CHAPTER II

THEORIES

The basic theories about this work were mentioned here such as polyimide definition, type of polyimide polymerization, polyhedral oligomeric silsesquioxanes (POSS), polyether characteristic and branched system.

2.1 Polyimide

Most of the developments in modern polyimide chemistry can be traced to pioneering work at DuPont in the 1950s and 1960s.
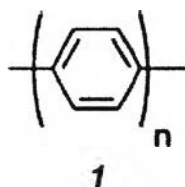

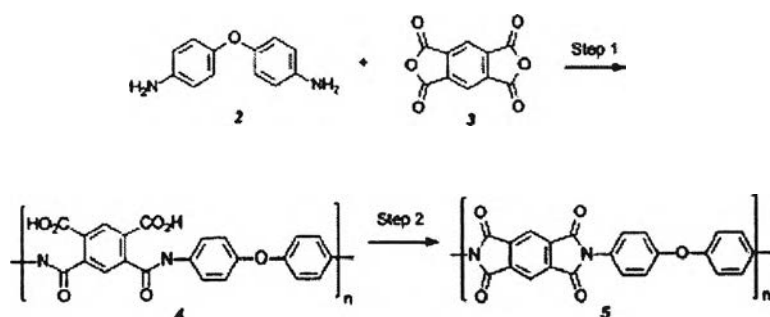**Figure 2.1** Poly (p-phenylene)

Figure 2.2 Two-step condensation polyimide synthesis, shown here for PMDA/ODA

These efforts revolved around the modification of nylon chemistry to produce polyimides in a two-step process [5] (Figure 2.2) that involved the condensation of an aromatic diamine, **2**, and dianhydride, **3**, to form poly(amic acid), **4**, followed by cyclodehydration to the polyimide, **5**. Research at DuPont led to the development of Pyralin™ soluble polyimides for use as wire coatings and Kapton-H™ polyimide

films. Since that time, a variety of condensation polyimides have been developed by many researchers in the United States, Japan, Europe, and the former USSR [6].

A major application of condensation polyimides is as thin films in electronics packaging, wire insulation, and gas separator membranes. However, condensation polyimides have also been used as composite matrix resins. A good example of this is DuPont's Avimid N, **8** (Figure 2.3) [7]. Avimid N has a Tg close to 360 ± °C, low weight loss, and good retention of mechanical properties after 100 h aging in air at 371 ± °C. However, the evolution of volatile condensation by-products (H_2O) and the low flow of this system render it difficult to process. While Avimid N was once considered to be a prime candidate for high-temperature composite applications, interest in this material has waned due, in large part, to these processing problems.

Addition-curing polyimides were investigated beginning in the early 1970s in an attempt to improve the processability of condensation polyimides without adversely affecting their stability and high-temperature performance.
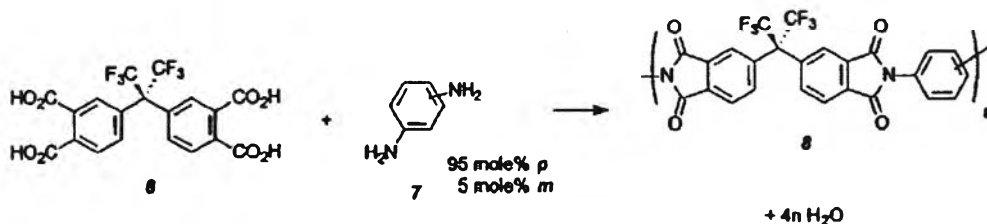

Figure 2.3 Avimid N chemistry.

2.1.1 One-step polymerization

A single-stage homogeneous solution polymerization technique can be employed for polyimides which are soluble in organic solvents at polymerization temperatures. In this process, a stoichiometric mixture of monomers is heated in a high boiling point solvent or a mixture of solvents in a temperature range of 140-250°C where the imidization reaction proceeds rapidly. Commonly used solvents are nitrobenzene,benzonitrile, α-chloronaphthalene, o-dichlorobenzene, trichlorobenzenes and phenolic solvents such as m-cresol and chlorophenols in addition to dipolar aprotic amide solvents. Toluene is often used as a cosolvent to facilitate the removal of the water of condensation. During polymerization, water is distilled off continually as an azeotrope along with the solvent. Preparation of high-molecular-weight

poly(amic acid) is not necessary in this procedure. Imidization still proceeds via amic acid intermediate. However, the concentration of amic acid group is very small at any time during the polymerization because it is unstable at high temperature and rapidly imidizes, or reverts to amine and anhydride. Because water is formed as the result of the imide formation, some of the anhydride groups are rapidly hydrolyzed to *o*-dicarboxylic acid. When a mixture composed of diamine, dianhydride, and a solvent is heated, a viscous solution is formed at intermediate temperature of 30-100 °C. The composition of the product is mainly poly(amic acid). At this stage, phase separation is usually observed in nonpolar solvents such as chlorinated aromatic hydrocarbons. However, on raising the temperature to 120-160 °C, a vigorous evolution of water occurs and the reaction mixture suddenly becomes homogeneous. At this stage the product is essentially a low-molecular-weight polyimide having *o*-dicarboxy and amino end groups. Thereafter, a slow stepwise polycondensation takes place according to the reaction between the end groups [8].

2.1.2 Formation of polyamic acids

When a diamine and a diahydride are added into a dipolar aprotic solvent such as *N,N*-dimethylacetamide, polyamic 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.

The most important aspect of this process is that it is an equilibrium reaction. 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 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 acid)s.

2.1.3 Reactivity of monomers

As mentioned earlier the mechanism of poly(amic acid) formation is a nucleophilic substitution reaction at one of the carbonyl carbon atoms of the dianhydride with diamine. Therefore, it is expected that the reaction rate is primarily governed by the electrophilicity of the carbomers are used in the beginning. If an additional dianhydride equivalent to the unreacted amino group is added to the above solution, it reacts with the amino end groups and the molecular weight increases. Although the high molecular weight of poly(amic acid) solutions is generally preferred in terms of process requirement for applications as films and coatings, it is not necessarily good to use additional dianhydride. Although the orthodicarboxylic acid group is inactive at ambient temperature, it thermally dehydrates to the anhydride and reacts with amine at higher temperatures, thus creating an off-stoichiometric situation with the dianhydride in excess. The molecular weight of poly(amic acid) intermediate is not important for one-step homogeneous high-temperature solution polymerization and the melt polymerization of polyimides. The molecular weight of the polyimide product is primarily determined by the stoichiometric relation of the monomers.

2.1.4 Thermal imidization of polyamic acid

Conversion of poly(amic acid)s to the corresponding polyimides it most commonly performed thermally in "solid state." This method is suitable for preparation of thin objects such as films, coating, fibers, and powders in order to allow the diffusion of by-product and solvent without forming bristles 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 (Tg) 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 intermediate stages of thermal imidization. The presence of residual solvent plays an important role. The imidization proceeds faster in the presence of dipolar amide solvents. The

observation is attributed to the specific salvation to allow the favorable conformation of amic acid group to cyclize. It may be also 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-carboxyamide 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, and it has not been possible to describe it by simple kinetic expression. The imidization process involves several interrelated elementary reactions, and dynamically changing physical properties such as diffusion rate, chain mobility, salvation, and acidity.

The imidization proceeds rapidly at the initial stage and tapers off at a plateau as same as a typical diffusion-limited kinetic process. As the degree of imidization increases, the Tg or stiffness of the polymer chain increase. When the Tg approaches the reaction temperature, the imidization rate slows down markedly. At a higher temperature, a higher degree of imidization is attained.

The initial rapid stage of imidization is attributed to the ring closure of amic acid in the favorable conformation. The slower rate in the later stage of imidization is attributed to the unfavorable conformation, which has to rearrange to conformation before ring closure.

2.2 Thermal curing in polyimide 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 aprotic 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 temperature in excess of 300 °C (thermal imidization) or through the addition of chemical dehydrating agents (chemical imidization). 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. 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.

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

Films can be prepared by removing the coating from the substrate anytime after steps 4, 5 or 6. Patterning of the coating is accomplished with the aid of a photoresist in the case of conventional (nonphotosensitive) polyimides, or by direct exposure of photosensitive polyimide coatings. All processing should be performed in standard clean room conditions to ensure defect-free coatings. A temperature controlled to 20-25 °C and a relative humidity between 40 and 50% are sufficient. Water acts as a plasticizer for polyimides and can affect the development of the polymer morphology. Therefore, the relative humidity should be controlled to within 5%.

2.2.1 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. The dehydration baked at 200 °C or higher may be necessary to remove adsorbed moisture.

2.2.2 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 or added as a separate processing step. To investigate the effect of the adhesion promoters on either the curing process or the properties of cured films or coating, 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.

2.2.3 Solution deposition

The objective of this step is to provide a uniform, defect-free polymeric coating over the surface of the substrate. The precursor solution can be deposited onto the substrate by a variety of techniques that are standard in the coatings industry, including spin coating, applicator blade coating, spray coating, roller coating, and dip coating. The morphology of the cured coating or film may be influenced by the technique used to deposit the solution and form the coating.

2.2.4 Drying

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 drying rate.

2.2.5 Spin Coating and Applicator Blade Coating (Casting)

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 or by slowly rotating the substrate while depositing a small quantity of the solution into the center of the substrate. 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.

The thickness, uniformity, and morphology of the film or coating are controlled by the solvent composition, polymer composition, molecular weight, solution concentration (viscosities), acceleration of the substrate, spin speed (angular velocity), spin time, and the environmental conditions(e.g., temperature, relative humidity, exhaust flow rate, etc.). For a given concentration, increasing the spin speed decreases the coating thickness. At constant spin speed, the coating thickness increases with increasing concentration. For a given precursor system with constant molecular weight and composition, the coating thickness depends only on the solution concentration and the spinning conditions.

Applicator Blade Coating (Casting) technique often used to prepare samples in the laboratory is applicator blade coating. 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 application 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 coating of uniform thickness.

2.2.6 Curing

This 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.

The parameters that must be controlled to ensure proper curing of the polyimide include the polymer composition and molecular weight; 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.). For a given polyimide with constant molecular weight and composition, the variables that control the drying process are time, temperature, and drying rate.
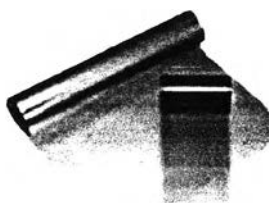

Figure 2.4 Polyimide film

2.3 Structures of dianhydride

2.3.1 Pyromellitic dianhydride (PMDA)

- Molecular Formula $C_{10}H_2O_6$
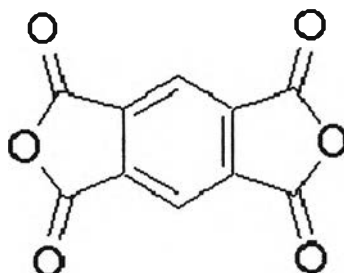- Molecular Weight 218.12

Figure 2.5 PMDA

2.3.2 (6 FDA) 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride

- Molecular Formula $C_{19}H_6F_6O_6$
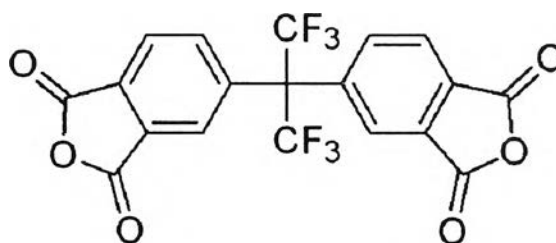- Molecular Weight 444.24

Figure 2.6 6 FDA

2.3.3 (BPDA) 3,3',4,4'-Biphenyltetracarboxylic dianhydride
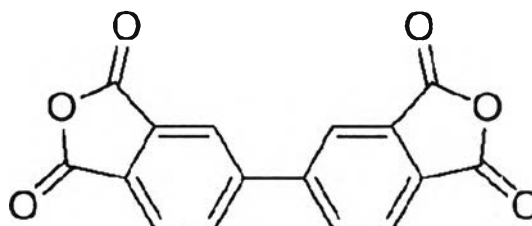
- Molecular Formula $C_{16}H_6O_6$
- Molecular Weight 294.22

Figure2.7 BPDA

2.4 Structures of diamine

2.4.1 3,4'- Oxydianiline (3,4'-ODA)

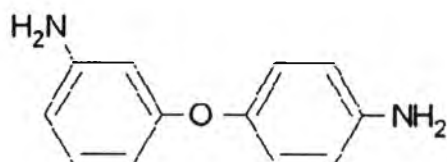- Molecular Formula $O(C_6H_4NH_2)_2$
- Molecular Weight   200.24

Figure 2.8 3,4'-ODA
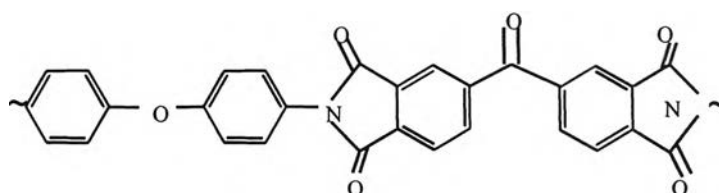
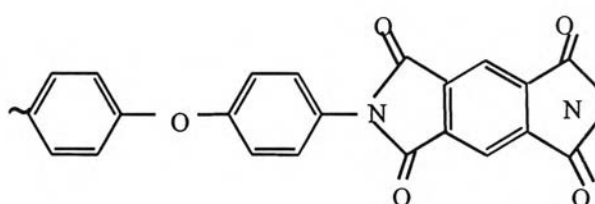## 2.5 Structures of polyimide

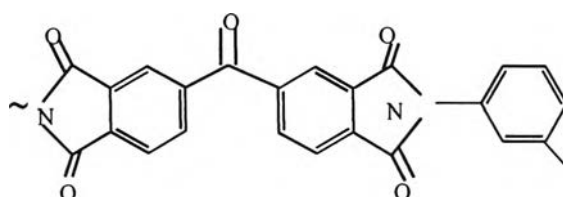**Figure 2.9**   BTDA-ODA

Figure 2.10 ODA-PMDA

Figure 2.11 BTDA-PDA

2.6 Properties of polyimide

- Thermosetting or Thermoplastic
- Crystalline,Semi-crystalline or Amorphorous polymer Kapton Polyimide
- Density 1.42 g/cm^3
- Max. Operating Temp. 260 °C
- Flexural Modulus 2.48 GPa
- Tensile Strength 72 MPa
- Dielectric Strength 22 MV/m

ADVANTAGES/DISADVANTAGES

Classification	Advantages
Characteristic	Molecular design suitable to need
	Purification
	Heat resistance and Low smoke emission
	Chemical resistance
	Low dielectric constant
Technological	Elasticity, absorption of mechanical stress

Disadvantages
Expensive
High moisture absorption and penetration
Poor resistance to alkali and hydrolysis

2.7 Dielectric properties

The dielectric requirements extracted from these considerations are first, low dielectric constant (between 2.0 and 3.5) over a very wide frequency range from DC to well into the GHz range. The dielectric constant, ε, should not at all, or only slightly, vary with frequency over the whole frequency range. Second, the dielectric loss tangent, tan δ_ε or dissipation factor, should be below 0.01 and independent of frequency.

Dielectric measurements are made mostly by parallel plate capacitance methods, which however, cover only a range of 0.1 kHz-1 MHz but allow variation of temperature over a wide range. Several methods for measuring dielectric constants at higher frequencies (usually at room temperature) are available but are not widely used. Fortunately, in most polyimide the dielectric constant does not vary significantly with frequency (on the order of 1.0). Some fluorocontaining polyimides, however, exhibit significant (on the order of 0.3-0.5) variations of dielectric constant, ε, with frequency.

Measurements of dielectric constants of thin polyimide films depend critically on the thickness uniformity of the film. Consequently, literature values are often inconsistent. A further source of methodical error can occur by insufficient contact between sample and electrodes, which can be eliminated by evaporation of thin layers of noble metals through masks onto both sides of the sample. This, however, can introduce another error caused by metal diffusion into the polyimide. In some cases metal diffusion can be avoided by high metal deposition rates. Furthermore, absorbed water can cause significant changes in ε up to a value of 0.5, depending on the overall water uptake of the polyimide. Finally errors can arise through contact resistance, edge effects, and pin holes. The many error sources are the origin for the large variations (up to 0.7) in ε found in the literature for identical polyimides.

A further complication arises in rigid-rod-like polyimides such as BPDA-PDA. In the presence of substrates all polyimides orient with respect to the substrate. The effect, however, is largest in polyimides of the rigid-rod type. Consequently, many of their properties are anisotropic. Refractive index measurements show clearly that these anisotropies are quite large. The relationship between refractive index and dielectric constant suggests that in such rigid-rod-like polyimides the dielectric constant in the plane is significantly higher than that perpendicular to the plane. The ε values obtainable by parallel plate capacitance measurements are always for the direction perpendicular to the film plane, that is, only the z-directional value can be measured. From birefringence values the differences between in-plane and out-of-plane dielectric constants are predicted to be 0.8 for BPDA-PDA and 1.0 for TPDA-PDA. Differences of this magnitude for the in- and out-of-plane dielectric constants of BPDA-PDA have been measured recently by using transmission lines and THz

spectroscopy. At 1-2.5 THz the in-plane dielectric constant was found to be 2.92±0.02 and the out-of-plane value was 3.69±0.08. With transmission lines (frequency range:10^3-10^6 Hz) the out-of-plane value was measured to be 3.7±0.24 for 1.2 μm thick conductor lines and polymer filled gaps of 1.5-3.5 μm. The magnitude of this anisotropy depends on the stiffness of the polymer backbone and on the film thickness. In more flexible polyimides the influence of the substrate is also observable but only in very thin films. In such materials (such as 6FDA-ODA), the refractive index is film-thickness-dependent below a certain film thickness. However, the birefringence observed in these films is much smaller and the dielectric constant difference can, for most packaging purposes, be neglected.

Table 2.1 Key requirement for electronics packaging dielectrics

Property	Comments
Dielectric constant	as low as possible; frequency independent
Dielectric loss	as low as possible; frequency independent
Stress	as low as possible either by matched CTE or low modulus
CTE	low if high modulus material
Modulus (usually Young's modulus)	low if high CTE material
Elongation-at-break	large>10%
Adhesion	good to metal, substrate, and self
Thermal stability (isothermal weight loss)	high (low outgasing, no degradation)
Glass transition temperature	high for low CTE polymer, low for low modulus polymer
Solvent up-take	as low as possible
Water up-take	as low as possible
Compatibility with other materials	No detrimental chemical reaction with other materials should occur
Ionics content	as low as possible; electromigration should not occur
Planarization	as high as possible

2.8 Mechanical properties

The material selection for a variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength [16]. These values are normally derived from the technical literature provided by material suppliers.

The basic understanding of stress-strain behavior of polymer is of almost importance to design engineers. One such typical stress-strain diagram is illustrated in Figure 2.12
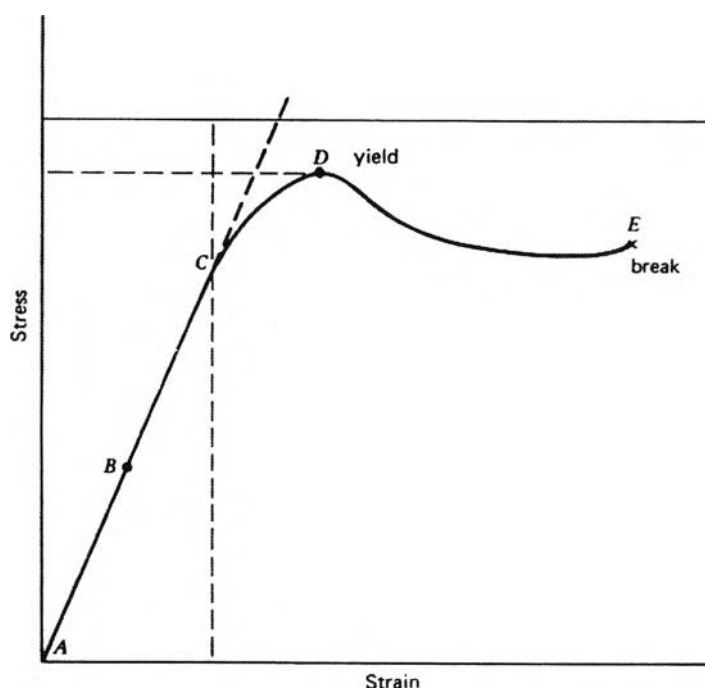

Figure 2.12 A typical stress-strain curve [16].

For a better understanding of the stress-strain curve, it is necessary to define a few basic terms that are associated with the stress-strain diagram.

2.8.1 Type of Stress-Strain Curve

The polymeric material can be broadly classified in term of their softness, brittleness, hardness, and toughness. The tensile stress-strain diagram serves as a basic for such a classification. Figure 2.13 illustrates typical tensile stress-strain curve for several type of polymer. The area under curve is considered as the toughness. Table 2.2 lists characteristic features of stress-strain curve as they relate to the polymer properties.
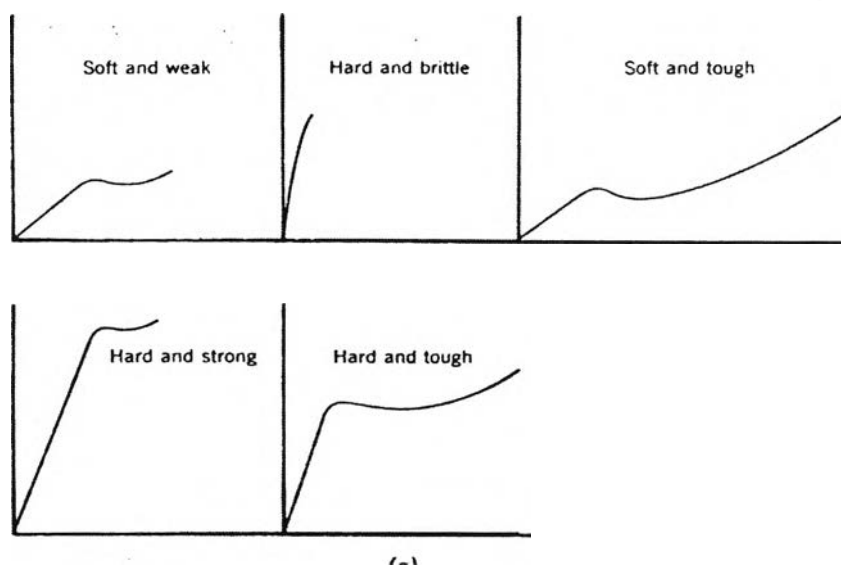
Figure 2.13 Types of stress-strain curve [16].

Table 2.2 Characteristic features of stress-strain curve as they relate to the polymer properties.

Description of polymer	Modulus	Yield stress	Ultimate strength	Elongation at break
Soft, weak	Low	Low	Low	Moderate
Soft, tough	Low	Low	Yield stress	High
Hard, brittle	High	None	Moderate	Low
Hard, strong	High	High	High	Moderate
Hard, tough	High	High	High	High

2.8.2 Tensile Tests

Tensile elongation and tensile modulus measurements are among the most important indication of strength in a polymer and are the most widely specified properties of polymer. Tensile test is normally a measurement of ability of a polymer to withstand forces that tend to pull it apart and to determine to what extent the polymer stretches before breaking. Tensile modulus, an indication of the relative stiffness of a polymer, can be determined from stress-strain diagram.
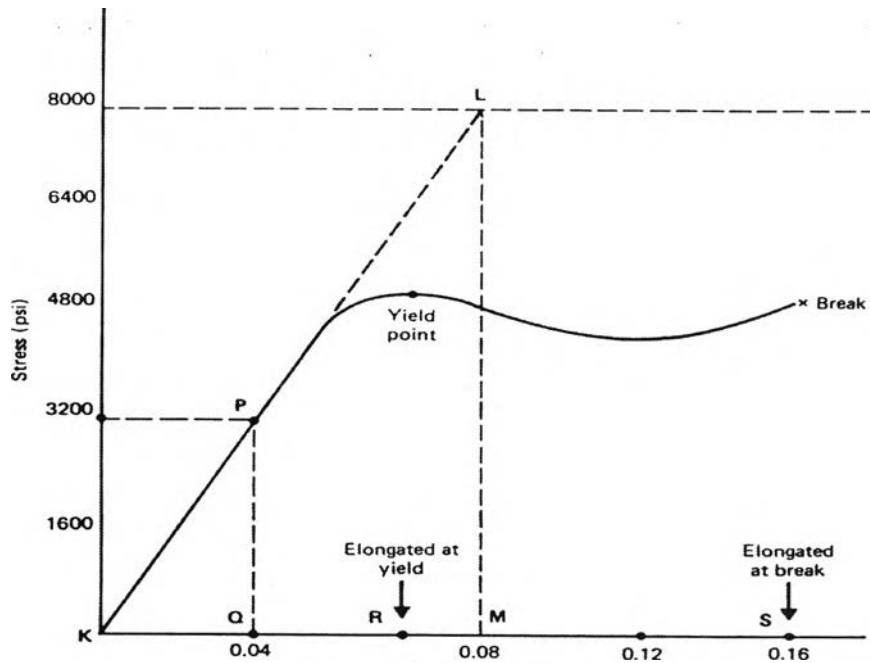
Figure 2.14 Diagram illustrating stress-strain curve form which modulus and elongation values are derived [16].

2.9 Dynamic mechanical analysis [18]

2.9.1 Introduction to dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is becoming more and more commonly seen in the analytical laboratory as a tool rather than a research curiosity. This technique is still treated with reluctance and unused, probably due its importation from the field of rheology. Rheology, the study of the deformation and flow of materials, has a reputation of requiring a fair degree of mathematical sophistication. Although many rheologists may disagree with this assessment, most chemists have neither the time nor the inclination to delve through enough literature to become fluent. Neither do they have an interest in developing the constituent equations that are a large part of the literature. However, DMA is a technique that does not require a lot of specialized training to use for material characterization. It supplies information about major transition as well as secondary and tertiary transitions not readily identifiable by other methods. It also allows characterization of bulk properties directly affecting material performance.

Depending on whom you talk to, the same technique may be called dynamic mechanical analysis (DMA), forced oscillatory measurements, dynamic mechanical thermal analysis (DMTA), dynamic thermomechanical analysis, and even dynamic rheology. This is a function of the development of early instruments by different specialties (engineering, chemistry, polymer physics) and for different markets. In addition, the names of early manufacturers are often used to refer to the technique, the same way that "Kleenex" has come to mean "tissues". DMA will be used to describe the technique of applying an oscillatory or pulsing force to a sample.

2.9.2 Basic principles

DMA can be simply described as applying an oscillating force to a sample and analyzing the material's response to that force. This is a simplification which needed further discussion. From this, one calculates properties like the tendency to flow (called viscosity) from the phase lag and the stiffness (modulus) from the sample recovery. These properties are often described as the ability to lose energy as heat (damping) and the ability to recover from deformation (elasticity). One way to describe what we are studying is the relaxation of the polymer chains. Another way would be to discuss the changes in the free volume of the polymer that occur. Both descriptions allow one to visualize and describe the changes in the sample.

2.10 POSS [19]

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. 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. The work also covers studies in the field of interfacial bonding compatibility, dispersion characteristics, ionic mobility and gelation effects. Studies on gelation, tether

structure and length are also presented. A brief overview of likely applications of POSS containing nanocomposites will be given.

2.10.1 Properties and Applications of POSS

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.
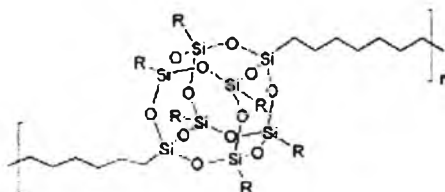
Figure 2.15 POSS

The POSS-based polymers can be roughly classified into three categories. One category is the 'cross-linked' architecture in which the POSS cage contains more than two multi-functional 4 polymerizable groups. Although these functional groups can form three-dimensional network materials, few of these materials can be characterized in detail because nearly all of these precursors are octafunctional, such as methacrylate and epoxy-functional R8T8. Essentially none of these materials is soluble. The second category is the 'bead-type' architecture in which two functional or active groups incorporate the T8-type cage into the backbone of polymer. Finally, the third category is the 'pendant-type' architecture, in which the single functional POSS can be polymerized as a monomer or a comonomer using the standard method of polymerization. These monomers or macromonomers include POSS-silanol, POSS-norbornenyl, POSS-acrylate, POSS-styrene, and POSS-bisphenol A systems. Other functional groups that have been employed in the preparation of hybrid materials include olefines, epoxies, imides, siloxanes, methacrylates and vinyl esters. Resultant nanocomposites include (but are not limited) to polystyrene, polysiloxanes, polyacrylates, polynorbornanes, and polyurethanes. The POSS nanocomposites are

designed to help create hybrid polymeric materials that have higher thermal and chemical stability than traditional polymers yet retaining the polymer's processibility and commodity. Dissimilar to typical inert additives, POSS directly binds to the polymer chains. A majority of the POSS molecules added to polymers have cubic Si-O cages, with 8 Si atoms forming the corners of the cube and 12 O atoms bridging each Si atom. The inner cage can be represented as $(SiO_{1.5})_8$ and is ~0.45 nm in diameter. They also generally contain seven inert functional groups (i.e., cyclohexane or cyclopentane) for solubility purposes and one reactive functional group, *e.g.* ester, epoxy, olefin or nitrile for linking to the polymer chain. In this respect, POSS nanostructured materials differ from other nanofillers in a number of aspects. Structurally, POSS units are precisely defined by their molecular architecture, unlike other nanofillers that possess relatively imprecisely defined structural units with distributions in both size and shape. An additional attractive characteristics is the ability to tailor properties of the molecule by attaching a variety of functional groups to the corners of the cage via the tetravalent Si atoms.

2.10.2 Properties of POSS nanocomposites

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 physical properties, such as impact strength or elongation at break performance even at relatively low concentrations of nanofiller. In general, nanocomposite materials incorporate extensive interfacial interactions that can result in nonlinear changes in composite properties. These changes can be so great that the rule-of-mixtures approximation, commonly used to estimate macroscopic composite properties. Thus, nanocomposites offer potential access to completely new classes of materials with unique properties. Regrettably, one of the most difficult problems in chemistry of nanomaterials is in developing synthetic and processing approaches that precisely define the volume and shape of the individual phases and their arrangement. Such efforts are needed to generate nanocomposite materials that permit one to probe how small changes in nanostructure affect macroscopic properties. A wide variety of octafunctional cubes have been prepared with polymerizable moieties that offer access to highly cross-linked nanocomposites (thermosets) having controlled porosities with high surface

areas, novel mechanical properties, and high thermal stabilities. In a complementary fashion, POSS materials offer access to robust thermoplastics with good-to-excellent properties including resistance to atomic oxygen.

2.10.3 Thermal properties

The introduction of the inorganic POSS promises to improve fire resistance, thermal properties and also act as mechanical reinforcements. POSS molecules are typically stable up to 300°C, which is higher than the thermal degradation temperatures of most organic macromolecules. Since the POSS derivatives containing amine functional groups can play the role of surfactants for the treatment of clays, the thermal stability of the resulting nanocomposite is generally enhanced. Also, there is experimental evidence that the polymer thermo-oxidative stability is increased by crystallization of POSS pendant groups. Small quantities of POSS (2%) in the hybrid polymer can markedly increase the Tg of the resultant polyhydroxystyrene (PHS) matrix.

2.10.4 Dielectric properties

The covalently tethering nanoporous POSS to presynthesized polyimide chain ends or the side chains results in organic-inorganic nanocomposite materials with much lower dielectric constant and controllable mechanical properties. The approach has also other limitations in that it requires particular functional groups to be present in polyimide to react with POSS. However, the dielectric constant of the resulting nanocomposites could be tuned by varying the molar ratio of POSS. Later work by the same researchers adopted a copolymer approach to directly synthesize polyimide-tethered POSS by the copolymerization of a diamine monomer, POSS-diamine, along with other diamines and dianhydride monomers. This copolymer approach provided a versatile way to design a variety of polyimide nanocomposites with a wide range of dielectric constants.

2.10.5 Applications

POSS have been regarded as new generation of high performance materials since they combine the advantages of the inorganic materials such as rigidity, high stability and the organic polymers flexibility, ductility and processibility. Moreover, in comparison with macroscopic composites made of the same component phases

they usually exhibit nonlinear changes in optical, electrical, electro-optical and thermal-mechanical properties. POSS nanocomposites are of considerable interest for among other articulate characteristics, their optical and electronic applications in addition to their thermal and mechanical stability, optical transparency, loading high functionality and easy processability. A large number of methods for the synthesis of these organic–inorganic nanocomposites with enhanced properties for real device applications have been reported. The POSS nanocomposites are likely to find applications in new nano- and mesoporous materials because of their utility and potential utility in many fields, e.g. as catalysts and catalyst supports due to high surface area and chemical functionality, dielectric materials for electronic applications, media for optics due to capability to incorporate chromophores, sensor and selectively permeable membranes. POSS nanocomposites also possess functionalities that make them good ligands for catalysts and advanced structured materials.

2.11 Branched systems

Branched and star polymers have lower intrinsic viscosities and better solubility than linear systems of the same molecular weight. This is particularly true for dendrimers, where the intrinsic viscosity tends to increase with increasing molecular weight, until it reaches a limiting value, whereupon it decreases. This is believed to be due to a change in molecular morphology from rod-like (low molecular weight) to globular (high-molecular weight). Branching and starred structures have been incorporated in polyimides, primarily to increase Tg. However, Jensen has recently shown that PETI-5 modified by the inclusion of small amounts of a trifunctional monomer, triaminopyrimidine, had a significantly lower melt viscosity (600 poise at 335 ± °C versus 10,000 poise for PETI-5 at 371 ± °C). The Tg of the modified system is higher than PETI-5 (291 versus 263 ± °C), and the mechanical properties of films prepared with this polyimide are better. An interesting approach to branched systems involves the use of a rotaxane as a means of mechanically cross-linking or branching polymer such as polyurethane. This self-threading approach to branching has also been employed with polyacrylates. While neither of these systems has the Tg and stability for use at high temperatures, it is likely that such an approach could be adapted for polyimides.

2.12 Polyurethane [11]

Polyurethanes are the results of the exothermal reaction between a polyisocyanate and a molecule containing two or more alcohol groups (-OH). Isocyanates contain a reactive group that can be made to react with –OH groups. Thus, if we react a diisocyanate with a molecule with an –OH group at each end, we create a basic building block of polyurethane; a prepolymer.

Notice that the ends of the prepolymer molecules are isocyanate groups. These are subsequently reacted to produce the solid foams and elastomers. As such, the material is usually a high-viscosity liquid. All polyurethanes go through this reaction, but this step might be immediately followed by the reaction that produces the foam or other finished product. In the so-called one-shot process, the isocyanate and polyol, as well as catalysts, crosslinkers, surfactants and blowing agents are blended together in one step and deposited into a mold or other receptacle for the reaction.

$$O=C=N-R-N=C=O + HO-(R'-O)x-H$$

$$O=C=N-R-N-\underset{\underset{O}{\|}}{C}-(R'-O)-\underset{\underset{O}{\|}}{C}-N-R-N=C=O$$
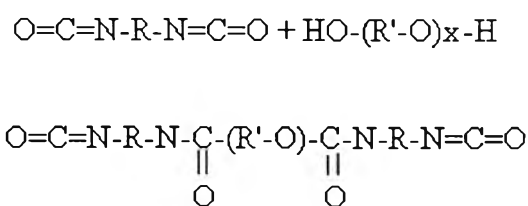
Figure 2.16 Prepolymer reaction

2.12.1 Isocyanate [12]

Isocyanates with two or more NCO groups in the molecule are needed for the formation of polyurethanes. Aromatic as well as aliphatic and cycloaliphatic di- and poly-isocyanates are suitable building blocks for polyurethane chemistry, the aromatic types being volumewise the more important. Reasons for this are that the aromatically linked isocyanate group is a significantly more reactive group than the aliphatic one and also that, in general terms, the aromatic isocynates are economically more readily available. Aliphatic isocyanates are only used if their reactivity fits specifically the polymer formation or if special properties are required regarding the final products. For example, light stable coating can only be obtained with aliphatic polyisocyanates.

There are also significant reactivity differences within the same class of isocyanates. These differences originate from their structure, from influences of substituents, and from steric effects which can be also play an important role. For example, in the case of 2,4-diisocyanato toluene, the isocyanate group which is in para position to the methyl group is significantly more reactive than the isocyanate group in the ortho position (the factor is about 2.5). Also, the reactivity of the second NCO group of a diisocyanate can change after the first one has reacted during polyurethane formation.
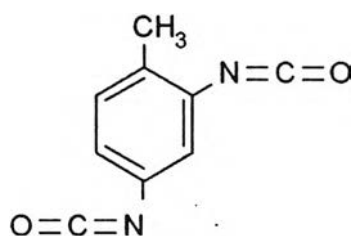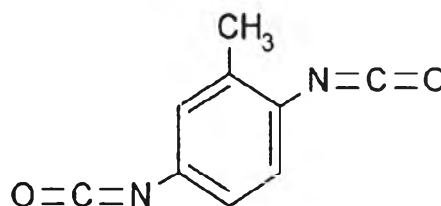
Figure 2.17 2, 4 -TDI   **Figure 2.18** 2, 5 -TDI
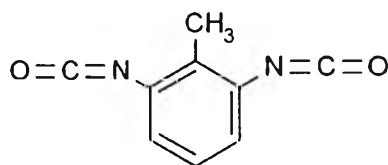
Figure 2.19 2,6 – TDI

2.13 ether

Ether is the general name for a class of chemical compounds which contain an ether group — an oxygen atom connected to two (substituted) alkyl groups. A typical example is the solvent and anesthetic diethyl ether, commonly referred to simply as "ether", (ethoxyethane, CH_3-CH_2-O-CH_2-CH_3).

2.13.1 Physical properties

Ether molecules cannot form hydrogen bonds among each other, resulting in a relatively low boiling point comparable to that of the analogous alcohols. However, the differences in the boiling points of the ethers and their isometric alcohols become

smaller as the carbon chains become longer, as the hydrophobic nature of the carbon chain becomes more predominant over the presence of hydrogen bonding.
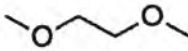
Ethers are slightly polar as the C - O - C bond angle in the functional group is about 110 degrees, and the C - O dipole does not cancel out. Ethers are more polar than alkenes but not as polar as alcohols, esters or amides of comparable structure. However, the presence of two lone pairs of electrons on the oxygen atoms makes hydrogen bonding with water molecules possible, causing the solubility of alcohols (for instance, butan-1-ol) and ethers (ethoxyethane) to be quite dissimilar.
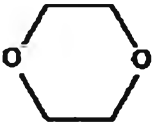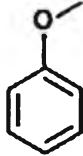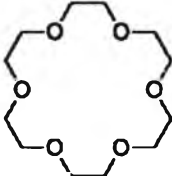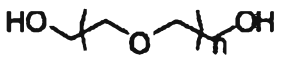
Cyclic ethers such as tetrahydrofuran and 1,4-dioxane are totally miscible in water because of the more exposed oxygen atom for hydrogen bonding as compared to aliphatic ethers.

2.13.2 Polyether

Polyethers are compounds with more than one ether group. While the term generally refers to polymers like polyethylene glycol and polypropylene glycol, low molecular compounds such as the crown ethers may sometimes be included.

Table 2.3 Important ethers

(structure)	Dimethyl ether	An aerosol spray propellant.
(structure)	Diethyl ether	A common low boiling solvent.
(structure)	Dimethoxyethane (DME)	A high boiling solvent:

	Dioxane	A cyclic ether and high boiling solvent.
	Tetrahydrofuran (THF)	A cyclic ether, one of the most polar simple ethers that is used as a solvent.
	Anisole (methoxybenzene)	An aryl ether and a major constituent of the essential oil of anise seed.
	Crown ethers	Cyclic polyethers that are used as phase transfer catalysts.
	Polyethylene glycol (PEG)	A linear polyether, e.g. used in cosmetics: