

CHAPTER II

LITERATURE REVIEWS



2.1 Polyimide

Recently, polyimides have drawn more and more attention because of their important role as dielectric layers in a variety of microelectronic devices. General speaking, they have relatively high glass transition temperatures, high processability, low dielectric constant, high thermal stability, high chemical resistance, and good mechanical properties. Due to the overall of their characteristics, there are many research works explaining many sides of view about polyimide.

Coating thickness effect on the orientation and thermal expansion coefficient of polyimide films was proposed by Jou *et al.* (1992). For films with rigid-rod polyimide, film orientation was especially prominent and decreased significantly as film thickness increased. From experiment, it was observed that the average film orientation decreased and the corresponding thermal expansion coefficient increased with increasing of film thickness.

Pryde (1993) reported an analysis of imide formation using the 1370 cm^{-1} band (C-N stretch) in conjunction with the 1500 cm^{-1} aromatic band as an internal standard. Examination of grazing incidence reflection spectra of ultrathin films of one polyimide on metal substrate indicated that there was a higher degree of imide-group orientation, particularly for films on aluminum. However, analysis of the growth of the normalized C-N band in these spectra indicated that this approach was capable of giving at least semiquantitative measurements of imidization.

The effect of orientation on thermal expansion behavior in polyimide films was suggested by Pottiger *et al.* (1994). Flexible (BTDA-ODA/MPD),

semirigid (PMDA-ODA), and rigid (BPDA-PPD) backbone polyimides were investigated. The backbone stiffness controls the degree of orientation that is developed during cure. The in-plane CTEs varied significantly with orientation ranging from 3 ppm/°C for the rigid BPDA-PPD to 47 ppm/°C for the flexible BTDA-ODA/MPD. A decrease in the in-plane CTEs therefore occurred with an increase in degree of orientation.

Ree *et al.* (1995) reported the relationship between polymer chain orientation and properties. For rigid type of polymers like BPDA-PDA, the thermal expansion and interfacial stress in thin films could not be reduced by the composite formation with silica aerogels having a low thermal expansivity. These properties still changed predominantly with the variation in the polymer chain orientation caused by silica aerogel particulates. However, the optical and dielectric properties were improved utilizing the low dielectric constant characteristics of silica aerogel.

Mascia *et al.* (1995) discussed about influence of siloxane composition and morphology on properties of polyimide-silica hybrids. The results illustrated the role of silica content in depressing the thermal expansion coefficient. These hybrids had both improved tensile strength and elongation at break. Kim *et al.* (1997) made great advance in this subject by providing dielectric properties of inorganic-organic silica-polyimide composite films prepared from tetraethoxysilane (TEOS) and polyimide precursors via sol-gel and thermal imidization processes. As the TEOS contents increased, the dielectric constant also increased. This increment of the dielectric constant was mainly due to the relatively high dielectric silica particles incorporated in the BPDA-PDA polyimide matrix.

Variations of the thermal expansion coefficient of thin polyimide films as a function of film thickness were studied by Saraf and Jordan-Sweet (1997). The effective expansion coefficient of the film decreased with

decreasing thickness. The expansion coefficient of surface or interfacial region was less than one-third the coefficient of the interior of the films.

In addition, polyimides have found widespread application in blending with others conductive polymers due to their superior chemical and mechanical properties coupled with excellent thermal stability. Selampinar *et al.* (1997) prepared polyimide-polypyrrole (PI-PPy) blends. Pyrrole and the dopant ion could easily penetrate through the polyimide matrix. PI-PPy composite films showed high electrical conductivity and electroactivity associated with stability to ambient conditions. Han *et al.* (1999) applied the same concept to polyaniline. The blend showed a more stable thermal behavior.

Beck Tan *et al.* (1998) studied about interface effects on moisture absorption in ultrathin polyimide films. Water absorption in thin films (<1000 Å) of a commercial polyimide adhered to polished silicon substrates was evaluated by monitoring dimensional changes induced by a humid environment. The results of this study showed that the moisture-induced change (percentage) in the thickness of a polyimide film adhered to a substrate depended on the dry film thickness. The use of an interfacial coupling agent has been shown to decrease water absorption, reducing the total moisture-induced swelling in a film of a given thickness.

FTIR study of the imidization process of an ester-type photosensitive polyimide, PMDA-ODA films on silicon wafer substrates, was reported by Li *et al.* (1998). The results indicated that the imidization reaction started near 100 °C and was completed at 270 °C. The IR peak at 588 cm⁻¹ was used to calculate the imidization degree for the first time, and the result calculated by using this peak agreed well with that obtained by the more commonly used peak at 1378 cm⁻¹. There was no evidence of any side reactions occurring along the imidization process. The change in thickness was also measured, and it was found that it shrank by as much as one third

during cure and that the temperature dependence of the thickness agreed very well with the degree of imidization.

Miscibility of polyimide with polymeric primer and its influence on adhesion of polyimide to the primed copper metal was purposed by Yu *et al.* (1999). Polyimide, BPDA-ODA, was synthesized from both poly(amic acid) (PAA) and poly(amic diethyl ester) (PAE) precursors and miscibility behaviors of these precursors with PAEBI, which is a good adhesion primer for copper metal, were investigated. The results indicate that the PAA-PAEBI blend over the whole range of compositions was completely miscible at the molecular level, consequently leading to the miscible PI/PAEBI blend. This miscibility might result from the strong interaction via the complex formation of imidazole groups of the PAEBI and carboxylic acid groups of the PAA precursor. In contrast, the miscibility of PAE/PAEBI blend in NMP was limited to a concentration of 13.5-36.3 wt%, leading to a phase separation. The immiscibility might result from the relative weak interactions of imidazole groups of PAEBI with both ester and amide linkages in the PAE precursor. The difference in the miscibilities of PAEBI with the PAA and PAE precursors was reflected in the adhesion of PI/PAEBI/copper joints. The higher miscibility gave the higher adhesion strength.

Kong *et al.* (1999) explained about effects of coupling agent thickness on residual stress in polyimide/ γ -APS/silicon wafer joints. The largest adhesion strength (780 N/m) was observed in the joint with 11 nm of γ -APS (coupling agent) and residual stress increased with increasing γ -APS thickness.

2.2 Clay

Montmorillonite(MMT) is a type of clay in smectic group made of silicate sheets with a thickness of about 1 nm. It has been reported that some organic compounds such as styrene, acrylic acid, and acrylonitrile may enter between the silicate sheets and undergo polymerization. However its structure is inorganic material while most of polymer is organic material. This is the reason why organically modified silicate layers have become of interest to apply in polymer. Generally, cations between silicate layers are exchanged with protonated form of amine group. Many kinds of amine have been studied in the modified organophilic-clay by intercalation into the space between silicate layers.

Organic compound of bentonite (clay) was prepared by Jordan (1948, 1949). The expansion of silicate layer depended on the length of hydrocarbon. The expansion of layer was multiple of 4 Å, which was about the thickness of one hydrocarbon chain. Moreover, the swelling ability of organic bentonite in various organic solvents was studied. Binary solvents showed better achievement to swell the organic compound of bentonite than monosolvent systems.

Jin-Ho Choy *et al.* (1997) reported the dispersion of quaternary alkylammonium modified montmorillonite in polar and nonpolar solvents. It was showed that the dispersibility of modified montmorillonite depended on compatibility between functional group on the modifying agent and type of solvents.

Yang *et al.* (1999) discussed about influence of intercalation agent on the structure of MMT. The Wide Angle X-ray Diffraction (WAXD) patterns showed the basal spacing of MMT with various intercalation agents. The basal spacing of MMT was increased by the organo-modification. For a

certain type of intercalation agent, the basal spacing of organo-modified MMT increased with length of the alkyl group in an agent.

2.3 Nanocomposite

In the past decade, nanotechnology has gained wide interest in the development of a novel polymeric composite. There has been increasing research about the molecular composite derived from the intercalation of organic polymers into smectic clays. In comparison with conventional polymer-matrix composites, polymer-layered silicate nanocomposites possess the following features: a very small fraction of silicate filler would give significant improvements in the strength and toughness of the materials; the composites possess excellent thermal stability and size stability; and the composite films possess excellent barrier properties.

Polyimide hybrid with montmorillonite clay mineral has been synthesized from dimethylacetamide (DMAC) solution of poly(amic acid) and a DMAC dispersion of montmorillonite intercalated with an ammonium salt of dodecylamine by Yano *et al.* (1993). Montmorillonite consists of stacked silicate sheets about 2000 Å in length, 10 Å in thickness. The organophilic-clay was uniformly dispersed in a polyimide film. This hybrid or nanocomposite material showed excellent gas barrier properties and low thermal expansion coefficient compared to an ordinary polyimide.

Poly(ϵ -caprolactone)-clay nanocomposites using 12-aminododecanoic acid together with concentrated hydrochloric acid as a cation exchanging reagent in sodium montmorillonite (clay) was prepared by Messersmith and Giannelis (1995). The results from Wide-Angle X-ray Scattering (WAXS) showed that the alumino-silicate layers produced fine dispersion in polymer matrix. The significant property of nanocomposites was a reduction in moisture permeability.

Pinnavaia *et al.* (1996) prepared epoxy-clay nanocomposites by *in-situ* polymerization of epoxy resin monomer in different types of organophilic-clay. Both the tensile strength and the modulus increased with increasing clay content. The reinforcement provided by the silicate layers at 15 wt% loading was manifested by a more than tenfold improvement in tensile strength.

Giannelis (1996) prepared poly(ethylene oxide)-clay nanocomposite by direct polymer melt intercalation. This process involves mixing the layer silicate with the polymer and heating the mixture above the softening point of the polymer. Differential Scanning Calorimetry (DSC) results show that as the intercalation reaction progresses, more poly(ethylene oxide), PEO, chains were intercalated and the area of endotherm corresponding to crystalline PEO was reduced. This result agreed with XRD patterns, which demonstrated the increment of intensity of the PEO-intercalated silicate peak. In addition to XRD, the nanocomposite was characterized by transmission electron microscopy, TEM. Well-dispersed individual silicate layers of thickness 10 Å were embedded in the epoxy matrix. This nanocomposite showed improvement in mechanical properties, barrier properties, heat resistance, and thermal stability. The conductivity of the melt-intercalated hybrid was much higher and more isotropic than that of pure matrix.

Wang and Pinnavaia (1998) reported nanolayer reinforcement of elastomeric polyurethane. From XRD patterns, d-spacing for clay layers increased after modified with organophilic ammonium ion due to arrangement of alkyl chain of organophilic ammonium ion perpendicular to the clay basal surface. The expansion of the organophilic-clay increased with increasing curing time at 95 °C. Clearly, the clay nanolayers, even when aggregated in the form of intercalated tactoids, strengthen, stiffen, and toughen the matrix. Another significant property of polyurethane-clay

nanocomposites was their high optical transparency. Furthermore, the dispersal of silicate nanolayers substantially reduced the permeability of the polymer.

Characterization of epoxy-clay hybrid composite prepared by emulsion polymerization was discussed by Lee and Jang (1998). The hybrid was prepared without any kind of ion-exchange reaction with alkyl or aryl onium ions or by employing special coupling agents. The structural characterizations by FTIR and XRD for the extracted product gave strong evidence that an overwhelming fraction of MMT was intercalated with the epoxy polymer. The enhanced thermal stability of those postcured products was confirmed by TGA and DSA analysis. The strong fixation of polymer to inorganic surface was believed to be due to the cooperative formation of the ion-dipole force acting between polar functional groups of polymer chain and interlayer ions.

Liu *et al.* (1999) demonstrated the studied on nylon 6-clay nanocomposites by melt-intercalate process. X-ray diffraction and DSC results showed that the crystal structure and crystallization behaviors of the nanocomposites were different from those of nylon 6. Mechanical and thermal testing showed that the properties of the nanocomposites were superior to nylon 6 in terms of heat-distortion temperature, strength, and modulus without sacrificing their impact strength. This is due to the nanoscale effects and the strong interaction between the nylon 6 matrix and the clay interface, as revealed by X-ray diffraction and transmission electron microscope.

Preparation and mechanical properties of polystyrene-clay hybrid were reported by Hasegawa *et al.* (1999). It was found that silicate layers of clay were delaminated and uniformly dispersed to the nanometer level. The strong moduli of the hybrid materials were higher than those of matrix polymer at all temperatures.

Noh *et al.* (1999) revealed intercalation of styrene-acrylonitrile copolymer in layered silicate by emulsion polymerization. Transmission electron microscopy (TEM) results showed orderly arrangement of 1-2 nm sized silicate layer in the copolymer matrix. The modulus of elasticity of the product increased with increasing content of MMT, whereas the stress at maximum load decreased with the increments of MMT.

Synthesis and characterization of polyaniline (PAn)-clay nanocomposite with extended chain conformation of polyaniline were presented by Wu *et al.* (2000). The conductive emeraldine salt form of polyaniline was inserted into the layers of montmorillonite clay to produce the hybrid with high conductivity. The results show that a real nanocomposite was obtained and over 90% of the polyaniline chain was inserted between the layers. It was a single chain with extended-chain conformation owing to the confined environment in the nanometer size gallery.

Recently, Chen *et al.* (2000) successfully prepared a new type of hybrid material of clay with poly(butyl acrylate) (PBA) using intercalation-polymerization process. Thermogravimetric analysis (TGA) result showed that the hybrid material had a decomposition temperature (485°C) higher than that of pure PBA (402°C).