

17. Silicone Oil was purchased from Merck KGaA Germany.

4.1.2 Equipments

All equipments used in the OAPS preparation and Polyimide film preparation are listed as below:

4.1.2.1 OAPS synthesis part

(a) reactor

The synthesis reactor was a 250 ml. three-neck flask. The reactor was equipped with several fittings for injecting the chemicals and condenser. A three-necked, round bottom flask equipped with a thermometer, a magnetic stir bar and a condenser are shown in Figure 4.1.
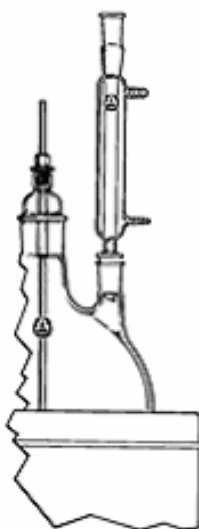
Figure 4.1 reactor

(b) Magnetic Stirrer and Hot Plate

The magnetic stirrer and hot plate model RCT basic from IKA Labortechnik were used.

(c) Cooling System

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

4.1.2.2 Polyimide synthesis part

Since the most of reagents were very sensitive to the oxygen and moisture therefore special techniques were taken in the handling of reagents and for loading into the reactor. Such equipments utilized for this purpose are as follows:

(a) Glove box

Glove box (Vacuum Atmospheres) with oxygen and moisture analyzer was used for transferring solid reagents under inert atmosphere and for storing air-sensitive reagents. The oxygen and moisture levels are normally below 2 ppm inside the glove box. The glove box is shown in Figure 4.2.
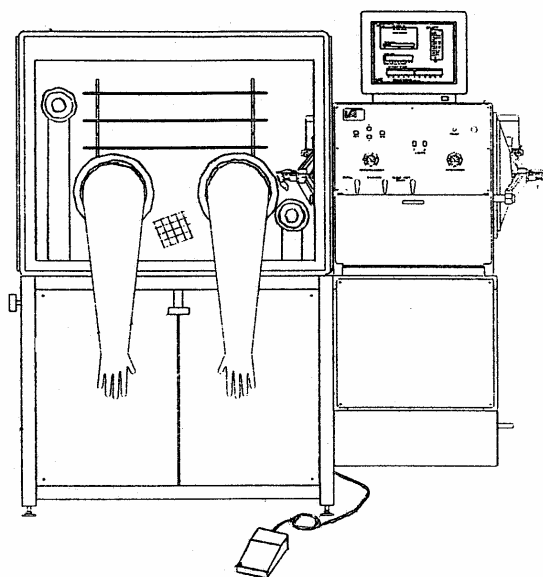
Figure 4.2 Glove box

(b) Syringe, Needle

The syringe was used in the experiment had a volume of 50 and 10 ml and the needle were No. 17 and 20, respectively.

4.1.2.3 Film preparation Part

(a) Vacuum oven

A Cole-Parmer vacuum oven model 282A was used for removing solvent. This vacuum oven is programmable. All functions can be set from digital panel and display their status on LCD. The temperature, pressure and time are controllable.

(b) Temperature controlled oven

A Carbolite LHT5/30 (201) Temperature controlled oven was used in these experiments. The maximum working temperature of this machine is 500°C. This equipment was used for thermal treated the film.

4.2 Preparation of octa(nitrophenyl)silsesquioxane (ONPS)

OPS (1 g, 0.968 mmol) was added in small potions to 20 mL of fuming nitric acid with stirring at 0°C. When the addition was complete, the solution was stirred at 0°C for 30 min and then at room temperature for 20 h. After filtration, the solution was poured onto 250 g of ice. When the ice was completely melt, the precipitate was collected and washed with water several times to remove acidic component. The obtained powder was dried under vacuum at 70°C for 10 h.

4.3 Preparation of octa(aminophenyl)silsesquioxane (OAPS)

A mixture of 1.5 mL of concentrated hydrochloric acid and 10 mL of 30%DMAc, 20%H$_2$O and 50% aqueous ethanol was added slowly to a mixture of 0.5 g of ONPS (0.3588 mmol), reductive iron (0.1202 g, 2.153 mmol), and 30 mL of 30%DMAc, 20%H$_2$O and 50% aqueous ethanol) in a 100 mL of three-necked round-bottom flask equipped with a mechanical stirrer, condenser and thermometer. The mixture was stirred with refluxing for 3 h, and 1 mL of ammonium hydroxide solution (10 wt%) was added slowly to the mixture during 10 min. The mixture was hot-filtered to remove the solvent, a light brown solid was obtained as OAPS, which was dried at 100°C for 10 h.

4.4 Titration of OAPS to determine quantitative of amine group in OAPS

4.4.1 Solution required

Perchloric acid was prepared to be 0.1 M solution by slowly adding 2.1 mL of 72% perchloric acid to dioxin and making up to 250 mL in a graduated flask.

4.4.2 Calibration curve

Various accurate weigh of ODA were dissolve in 2 mL NMP and glacial acetic acid was added 70 mL . Then crystal violet as indicator was used in the amount of 3 drops and titrate against 0.1 M perchloric acid.

4.4.3   Procedure

Accurately weight, 0.0056 g of OAPS was dissolved in 2 mL NMP and added 70 ml glacial acetic acid. With the amount of 3 drops of crystal violet, the solution

was titrated with 0.1 M perchloric acid. We obtained all amine groups of OAPS by compared calibration curve of ODA and in this thesis, they were approximate 18 amine groups per one molecule of POSS. Further, we could calculate amount of phthalic anhydride to end capped amine group of OAPS according to the specifications.

4.5 Preaparation of Polyimide films

Polyimide were synthesized by two step polymerization of OAPS, phthalic anhydride, ODA and PMDA in NMP. This thesis (1) Various amine groups of OAPS (18, 10 and 4 groups) were reacted with phthalic anhydride. (2) Various amount of OAPS were 50%, 75%, 100%, 125% and 150% of 0.00588 g OAPS. Therefore, synthesize polyimides can be represented by PI50-18, PI50-10, PI50-4, PI75-18, PI75-10, PI75-4, PI100-18, PI100-10, PI100-4, PI125-18, PI125-10, PI125-4, PI150-18, PI150-10 and PI150-4.

In typical experiment for an example, PI50-10 was prepared in glove box as follows: OAPS (0.00294 g, 0.00225 mmol) was dissolved in 1 mL of NMP and added phthalic anhydride (0.0027 g, 0.01869 mmol). The mixture was stirred at room temperature for 2 h. Then ODA (0.32999 g, 1.64998 mmol) and PMDA (0.35970 g, 1.65 mmol) were added to the solution to obtain 15% of solid content with stirring at room temperature for 8 h. The obtained viscous poly(amic acid) solution (PAA solution) was converted into a polyimide by further imidization at high temperature. The PAA solution was casted to clean glass substrate and heated at 50°C for overnight and cured according as temperature procedure of 100°C, 150°C for 0.5 h and 300°C for 1 h. Then polyimide film was removed from glass substrate by immersing into water and then it was dried at 100°C for 1 h, successively.

The other polyimides were prepared from the polymerization of 1 equiv. diamine and 1 equiv. dianhydride by mol at 15% solid content in NMP by the same method as polyimide PI50-10.

4.6 Characterization Instruments

4.6.1 Infrared Spectroscopy (FTIR)

Infrared survey spectra were recorded with Nicolet 6700 FTIR spectrometer. The scanning ranged from 400 to 4000 cm^{-1} with scanning 64 times and KBr tybe.


Figure 4.3 Infrared Spectroscopy (FTIR) Equipment**.**

4.6.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of all polyimide products were determined by using Dynamic Mechanical Analysis (DMA) with a Perkin-Elmer Pyris Diamond DMA. The samples were prepared according to standard DMA samples (10x25 mm). Conditions and parameters during the experiments were shown as the Table below.

Table 4.1 Conditions and parameter for running DMA

Conditions and parameter	Value
Sample size(w x l) (mm)	10 x 20
DMS Measurement Mode	Tension
Temperature Control Mode	Ramp (5.0 ^{o}C/min)
DMS frequency (Hz)	1.0, 5.0, 10.0
Temperature range	50 to 450 ^{o}C
L Amplitude (μm)	10
Minimum Tension/Compression Force(mN)	200
Tension/Compression Force gain	1.5
Force Amplitude Default Value (mN)	4000
Nitrogen as carrier gas (ml/min)	100
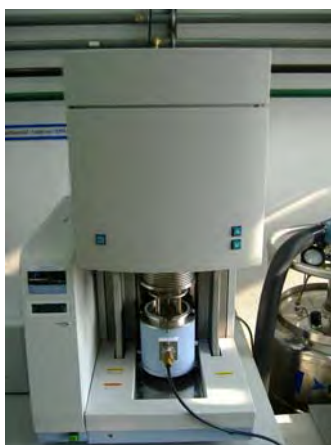
Figure 4.4 Dynamic Mechanical Analysis (DMA) Equipment**.**

4.6.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) thermograms were performed using a SDT Analyzer Model Q600 from TA Instruments, USA. The temperature range of 50-600°C at a heating rate of 10°C/min was applied. O_2 UPH at flow rate 100 mL/min.
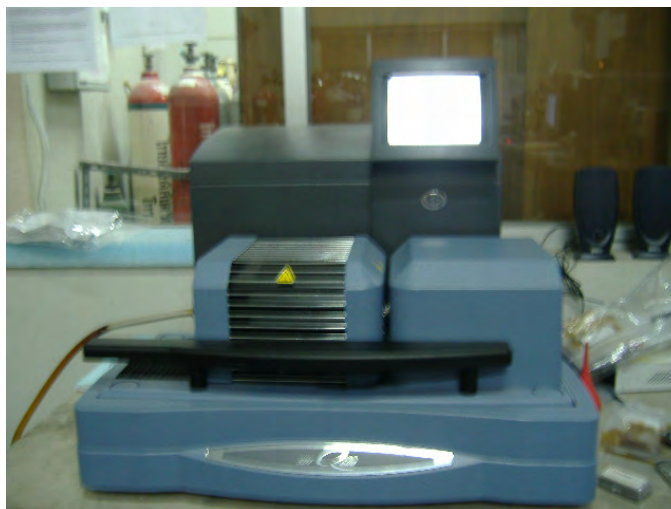

Figure 4.5 Thermogravimetric analysis (TGA) Equipment**.**

4.6.4 Dielectric properties

The dielectric properties of the polyimide films were obtained via the capacitance method and sample size 1.5x1.5 cm were measured at room temperature, 500 mV with frequency 1, 10, 100 and 1000 KHz by a Agilent E 4980A Precision LCR Meter. The films for dielectric properties analysis were coated with gold layer by JEOL JFC-1100E ion sputtering device on both sides to provide electrical contact to the specimens.
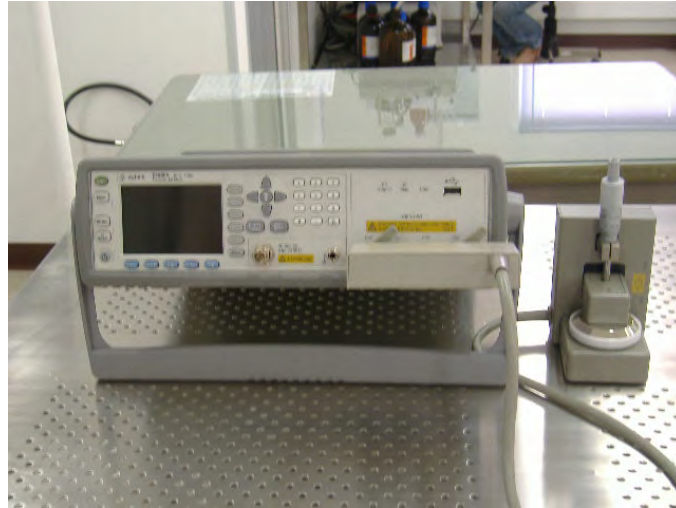
Figure 4.6 Dielectric analysis (DEA) Equipment**.**

4.6.5   Tensile testing machine

Tensile properties were characterized using an Instron universal testing machine with a test speed of 12.5 mm/min. Sample size 2 x 10 cm. The tests were conducted according to ASTM D 882-02.

The tensile testing machine of a constant-rate-of-crosshead movement is used. It has a fixed or essentially stationary member carrying one grip, and a moveable member carrying a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and moveable member to prevent the alignment problem. An extension indicator is used to determine the distance between two designated points located within the length of the test specimen as the specimen is stretched.
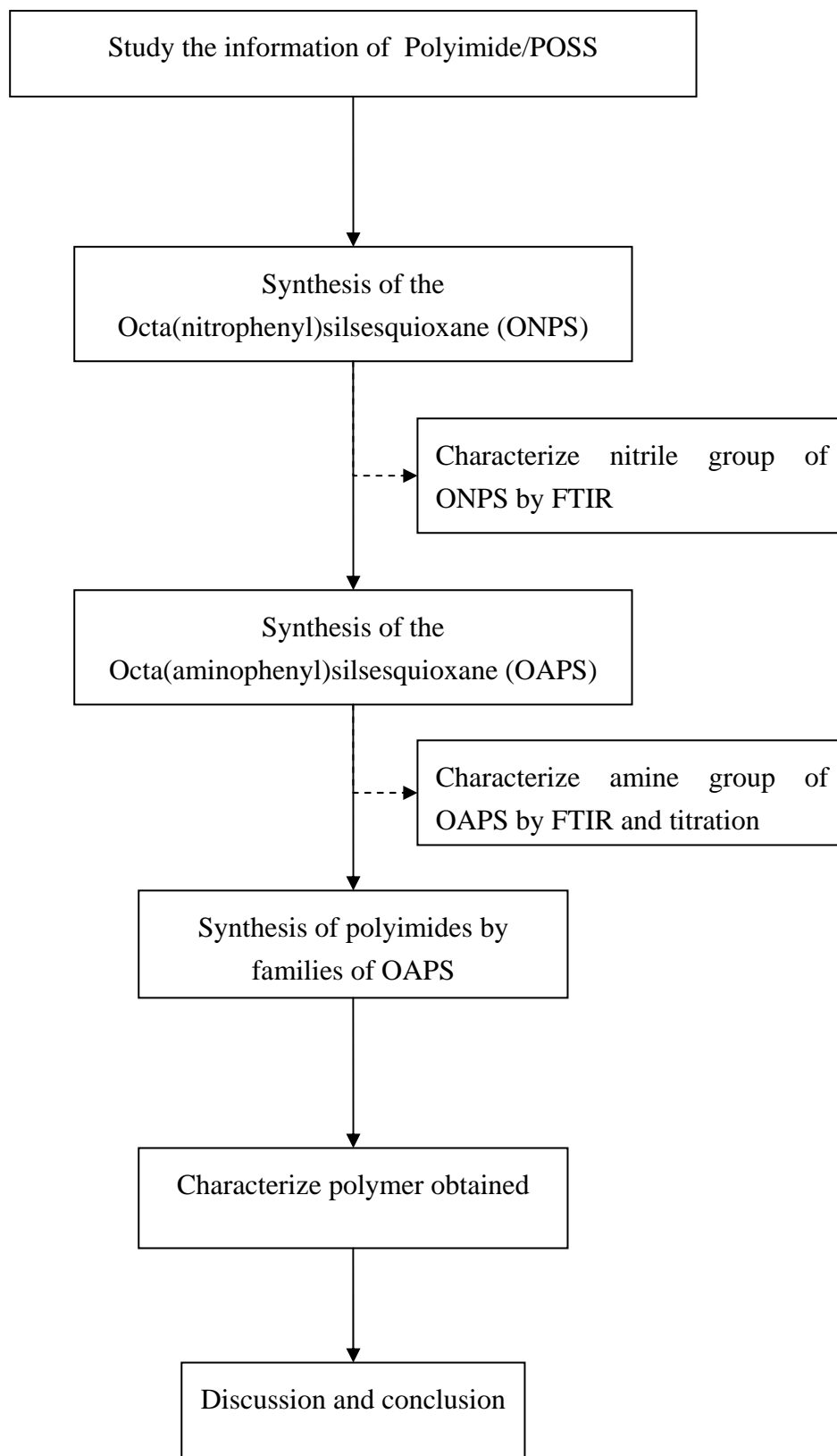
Figure 4.7 Tensile testing machine Equipment.

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┌─────────────────────────────────────────────┐
│      Study the information of  Polyimide/POSS │
└─────────────────────────────────────────────┘
                      │
                      ▼
┌─────────────────────────────────────────────┐
│              Synthesis of the                │
│   Octa(nitrophenyl)silsesquioxane (ONPS)     │
└─────────────────────────────────────────────┘
                      │         ┌──────────────────────────────┐
                      │  - - - ▶│ Characterize  nitrile  group  of │
                      │         │ ONPS by FTIR                 │
                      ▼         └──────────────────────────────┘
┌─────────────────────────────────────────────┐
│              Synthesis of the                │
│   Octa(aminophenyl)silsesquioxane (OAPS)     │
└─────────────────────────────────────────────┘
                      │         ┌──────────────────────────────┐
                      │  - - - ▶│ Characterize  amine  group  of │
                      │         │ OAPS by FTIR and titration   │
                      ▼         └──────────────────────────────┘
┌─────────────────────────────────────────────┐
│         Synthesis of polyimides by           │
│            families of OAPS                  │
└─────────────────────────────────────────────┘
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                      ▼
┌─────────────────────────────────────────────┐
│         Characterize polymer obtained        │
└─────────────────────────────────────────────┘
                      │
                      ▼
┌─────────────────────────────────────────────┐
│          Discussion and conclusion           │
└─────────────────────────────────────────────┘
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Figure 4.8 Flow diagram of research methodology.

CHAPTER V

RESULTS AND DISCUSSION

This chapter provides the identification information of the POSS, PI/POSS nanocomposites and the characterization information of PI/POSS nanocomposites with various controlled amine OAPS (Octa(aminophenyl)silsesquioxane). The thermal properties, mechanical properties and electrical properties of the PI/POSS nanocomposites were obtained and verified.

5.1. Synthesis of OAPS monomer

OAPS monomer was prepared by two-step reaction.

i)   nitration of POSS to form ONPS (Octa(nitrophenyl)silsesquioxane).

ii)   hydrogenation of ONPS to form OAPS.

FTIR of the products from those reactions can be shown and confirmed the functional group of the ONPS and OAPS as in figure 5.1.
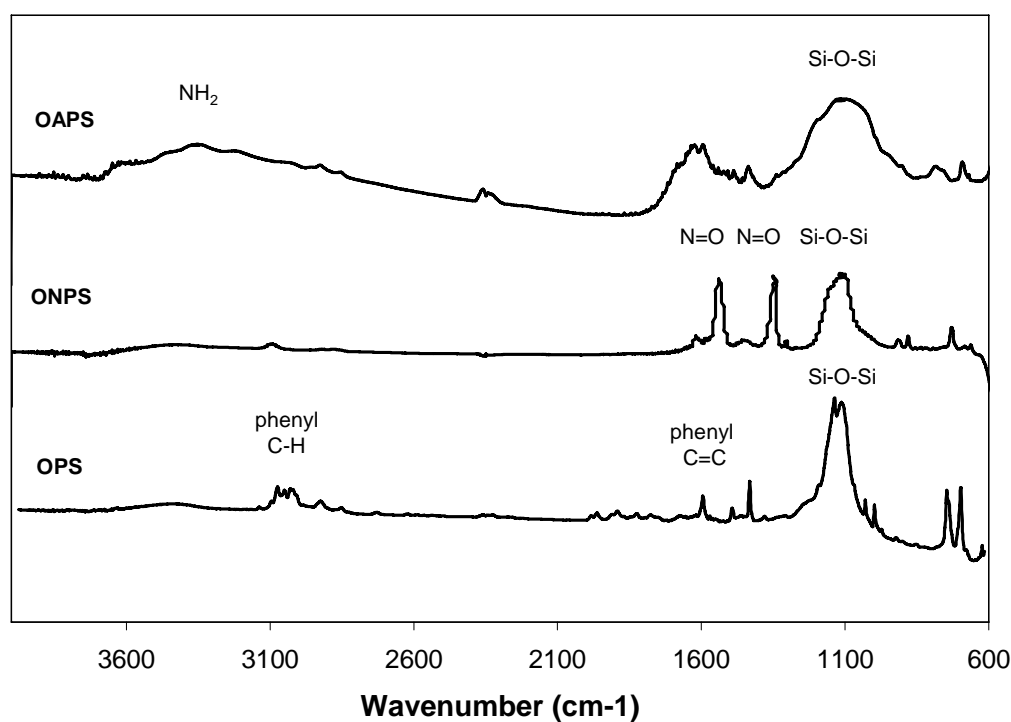
Figure 5.1 FTIR spectra of OPS, ONPS and OAPS monomer.

Figure 5.1 show the FTIR spectra of OPS, ONPS and OAPS. Functional group after nitration of OPS to form ONPS were confirmed at the peak of 1347 and 1540 cm^{-1} resulting from asymmetric and symmetric stretching vibration of –NO$_2$ group. These peaks are disappeared after ONPS reduced (hydrogenation) to form OAPS. The FTIR spectra of OAPS indicated a completed hydrogenation of nitro-compound into amine functional monomers because the peaks of 1347 and 1540 cm^{-1} were disappeared while band of –NH$_2$ group were instate presented at 3376 cm^{-1} (N-H stretching) and 1620 cm^{-1} (N-H banding) [34].

The amount of amine groups per one OAPS can be measure by titration method with slight modifacation [37]. The detail of the method can be summarized as follows,

1. Dissolve 0.0056 g of OAPS in 2 mL NMP and added 70 ml glacial acetic acid.
2. With the amount of 3 drops of crystal violet.
3. The solution was titrated with 0.1 M perchloric acid.

The calibration curve was made from known amount of amine of ODA at various concentration and the calibration equation can be shown as below.

$$y \quad = \quad 7.3925e^{-5}(x) \; - \; 0.001332$$

y : mole of the amount of OAPS.

x : Volume of 0.1 M perchloric acid.

The amount of amine groups per one OAPS systhesis were 18 functional groups per POSS molecule. The as made OAPS was further mixed with the compensate amount of ODA to obtain 1:1 ratio of dianhydride and diamine group. As calculated [34], the molecular weight of polyimide obtained should be maximum at the ratio of dianhydride and diamine of 1:1. The functional amines in OAPS were further reacted with phtalic anhydride to change the amine in OAPS to imide before further reaction with ODA and PMDA. In this case, the controlled functional amount

of amines were 18 (as made), 10, 4 arms of amine per one OAPS. These controlled amine OAPS were further reacted with PMDA together with the compensation amount of amine in ODA.

5.2 Synthesis of PI-POSS nanocomposites

5.2.1 Polymer synthesis condition

All synthesized conditions and name definitions of synthesized polymers are shown in Table 5.1. Polymers are synthesized from diamine and carboxylic dianhydride by two step polymerization in 15 wt% solid under argon atmosphere at room temperature.

The effects of the amount of amine group in PI/POSS nanocomposites were observed as 4, 10 and 18 functional amine group per one POSS molecule. In addition; various concentration of OAPS content in PI/POSS nanocomposites with various functional were investigated as 50, 75, 100, 125 and 150% of 0.00588 g of OAPS in 0.69557 g of polyimide respectively. The larger amount of OAPS in polyimide will deteriorate the strength of the obtained film. In other word, no strong polyimide films were obtained at the higher concentration than 0.00882 g of OAPS in 0.69851 g of polyimide. (150% of 0.00588 g)

(a)   (b)
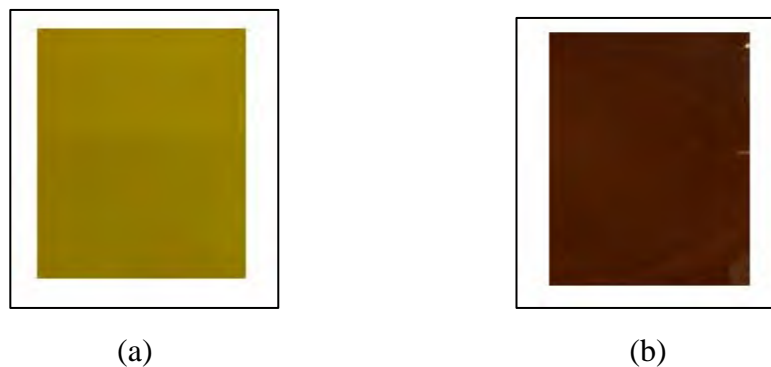
Figure 5.2 Polyimide films a) pure polyimide b) PI/POSS nanocomposite (PI100-18).

Table 5.1 The series of the PI/POSS nanocomposites

Sample name	Amine group (-NH$_2$)	Content of OAPS (g)	Mole ratio[a] PMDA:ODA:OAPS:PA
Pure PI	-	-	100: 100: 0: 0
PI50-4	4	0.00294	100: 99.999: 0.137: 1.983
PI50-10	10	0.00294	100: 99.999: 0.137: 1.133
PI50-18	18	0.00294	100: 99.999: 0.137: 0
PI75-4	4	0.00441	100: 99.998: 0.205: 3.007
PI75-10	10	0.00441	100: 99.998: 0.205: 1.718
PI75-18	18	0.00441	100: 99.998: 0.205: 0
PI100-4	4	0.00588	100: 99.997: 0.273: 4.018
PI100-10	10	0.00588	100: 99.997: 0.273: 2.296
PI100-18	18	0.00588	100: 99.997: 0.273: 0
PI125-4	4	0.00735	100: 99.997: 0.342: 5.022
PI125-10	10	0.00735	100: 99.997: 0.342: 2.871
PI125-18	18	0.00735	100: 99.997: 0.342: 0
PI150-4	4	0.00882	100: 99.996: 0.410: 6.028
PI150-10	10	0.00882	100: 99.996: 0.410: 3.444
PI150-18	18	0.00882	100: 99.996: 0.410: 0

[a] Mole ratio is the mole ratio of PMDA:ODA:OAPS:Phthalic anhydride

5.2.2 FTIR spectra

The pure polyimide and the PI/POSS nanocomposites were prepared by two step reaction of carboxylic dianhydride and diamine as in table 5.1. The Selected FTIR spectra of pure PI and PI/POSS nanocomposite (PI50-18 and PI75-18) are show in Fig. 5.2. Both pure PI and PI/POSS nanocomposite exhibit characteristic absorption bands at 1778 and 1729 cm^{-1} resulting from asymmetric and symmetric of imide ring C=O [34,36], which confirmed the complete imidization. The

characteristic absorption band of POSS can be observed at 1103 cm^{-1}, which also confirm the incorporation of OAPS in PI/POSS nanocomposites.
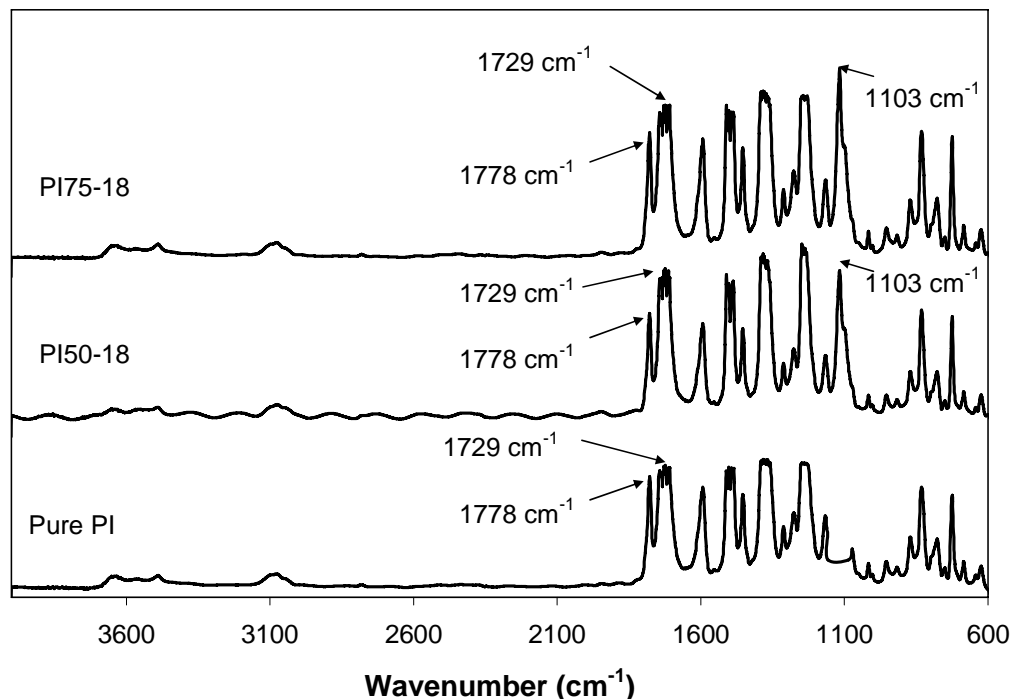
Figure 5.3 FTIR spectra of the pure PI and the PI/POSS nanocomposites.

5.2.3 Densities and dielectric constant

Dielectric constant of the pure PI and the PI/POSS nanocomposites were measured by a dielectric analysis at 1 MHz. Figure 5.3 shows the relationship of the dielectric constant of pure PI and PI/POSS nanocomposites at different OAPS content of various amount of amine group, while Figure 5.4 shows the densities at different conditions as above.

The dielectric constant of PI/POSS nanocoposites were decreased as the amount of OAPS loading increase. Moreover, decreasing of dielectric constant is observed while the amount of amine groups per one OAPS was decreased. The lowest dielectric constant at 2.75 was observed for series of the PI/POSS nanocomposites (PI150-10). Compared with the dielectric constant of pure PI (k=3.56, 1MHz); the

maximum reduction in the dielectric constant of the PI/POSS nanocomposites is about 23%.

Table 5.2 The dielectric constant and densities.

name	d (g/cm^3)	k
PI50-18	1.433	3.26
PI50-10	1.353	3.09
PI50-4	1.307	2.89
PI75-18	1.444	3.27
PI75-10	1.350	3.10
PI75-4	1.222	2.88
PI100-18	1.417	3.19
PI100-10	1.304	3.09
PI100-4	1.237	2.83
PI125-18	1.398	3.18
PI125-10	1.167	2.95
PI125-4	1.111	2.85
PI150-18	1.319	3.04
PI150-10	1.237	2.75
PI150-4	na	na
kapton	1.498	3.65
pure	1.357	3.56

The dielectric constant values are also in accordance with the relative relationship of their density. The lower are the density, the lower are the dielectric constant in the polymer films and the lower are the free volume. The reduction in the dielectric constant of polyimide films can be explained in term the free volume of the polymer nanocomposites due to the nanoporosity in the core of the OAPS molecules and the external porosity incorporated by the large volume branches of OAPS molecules within the polyimide films. Furthermore, the dielectric constant of POSS cubic silica structure was about 2.1 [26,36] while the polyimide matrix has the dielectric constant of about 3.5. Therefore, the dielectric constant of OAPS blends tend to decreased and the chemical binding OAPS with polyimide will results in the reduction of dielectric constant of PI/POSS nanocomposites while maintained the mechanical properties.
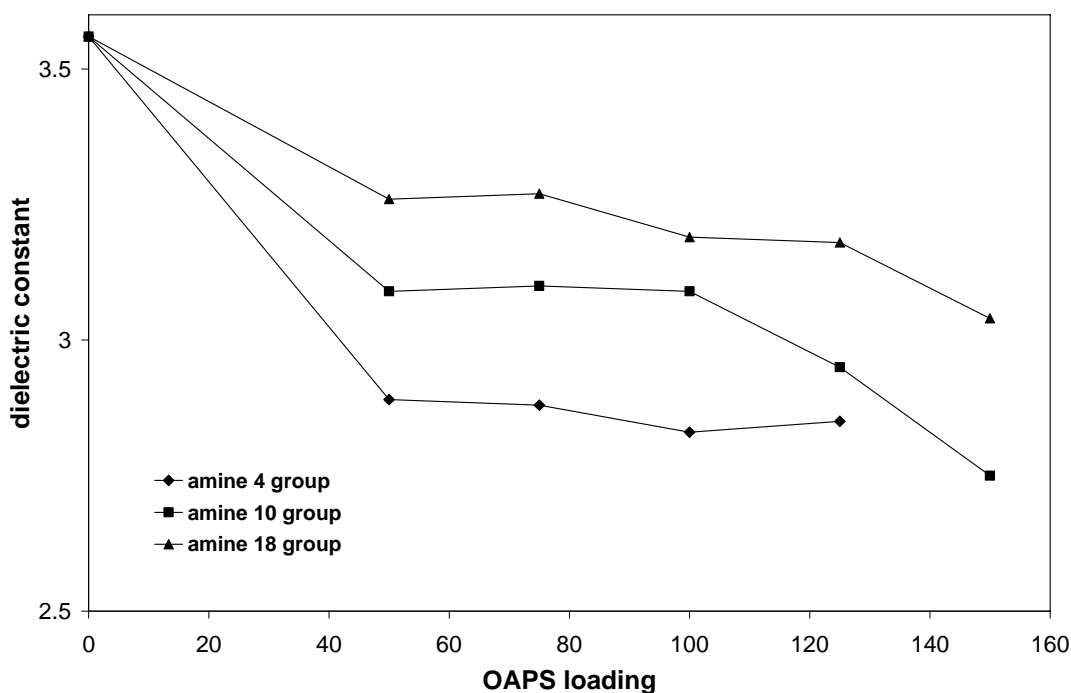
Fig. 5.4 Dielectric constants of the pure PI and the POSS nanocomposites at various OAPS loading.
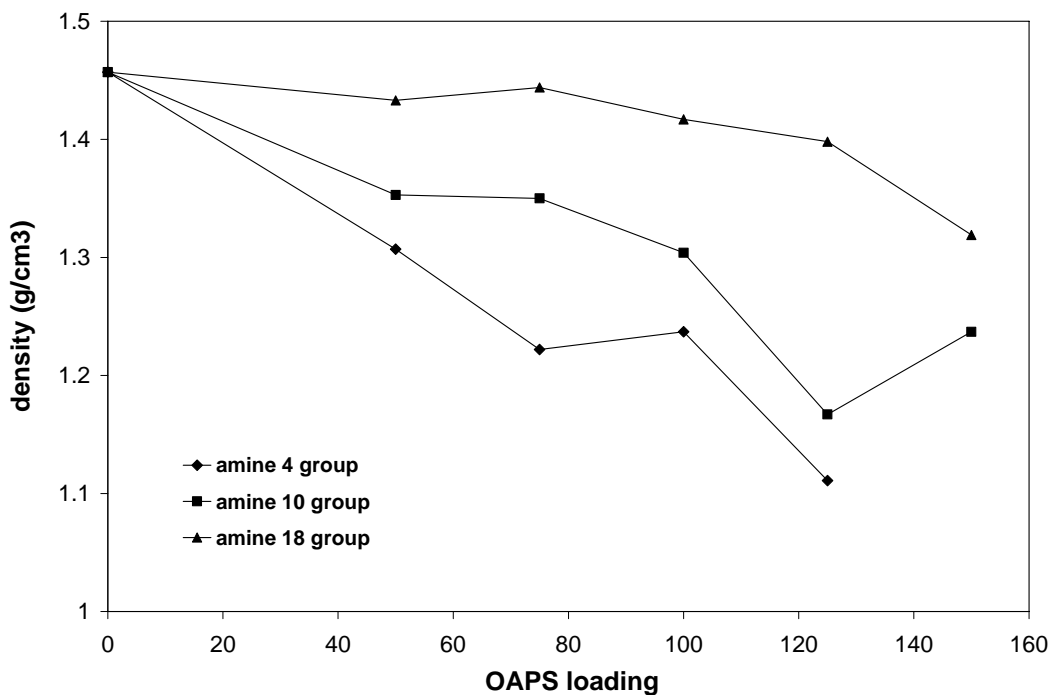
Fig. 5.5 Densities of the pure PI and the POSS nanocomposites at various OAPS
loading.

5.2.4 Mechanical properties

Mechanical properties of the pure PI and the PI/POSS nanocomposites were
investigated by tensile testing. The effects of the amount of amine group and
concentration of OAPS on the mechanical properties of the pure PI and the PI/POSS
nanocomposites are shown in Fig. 5.5 – 5.6 and Table 5.2.

Increasing of both the tensile strength (Fig. 5.5) and the elongation at break
(Fig. 5.6) are depended on the amount of amine group per molecules OAPS. The
increases in tensile strength from 82.3 MPa, 5.86% (pure PI) to 90 MPa, 6.33%
(PI100-10) can be observed. However, the lower amount of amine group per OAPS
resulted in the lower both tensile strength and elongation at break. The reaction of
OAPS with phthalic anhydride which are increase at the low amine functional group
per molecule OAPS might deteriorate the strength of the films.
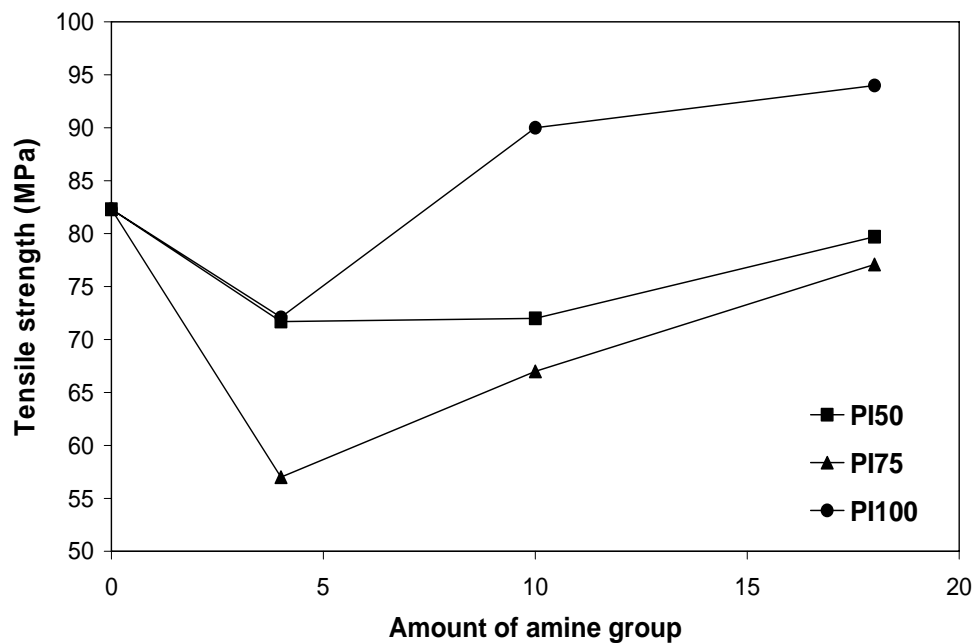
Fig. 5.6 The tensile strength of the pure PI and the POSS nanocomposites vs the amount of amine group.
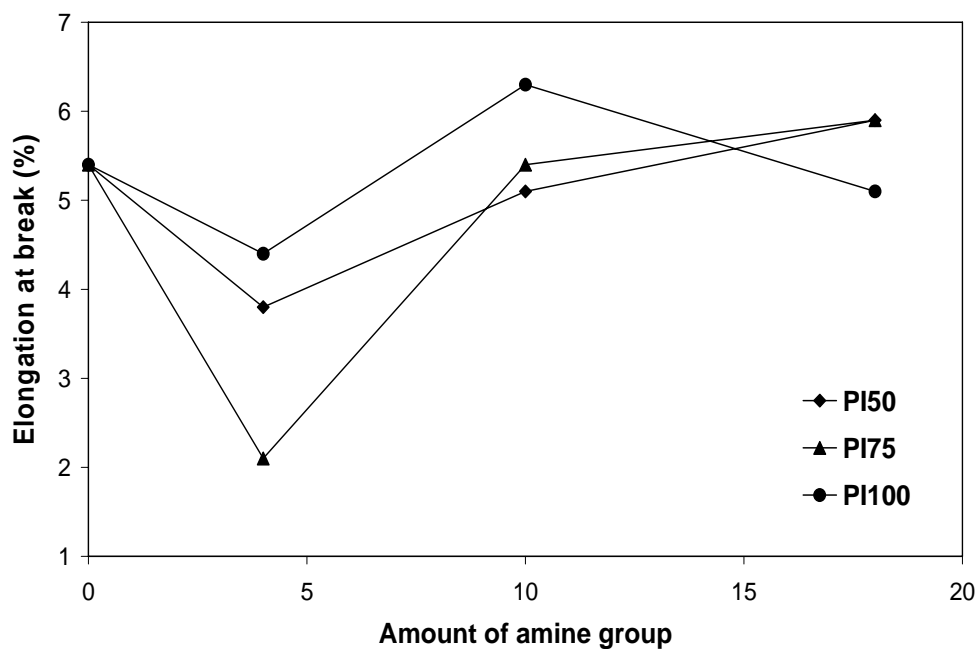
Fig. 5.7 The elongation at break of the pure PI and the POSS nanocomposites vs the amount of amine group.

Table 5.3 The mechanical properties of pure PI and PI?POSS nanocomposites.

Sample	Tensile Modulus (GPa)	Tensile Strength (MPa)	% elongation	Toughness
pure	2.34	82.3	5.4	388.8
PI50-18	2.45	79.7	5.9	312.3
PI50-10	2.37	72.0	5.1	241.2
PI50-4	2.66	71.7	3.8	167.8
PI75-18	2.48	77.1	5.9	328.3
PI75-10	2.39	67.6	5.4	162.4
PI75-4	2.82	57.7	2.1	54.8
PI100-18	3.06	94.4	5.1	286.0
PI100-10	2.67	90.2	6.3	388.3
PI100-4	2.31	72.1	4.4	194.9

5.2.5 Dynamic mechanical analysis (DMA)

Dynamic Mechanical Analysis (DMA) of the blend were perform under N_2 at range 50-450ºC rate 5ºC/min. The results from pure PI and PI/POSS nanocomposites are shown in Fig. 5.7-5.8. It can be see that when OAPS content increased , Tg and storage modulus increased from 399.2°C, 3.58 GPa at 50ºC (pure PI) to 402.7°C, 4.33 GPa at 50ºC (PI100-18) due to rigidity body of POSS and introduction of OAPS loading increased crosslink density [34].
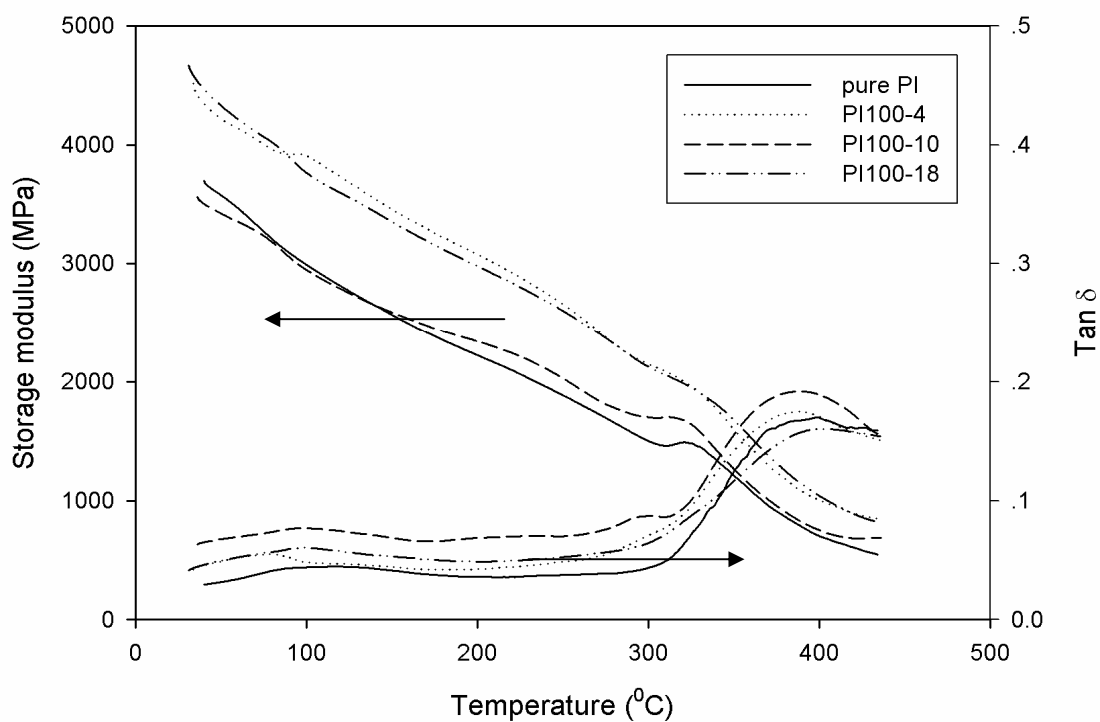
Fig. 5.8 DMA curve of the pure PI and the POSS nanocomposites.
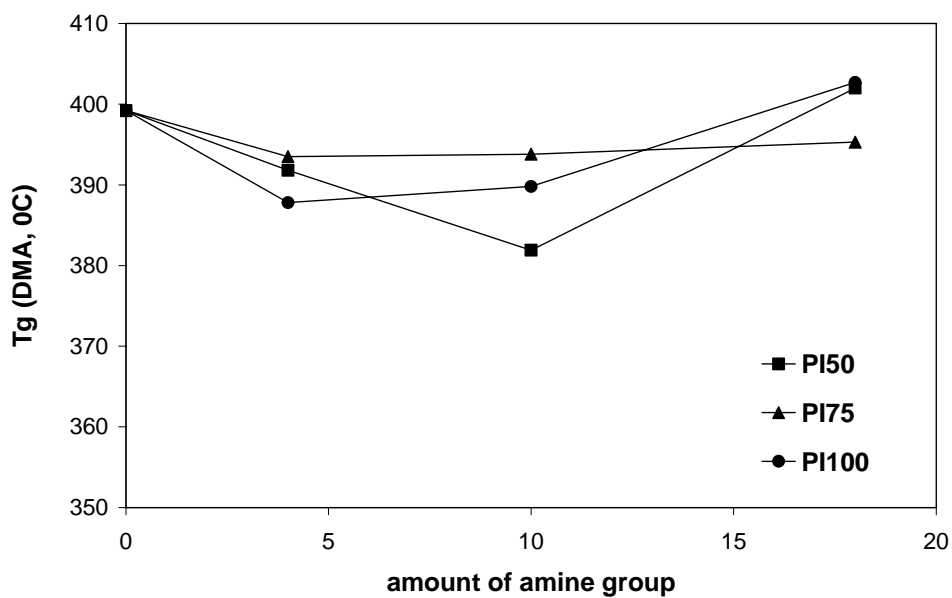
Fig. 5.9 DMA curve of the pure PI and the POSS nanocomposites vs the amount of amine group.

5.2.6 Thermal properties

The thermal properties of pure PI and PI/PSS nanocoposites were investigated by Thermogravimetric Analysis (TGA) in O_2 at range 35-600 ℃ rate 10℃/min during the close cup condition. The results are shown in the following figure.
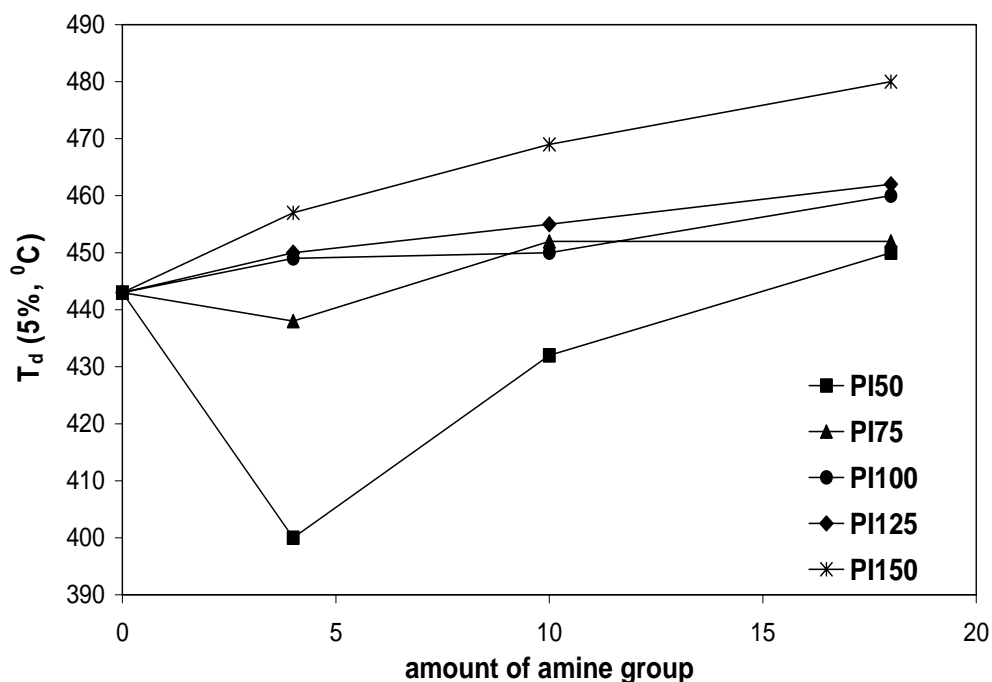
Fig. 5.10 TGA curve of the pure PI and the POSS nanocomposites vs the amount of amine group.

From Fig. 5.10, it showed the thermal stability of PI/POSS nanocomposites which increased as the increased amount of amine group from 4 to 18. In addition, the thermal stability increased according to the concentration of OAPS. Compared with the thermal decomposition temperature of 5% mass loss of the pure polyimide ($T_{d,5\%}$ = 443 ℃), the thermal decomposition temperature of 5% mass loss increased to 480℃ for the PI150-18. The increasing thermal stability of PI/POSS nanocomposites as the increasing concentration of OAPS might be because the good thermal stability of the

cubic silica core, the phenyl group in OAPS molecules and the crosslinked covalent bond between both components and the polyimide chains.

CHAPTER VI

CONCLUSIONS & RECOMMENDATIONS

6.1 Conclusions

In this research, the preparation of PI/POSS nanocomposites was studied and verified. The properties of the synthesized polyimide with OAPS (Octa(Amino Phenyl) Silsesquioxane) that have well defined amine functional group were investigated. The OAPS having 4, 10 and 18 amine group with various amount of loading OAPS (50%, 75%, 100%, 125% and 150% of 0.00588 g OAPS) were added to the stoichiometric balance of polyimides. The titration amount of amine in the fresh OAPS was 18 groups and the amine groups of 10 and 4 were prepared by reactions of fresh OAPS with controlled amount of Phthalic anhydride. The effect of adding POSS were assessed by thermal, mechanical and dielectric properties. From this work, it can be concluded as follows;

1. The reduction of ONPS to OAPS was confirmed by the FTIR spectra. The FTIR spectra of OAPS indicated a completed hydrogenation of nitro-compound into amine functional monomers because the peaks of 1347 and 1540 cm^{-1} (–NO_2 group) were disappeared while band of –NH_2 group were instate presented at 3376 cm^{-1} (N-H stretching) and 1620 cm^{-1} (N-H banding)

2. The amine groups per OAPS can be measured by the titration method which the freshly made OAPS contained 18 groups of amine per OAPS. The 10 and 4 amine groups per OAPS can be made by reaction of the fresh OAPS with controlled amount of phthalic anhydride and the titration confirmed the results.

3. The pure polyimide and the PI/POSS nanocomposites were prepared by two step reaction of stoichiometric balance of carboxylic dianhydride and diamine. Both pure PI and PI/POSS nanocomposite exhibit characteristic absorption bands at 1778 and 1729 cm^{-1} resulting from asymmetric and symmetric of imide ring C=O, which confirmed the complete imidization. The characteristic absorption band of POSS can be observed at 1103 cm^{-1}, which also confirm the incorporation of OAPS in PI/POSS nanocomposites by FTIR.

4. The dielectric constants and densities of the nanocoposites were decreased as OAPS loading increase and as the amine groups per one OAPS decreased. The lowest dielectric constant was 2.75 for PI150-10, but PI/POSS films of OAPS loading at 125% and 150% exhibited the poor mechanical properties. It can be seen that the optimum OAPS loading for synthesis PI/POSS films were at 100%. The dielectric constant and densities of PI/POSS films at 100% OAPS loading were 2.83 and 1.237 g/cm^3 for PI100-4 < 3.09 and 1.304 g/cm^3 for PI100-10 < 3.19 and 1.417 g/cm^3 for PI100-18.

5. The mechanical properties of PI/POSS nanocomposites were improved by incorporation OAPS. The nanocomposites' tensile strength and modulus increased while the amount of amine group increased. Both tensile strength and tensile moduli of PI/POSS nanocomposites at 100% OAPS loading are 72.1 MPa, 2.31 GPa (PI100-4) < 90.2 MPa, 2.67 GPa (PI100-10) < 94.4 MPa, 3.06 GPa (PI100-18).

6. From the thermogravimetric analysis (TGA), the nanocomposites exhibited the good the thermal stability. At 100% OAPS loading, the thermal degradation (T$_{d,5\%}$) were 443ºC for pure PI < 449 ºC for PI100-4, < 450 ºC for PI100-10 and < 460 ºC for PI100-18. The temperature

increased while the OAPS loading and the amount of amine group increased.

6.2 Recommendations

From the experiments, the thicknesses of films should be controlled because they strongly affected on the analysis result. Moreover, Coefficient of Thermal Expansion (CTE) from Thermalmechanical analysis (TMA) should be measured in order to study the complete effects on thermal properties to PI/POSS nanocomposites.

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APPENDICES

APPENDIX A

DETERMINE QUATITATIVE OF AMINE GROUP

IN OAPS BY TITRATION

Table A-1 Data from titration

	weight (g)	Mw	volume $HClO_4$	mol	mol of NH_2 group
ODA1[a]	0.001	200	1.7	0.000005	0.00001
ODA2[a]	0.0022	200	2	0.000011	0.000022
ODA3[a]	0.0034	200	2.3	0.000017	0.000034
ODA4[a]	0.0056	200	2.6	0.000028	0.000056
ODA5[a]	0.0114	200	3.4	0.000057	0.000114
ODA6[a]	0.0225	200	4.6	0.0001125	0.000225
OAPS	0.0056	1153.7	**3.0**	4.85395E-6	C[b]

a is data for calibration curve
b : calculated from calibration curve
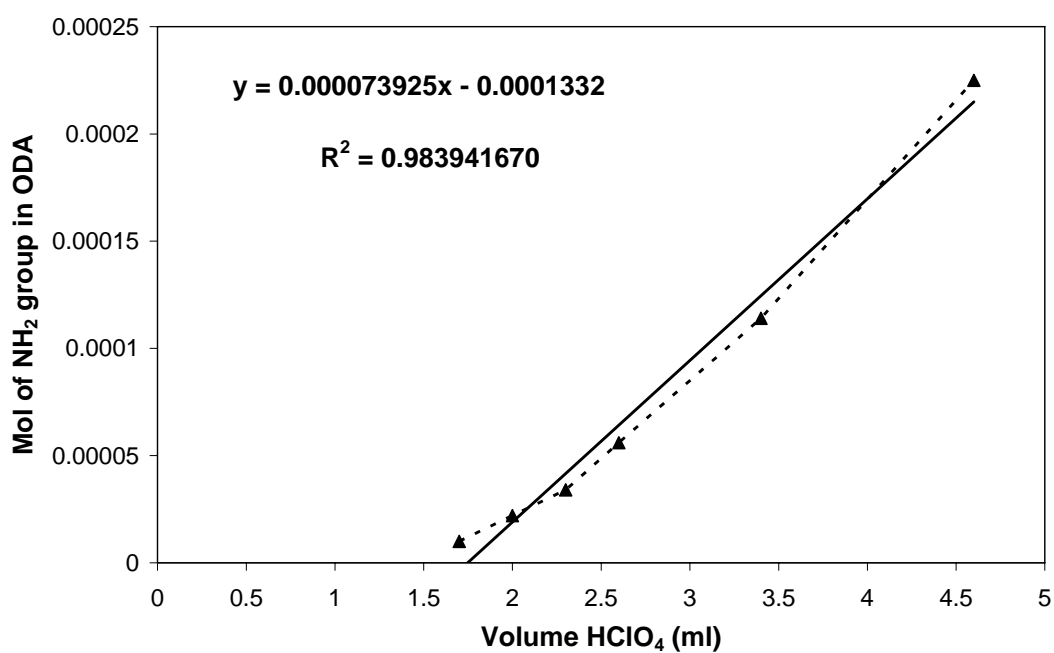
Figure A-1 Calibration curve of ODA.

From;

$$y = 0.000073925x - 0.0001332$$

Determine mol of NH_2 group in OAPS;

$$C = 0.000073925*(3.0) – 0.0001332$$

$$C = 8.8575E-5$$

Determine the amount of NH_2 group in OAPS (D)

$$D = (\text{mol of } NH_2 \text{ group in OAPS})/(\text{mol})$$

$$D = (8.8575E-5)/(4.85395E-6)$$

$$D = 18.2$$

The amount of HN_2 group in OAPS is 18 groups   ##

APPENDIX B

DYNAMIC MECHANICAL ANLYSIS (DMA) CHARACTERIZATION

These DMA diagrams showed E', E", and tanD at various frequencies of each sample.
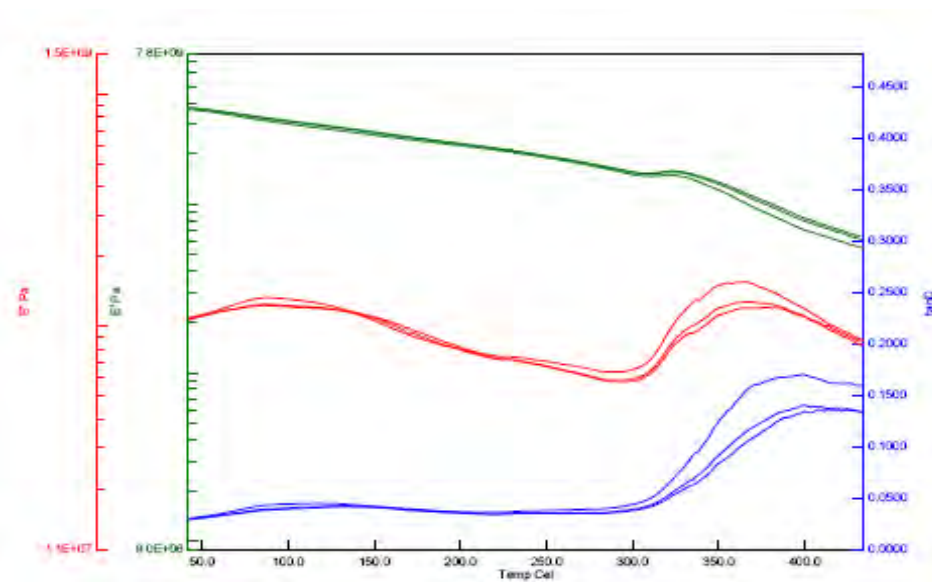
Figure B-1 DMA diagram of pure polyimide
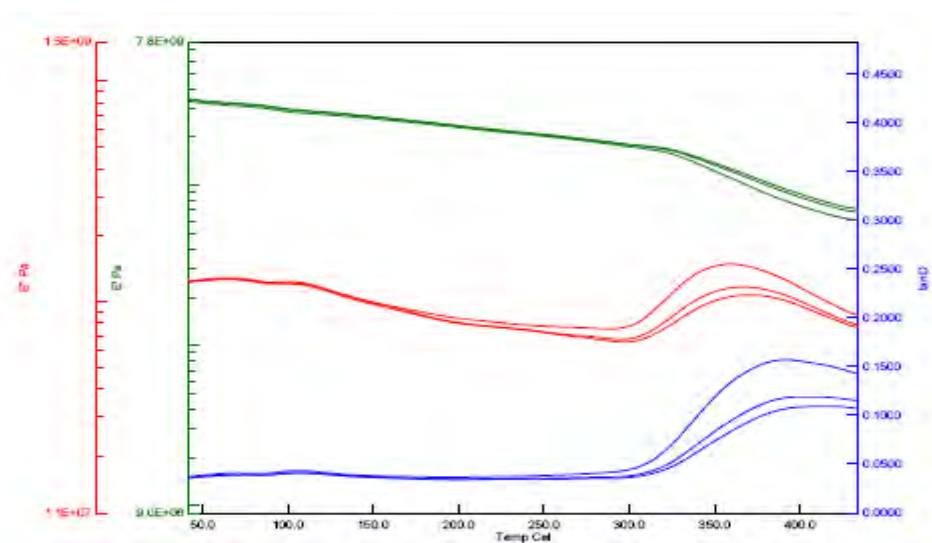
Figure B-2 DMA diagram of PI50-4
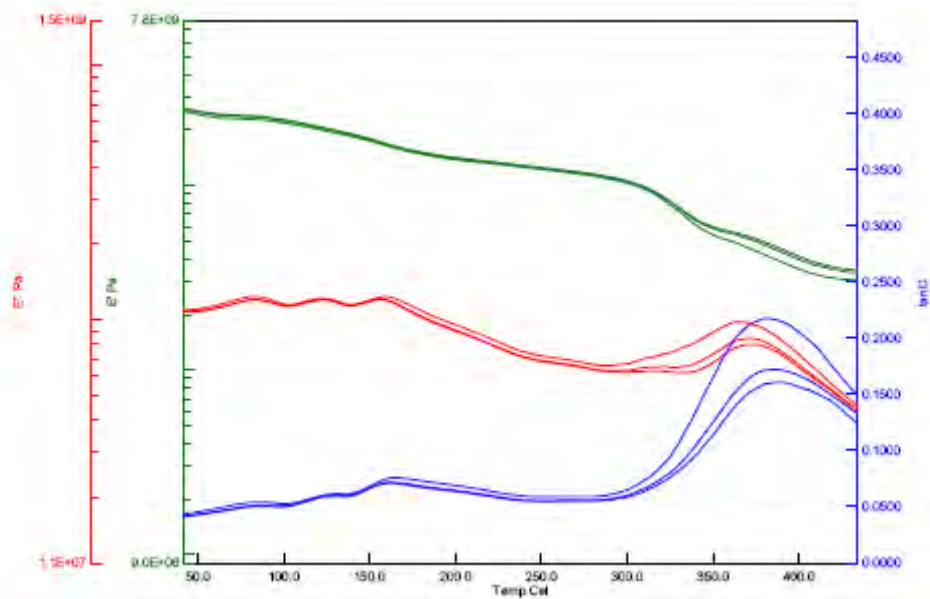
Figure B-3 DMA diagram of PI50-10.
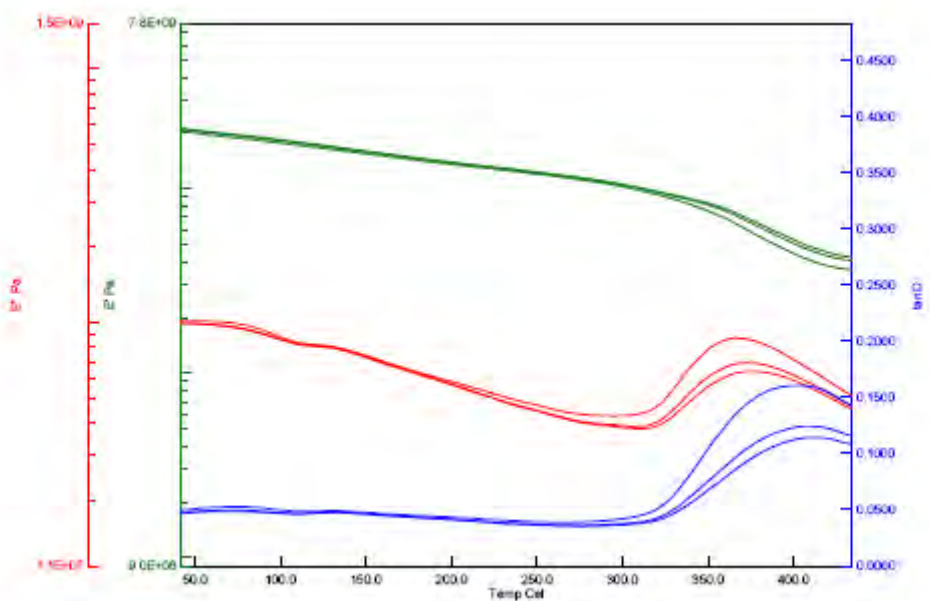
Figure B-4 DMA diagram of PI50-18.
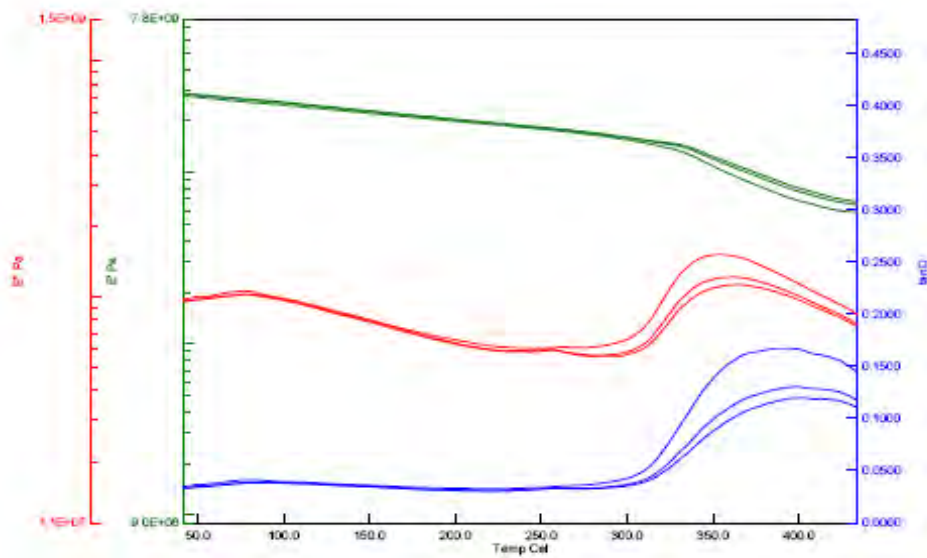
Figure B-5 DMA diagram of PI75-4.
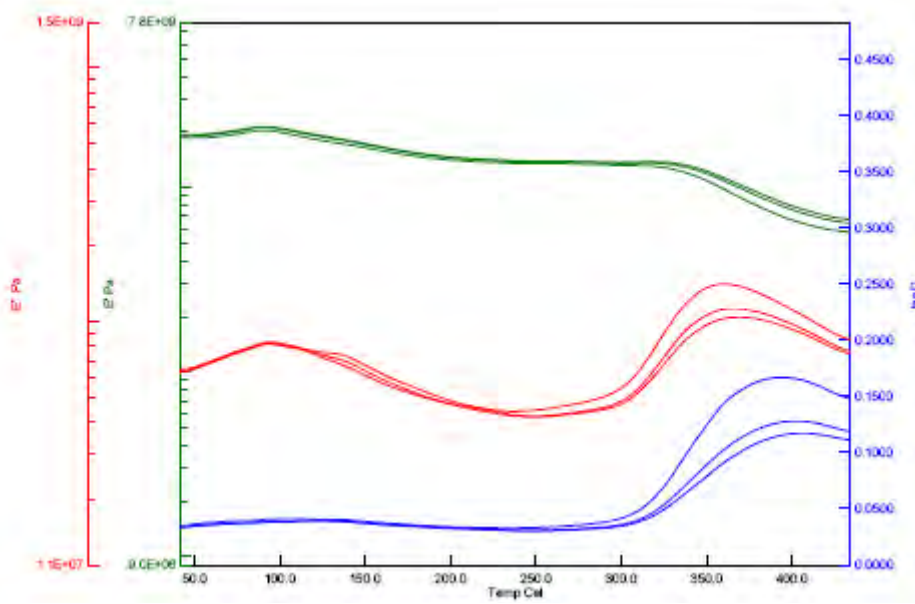
Figure B-6 DMA diagram of PI75-10.
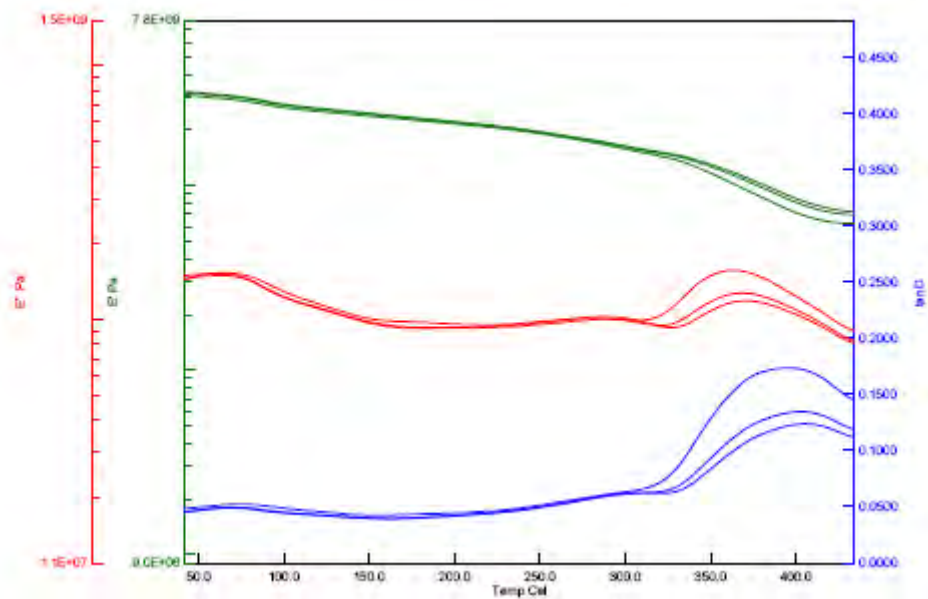
Figure B-7 DMA diagram of PI75-18.

APPENDIX C

THERMALGAVIMETRIC ANALYSIS (TGA)
CHARACTERIZATION
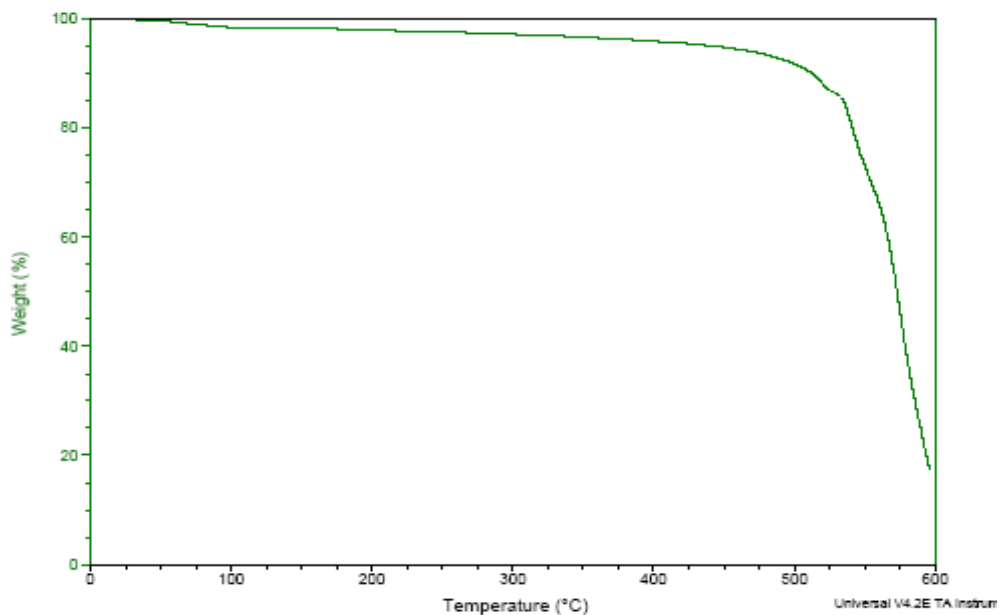
Figure C-1 TGA curve of pure polyimide
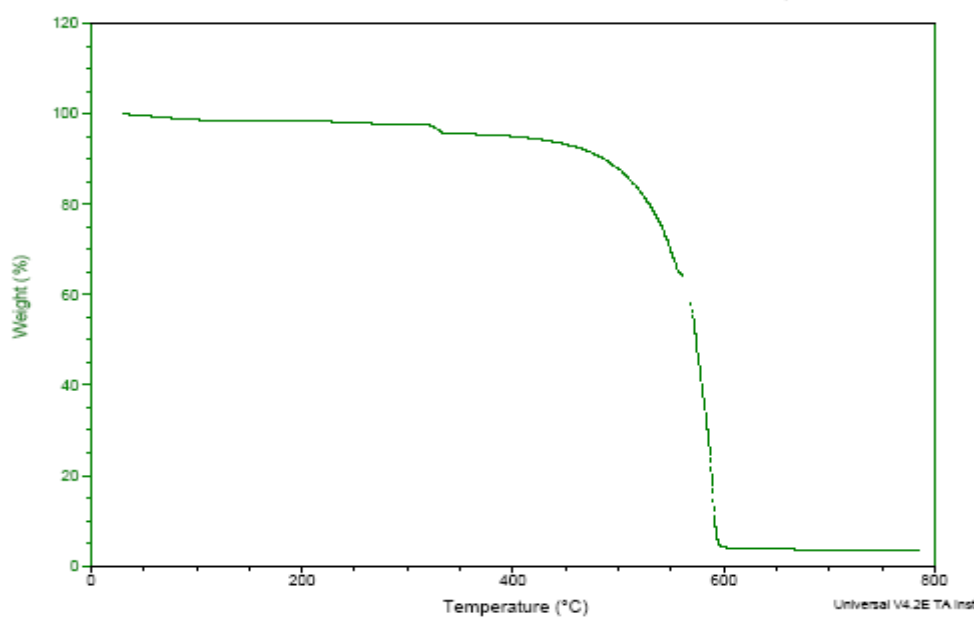
Figure C-2 TGA curve of PI50-4
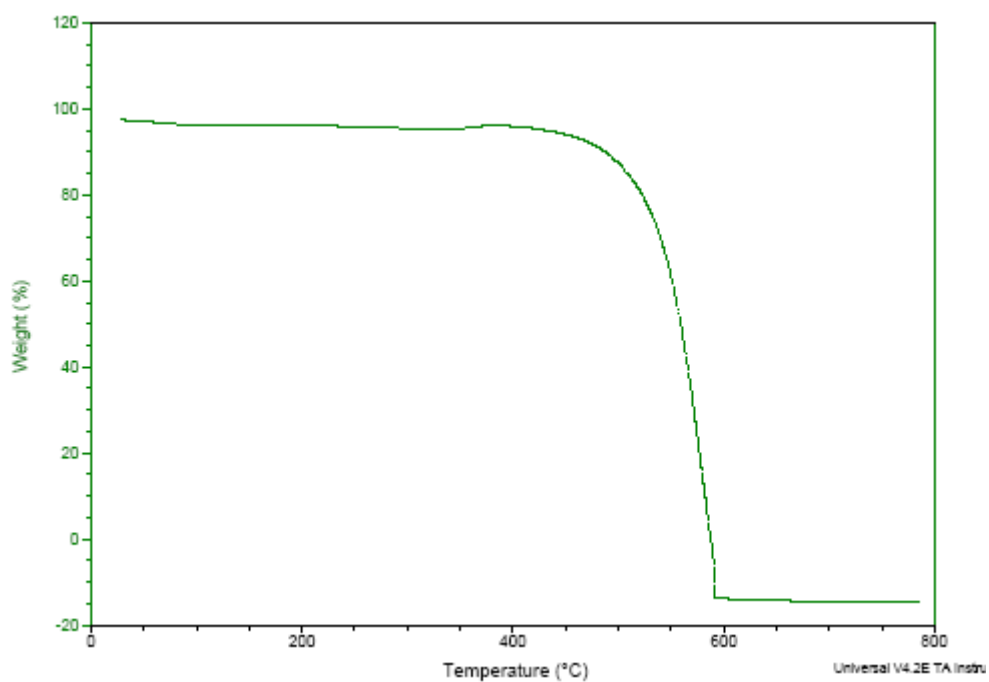
Figure C-3 TGA curve of PI50-10.
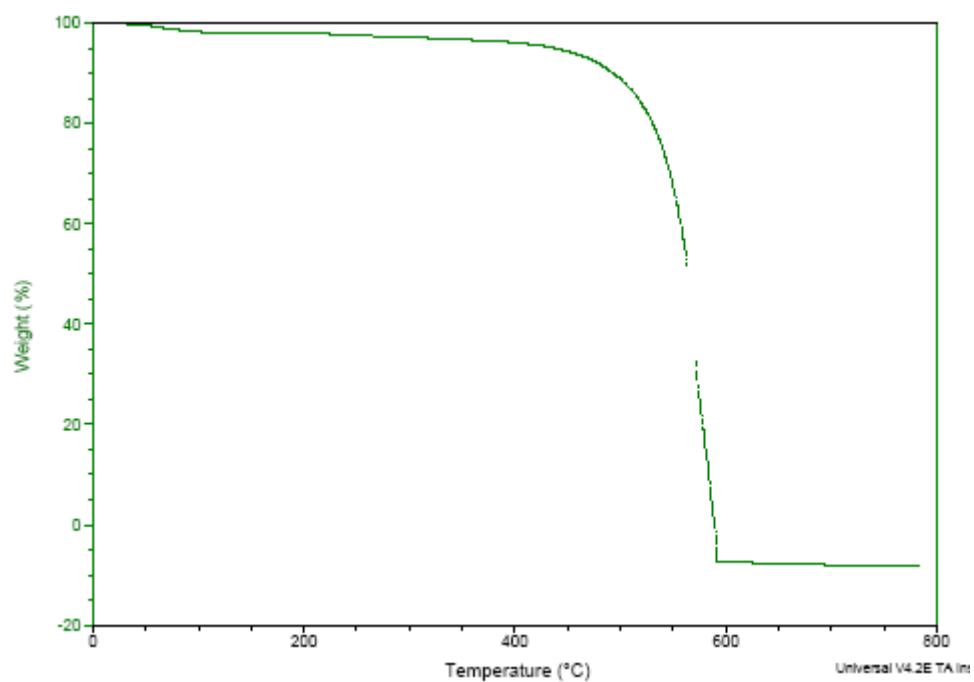
Figure C-4 TGA curve of PI50-18.
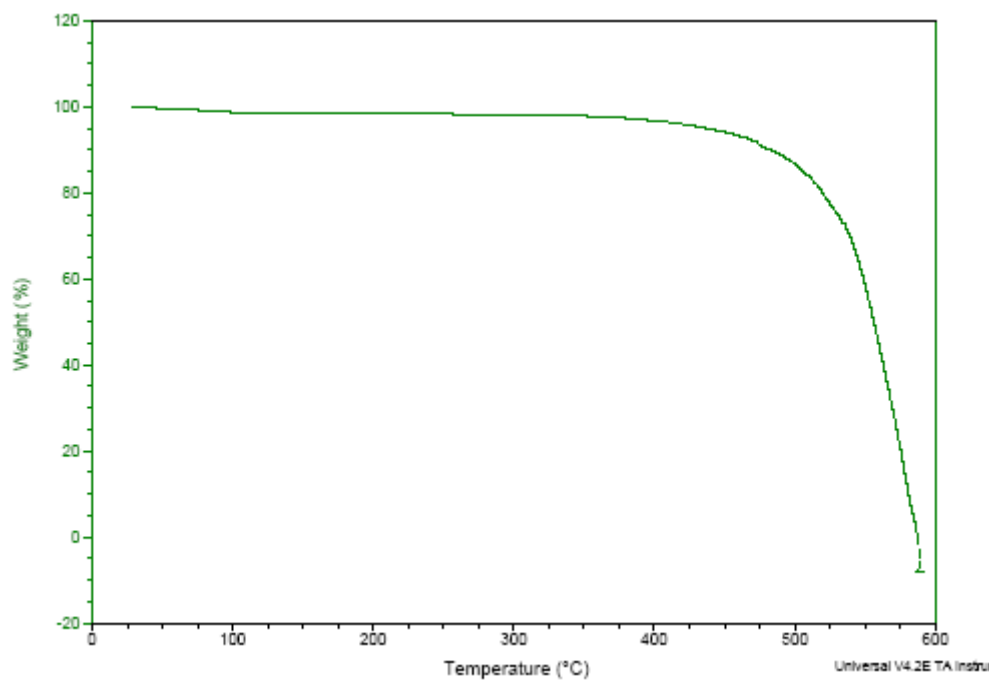
Figure C-5 TGA curve of PI75-4.
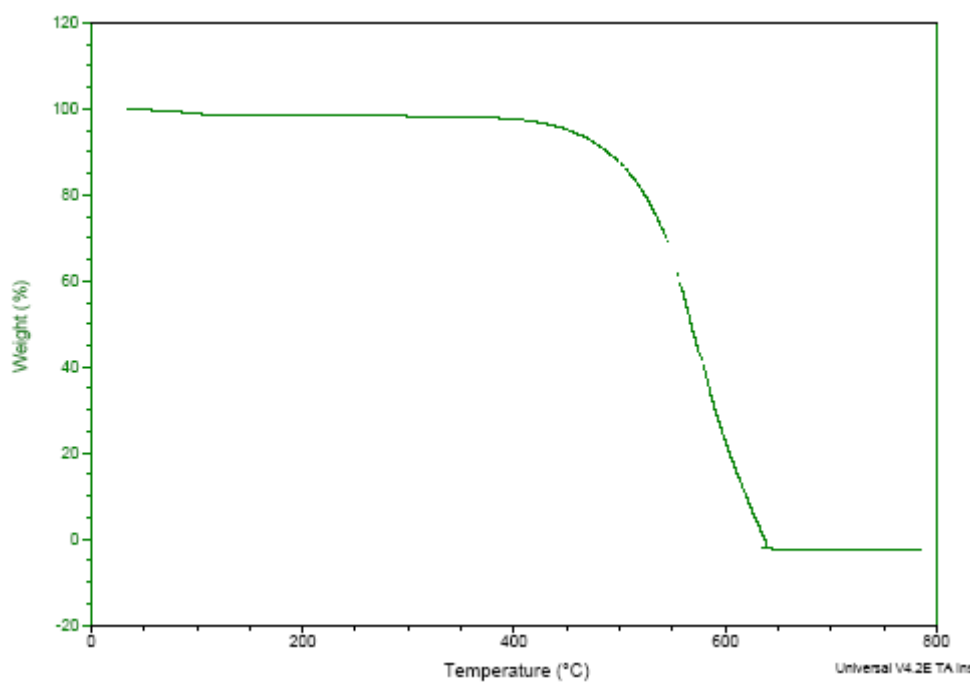
Figure C-6 TGA curve of PI75-10.
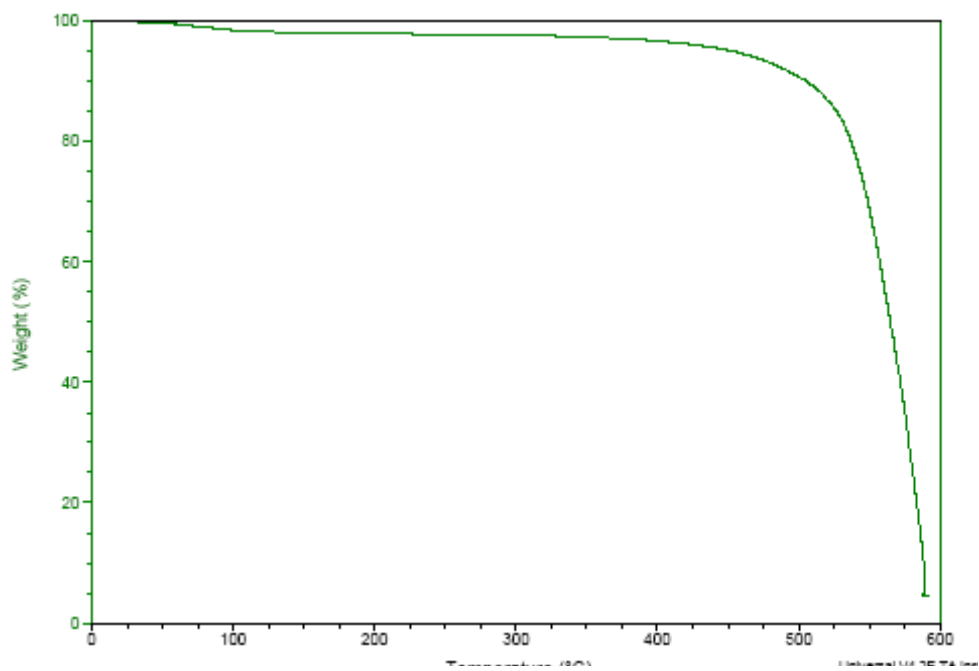
Figure C-7 TGA curve of PI75-18.
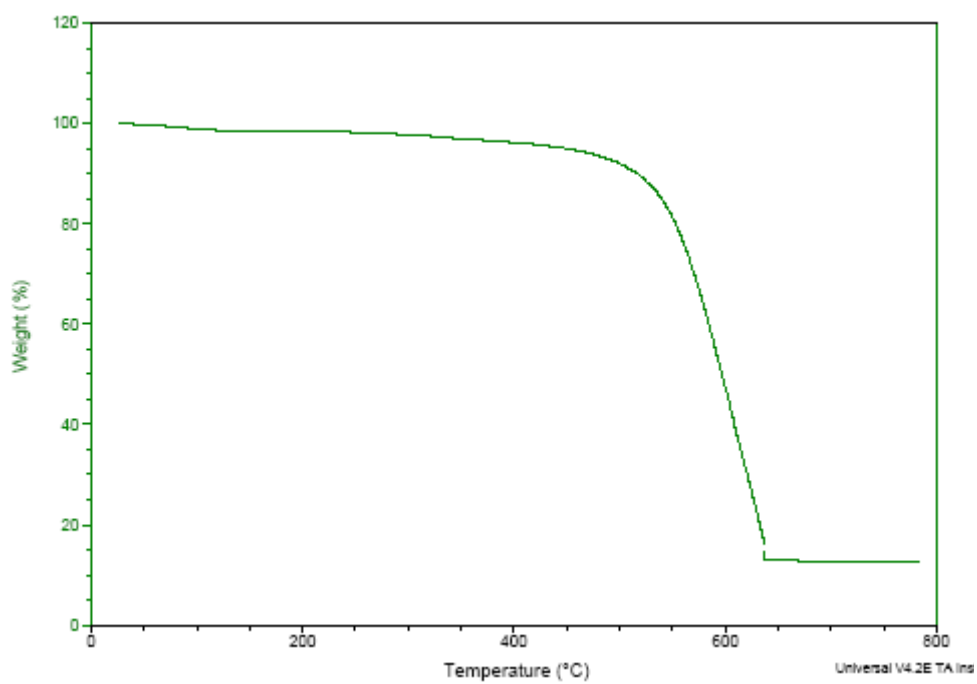
Figure C-8 TGA curve of PI100-4.
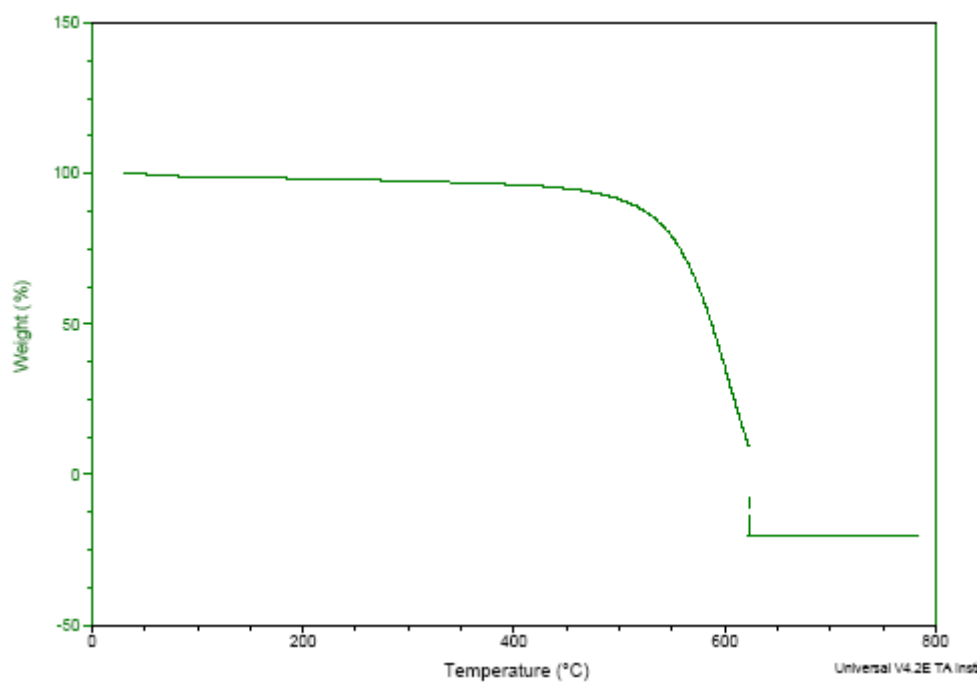
Figure C-9 TGA curve of PI100-10.
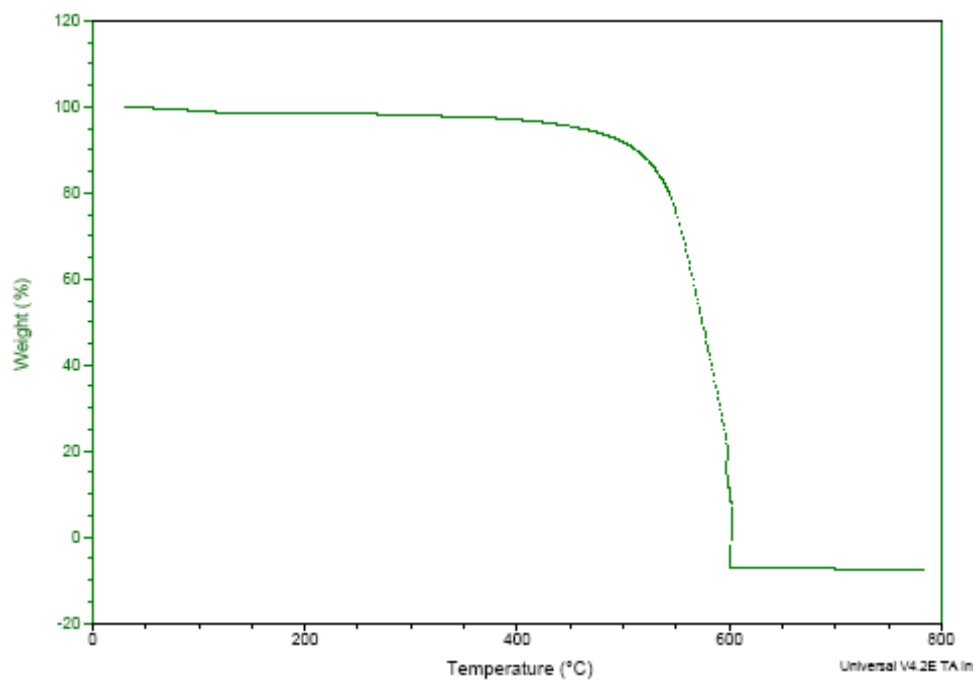
Figure C-10 TGA curve of PI100-18.
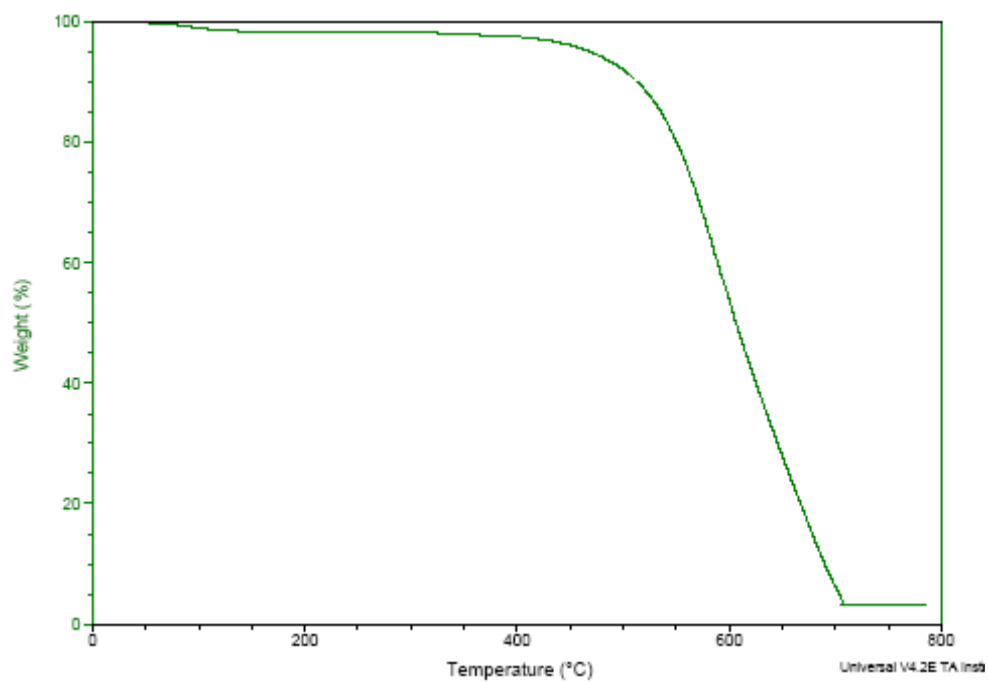
Figure C-11 TGA curve of PI150-10.
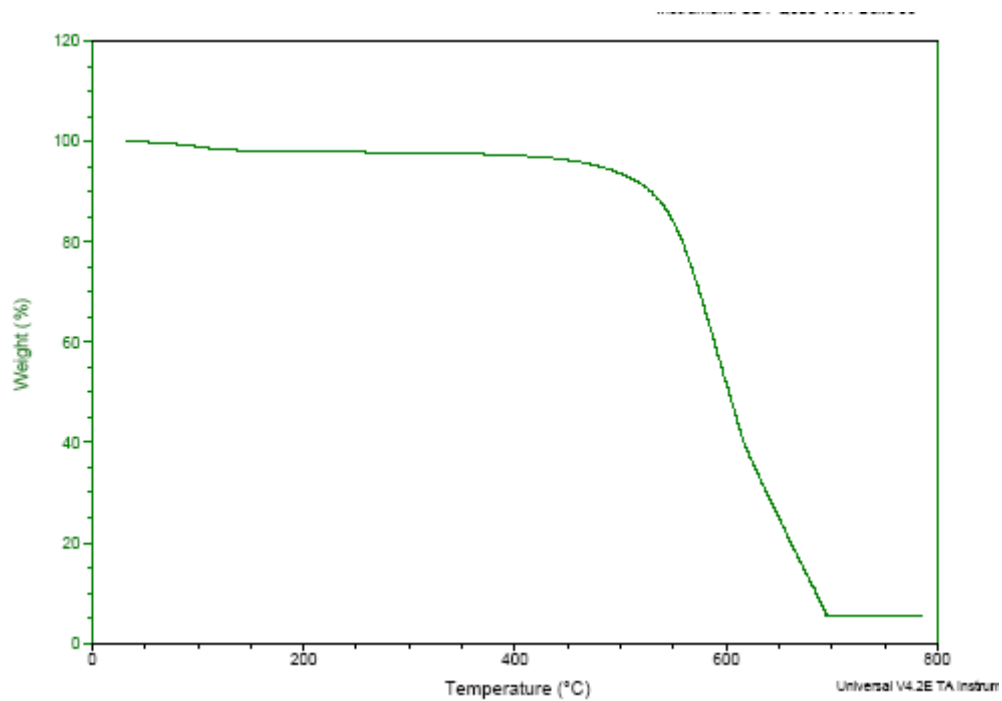
Figure C-12 TGA curve of PI150-18.
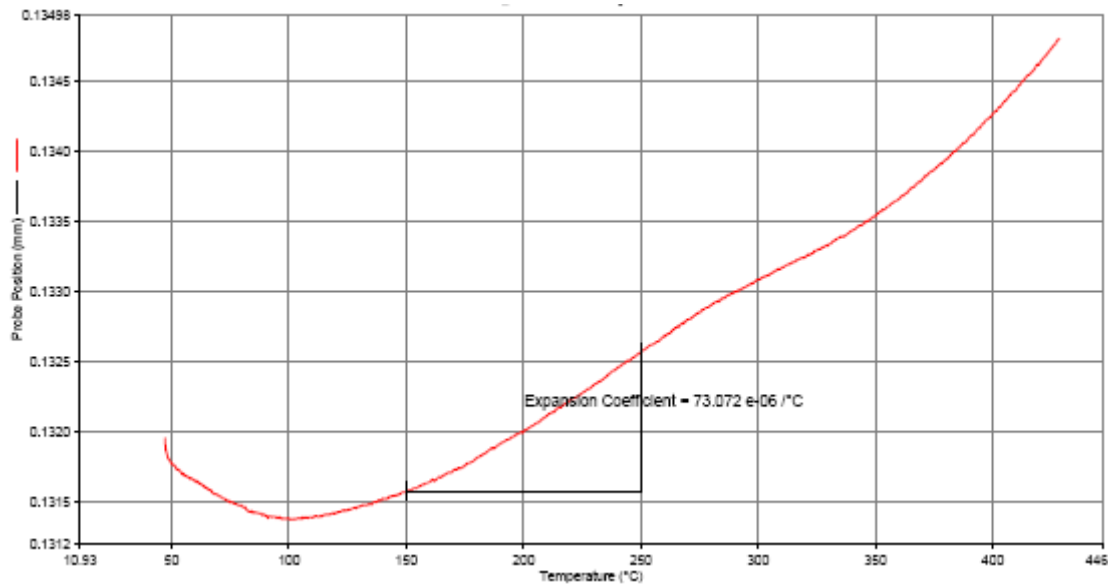
APPENDIX D

THERMALMECHANICAL ANALYSIS (TMA)
CHARACTERIZATION
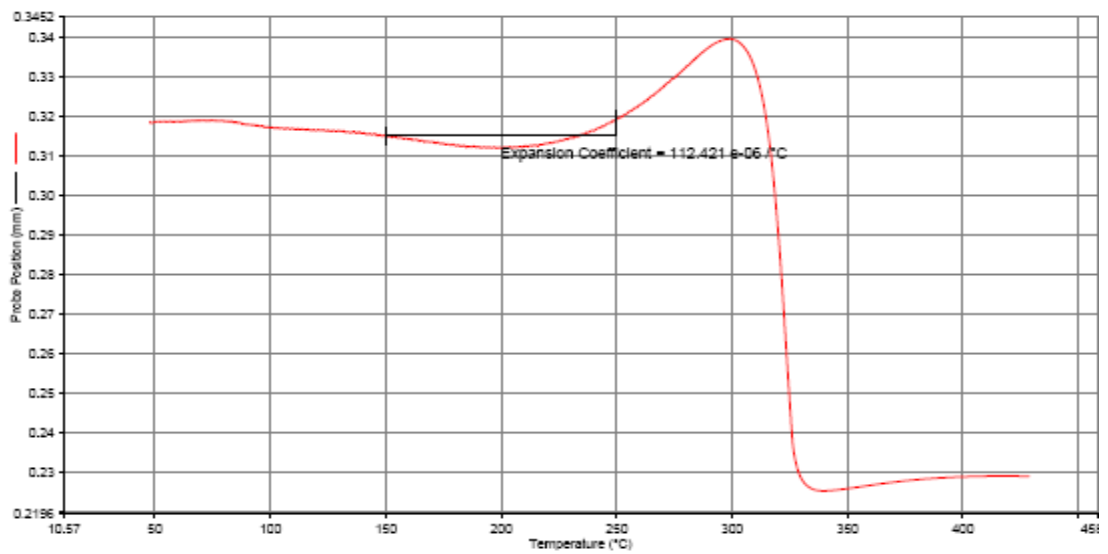

Figure D-1 TMA curve of Kapton^R (50 mN)

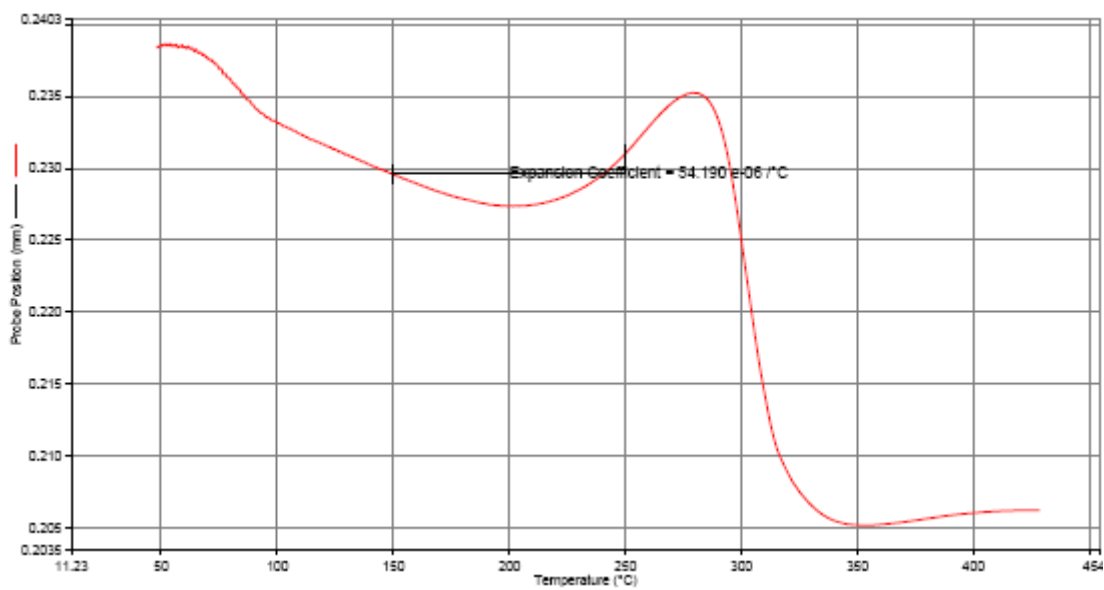**Figure D-2** TMA curve of pure polyimide (50 mN)

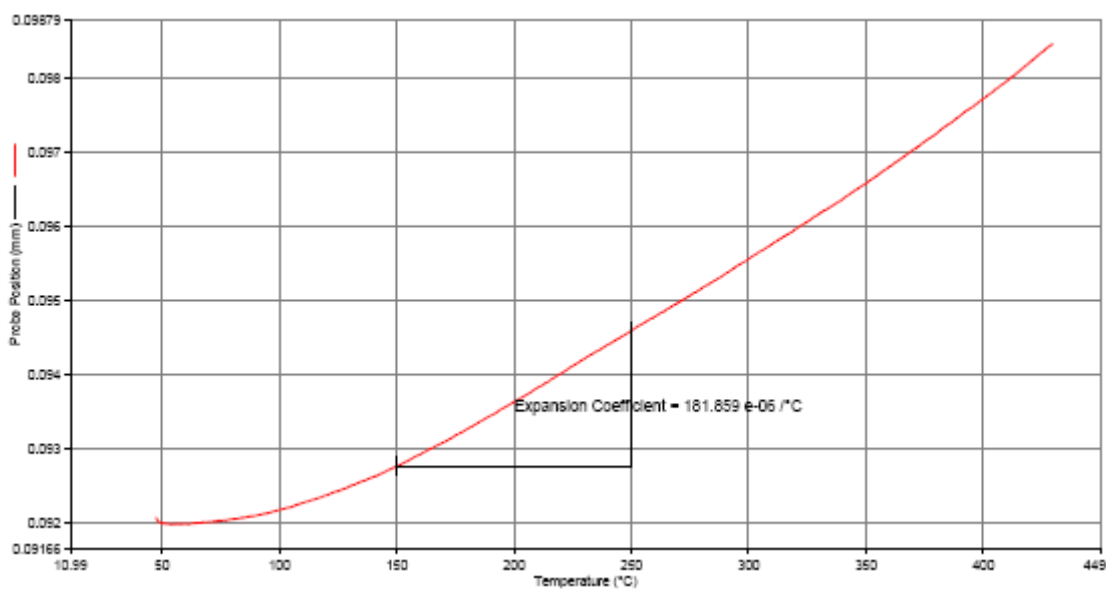**Figure D-3** TMA curve of PI100-4 (50 mN).

Figure D-4 TMA curve of Kapton^R (500 mN).

VITA

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