

CHAPTER III

LITERATURE REVIEWS



This chapter presents the literature reviews of the previous works related to this research. Polyimide synthesis part, polyhedral oligomeric silsesquioxane (POSS) part, poly (urethane-imide) part and hyperbranched polyether part are shown as below.

3.1 Polyimide synthesis.

C. D. Simone and D. A. Scola [3] succeeded in synthesis and characterization of phenylethynyl (PE) end-capped polyimides derived from 4,4'-(2,2,2-trifluoro-1 phenylethylidene) diphthalic anhydride (3FDA), 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), and 3,3',4,4'-biphenylene dianhydride (s-BPDA), with particular emphasis on the glass transition temperatures and viscosities. The phenylethynyl endcapped 3FDA- and 6FDA-containing oligomides demonstrate much lower minimum complex melt viscosities than s-BPDA-containing oligomides. The PE-3F and PE-6F oligomers also show greater viscosity stability at elevated temperature (310°C) than s-BPDA oligomides. The lower viscosities can be explained by the presence of the bulky groups CF_3 and phenyl on 3FDA and 6FDA relative to the planar configuration of the s-BPDA dianhydride. The greater viscosity stability of the PE-3F and PE-6F oligomers over the s-BPDA oligomers at 310 °C may be explained by the decreased electron density and hence lower reactivity of the ethynyl group in the PE-3F and PE-6F oligomers due to the influence of fluorine in the polymer chain.

Tomoyuki Suzuki and Yasuharu Yamada [9] studied two physical and gas transport properties of the hyperbranched polyimides. The first polyimide prepared from a triamine, 1,3,5-tris(4-aminophenoxy)benzene (TAPOB), and a dianhydride, 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), were investigated and compared with the second linear-type polyimides with similar chemical structures but prepared from diamines, 1,4-bis(4-aminophenoxy)benzene (TPEQ) or 1,3-bis(4-aminophenoxy)benzene (TPER), and 6FDA. 6FDA-TAPOB hyperbranched

polyimide exhibited a good thermal stability as well as linear type analogues. Fractional free volume (FFV) value of 6FDA-TAPOB was higher than those of the linear-type analogues, indicating looser packing of molecular chains attributed to the characteristic hyperbranched structure. It was found that the increased resistance to the segmental mobility decreases the gas diffusivity of 6FDA-TAPOB, in spite of the higher FFV value. However, 6FDA-TAPOB exhibited considerably high gas solubility, resulting in high gas permeability. It was suggested that low segmental mobility and unique size and distribution of free volume holes arising from the characteristic hyperbranched structure of 6FDA-TAPOB provide effective O₂/N₂ selectivity. It is concluded that the 6FDA-TAPOB hyperbranched polyimide has relatively high permeability and O₂/N₂ selectivity, and is expected to apply to a high performance gas separation membrane.

Lizhong Jiang *et al.* [24] have found a method to generate nanoporous polyimide films with low dielectric constants. The preparation consisted of two steps. Firstly, a polyimide/silica hybrid film was prepared via sol-gel process. Secondly, the hybrid film was treated with hydrofluoric acid to remove the dispersed silica particles, leaving pores with diameters between 20 and 120 nm, depending on the size of silica particles. Both hybrid and porous films were subjected to a variety of characterizations including transmission electron microscopy observation, dielectric constant measurement and tensile strength measurement.

I. Rozhanskii *et al.* [25] examined 2,2',3,3'-Biphenyltetracarboxylic dianhydride (i-BPDA) as a monomer for the synthesis of soluble polyimides with high thermal stability, and developed the efficient method of its preparation. Polyimides derived from i-BPDA and aromatic diamines (i.e. 4,4'-oxydianiline, 2,2'-bis(trifluoromethyl)benzidine and 9,9'-fluorenylidene-4,4'-dianiline) showed high glass transition ($T_g > 330$ °C) and degradation ($T_d5 > 550$ °C), temperatures, and were soluble in organic solvents (i.e. NMP, DMF, γ -butyrolactone, CHCl₃), although their mechanical properties were inferior to those of polyimides composed of semirigid 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA). Random copolymers, derived from i-BPDA and s-BPDA, retained superior mechanical properties of s-BPDA-based polyimides and showed improved solubilities, depending on the i-BPDA

content. A regular increase of glass transition temperatures and a decrease of inherent viscosities of copolymers with increasing content of i-BPDA were observed, whereas the dielectric constants and degradation temperatures were found to be independent of the ratios of dianhydride units.

Shu-Hui Xie *et al.* [26] have prepared polyimide/aluminum nitride (AlN) composites based on pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) by in situ polymerization. To disperse the AlN particles in the polyimide matrix homogeneously, γ -glycidoxypropyltrimethoxysilane (GPTS) was used as coupling agent for the preparation of the composites. It was found that, with the inclusion of aluminum nitride powder into the polyimide matrix, the thermal properties of the resulting polyimide–AlN composite were improved without obvious loss in the dielectric properties. The results indicated that the thermal stability and the thermal conductivity of the composite were enhanced, while the dielectric constant increased slightly and the electrical properties altered to less degree with the increase of AlN fraction. Meanwhile, the dielectric and thermally conducting properties were also influenced by the content of the coupling agent. In addition, the thermally conducting and dielectric properties of the studied composites followed the classic composite theories.

Jingling Yan *et al.* [4] have synthesized 4,4'-Bis(3,4-dicarboxy phenylthio) diphenyl sulfone dianhydride(4,4'-PTPSDA) and 4,4'-bis(2,3-dicarboxy phenylthio) diphenyl sulfone dianhydride(3,3'-PTPSDA) from chlorophthalic anhydrides and bis(4-mercaptophenyl) sulfone. Their structures were determined via IR spectra, ¹H NMR and elemental analysis. A series of polyimides were prepared from isomeric PTPSDAs and aromatic diamines in 1-methyl-2-pyrrolidinone (NMP) via the conventional two-step method. Polyimides based on 4,4'-PTPSDA and 3,3'-PTPSDA have good solubility in polar aprotic solvents and phenols. The 5% weight loss temperatures of isomeric polyimides were near 500 °C in N₂. DMTA and DSC analyses indicated that the glass-transition temperatures of polyimides from 3,3'-PTPSDA are higher than those of polyimides from 4,4'-PTPSDA. The wide-angle X ray diffraction showed that all the polyimides are amorphous. The polyimides from

3,3'-PTPSDA showed higher permeability but lower permselectivity compared with those from 4,4'-PTPSDA.

Z. Y. Ge *et al.* [2] examined a series of novel fluorinated polyimides, which could be easily dissolve in many organic solvents to give homogeneous and stable polyimide solution with solid content as high as 35-40 wt.%. The polyimide films obtained by casting the polymer solution followed by thermal imidization exhibited good thermal stability with high glass transition temperature and the temperature at 5% weight loss, and have outstanding mechanical properties. In addition, the fluorinated polyimides have low dielectric constants and dissipation factor, and very low moisture absorption.

3.2 Polyhedral oligomeric silsesquioxane (POSS)

Chyi-Ming Leu *et al.* [20] investigated low-dielectric-constant nanoporous films (dielectric constant, $k = 2.4$) with thermal integrity and controllable mechanical strength 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 retained a nanoporous crystal structure, but formed 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 while the polyimide molecules offer additional advantages of maintaining certain thermal and mechanical strengths.

Chyi-Ming Leu *et al.* [21] investigated nanoporous POSS/polyimide nanocomposites that contained polyhedral oligomeric silsesquioxanes (POSS) having amine groups (NH_2 -POSS). The NH_2 -POSS reacted with poly(amic acid) that having free anhydride end groups to form porous nanocomposites. The van der Waals interactions between tethered POSS molecules were 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 resulted in a reduction of the dielectric constant of the polyimide nanocomposite from 3.40 for the pure polyimide to 3.09 without detrimental to mechanical strength.

Mei-Hui Tsai, Wha-Tzong Whang [22] prepared new type of low dielectric polyimide/poly(silsesquioxane)-like (PI/PSSQ-like) hybrid nanocomposite material from the polyimide (ODA-ODPA) precursor containing phenyltrialkoxysilane (PTS) at two chain ends and monoaryltrialkoxysilane with a self-catalyzed sol-gel process. We employ *p*-aminophenyltrimethoxysilane (APTS) to provide bonding between the PTS and ODPA-ODA phase. It is shown by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) that the PSSQ-like domain sizes with uniform size are fairly well separated in the hybrid films. The silica domain sizes of 5000-PIS and 5000-PIS-50-PTS films are in the range of 30-100 nm, of 5000-PIS-100-PTS and 10000-PIS-100-PTS in the range of 80-200 and 300-600 nm, respectively. The dielectric constant can be 2.79 for 5000-PIS-140-PTS with fairly good mechanical properties. The PI/PSSQ-like hybrid films have higher onset decomposition temperature and char yield in thermogravimetric analysis (TGA) and higher T_g in differential scanning calorimetry (DSC) than the pure PI. Moreover, the PI/PSSQ-like hybrid films have excellent transparency even under high PTS content. In the series of X-PIS hybrid films, the coefficient of thermal expansion (CTE) below T_g increases with the PI block chain length, but in the series of X-PIS-*y*-PTS films, it slightly increases with the PTS content. However, above T_g the CTE of X-PIS and X-PIS-24-PTS is much lower than that of the pure PI. The dielectric constant and water absorption of X-PIS-*y*-PTS films decrease with the PTS content because of the higher free volume and hydrophobicity.

Yuan-Jyh Lee *et al.* [23] studied novel polyimide (PI) hybrid nanocomposite containing polyhedral oligomeric silsesquioxane (POSS) with well defined architecture prepared by copolymerization of octakis (glycidyl dimethyl siloxy) octasilsesquioxane (Epoxy-POSS), 4,4'-oxydianiline diamine (ODA), and 4,4'-carbonyldiphthalic anhydride (BTDA). In these nanocomposite materials, the equivalent ratio of the Epoxy-POSS and ODA are adjustable, and the resultant PI-POSS nanocomposites give various thermal and mechanical properties. More importantly, we 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.

Leu *et al.* [20] have recently demonstrated that 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.

3.3 Poly (urethane-imide)

Min Zuo, Tsutomu Takeichi [13] succeed in novel type of poly(urethane-imide) that was prepared by a reaction of a polyurethane prepolymer and a soluble polyimide containing hydroxyl functional group. Polyurethane prepolymer was prepared by a reaction of polyester polyol and 2,4-tolylenediisocyanate and then end capped with phenol. Soluble polyimide was prepared by the two-step synthesis from 2,2'-bis (3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 3,3'-diamino-4,4'-dihydroxybiphenyl (AHBP). Soluble polyimides having various contents of hydroxyl functional groups were prepared similarly by adjusting diamine mixtures ratio of AHBP and oxydianiline. Cast films were obtained from blend solutions of the polyurethane prepolymer and the polyimide. The cast films were thermally treated at various temperatures to give a series of transparent poly(urethane-imide) films. By changing the ratio of polyurethane and polyimide components, poly(urethane-imide) films having various properties from plastic to elastomer were prepared. Dynamic mechanical analysis showed that lower glass transition temperature (T_g) of the films shift to high temperature with the increase of polyimide component, suggesting that the two polymer components are miscible to some extent. Thermogravimetric analyses indicated that the thermal degradation of

poly(urethane-imide) occurs at ca. 270 °C, which is ca. 30 °C, higher than the conventional polyurethane, confirming that the introduction of polyimide component improved the thermal stability of polyurethane.

3.4 Hyperbranched polyether

Panagiotis Maroulas *et al.* [27] investigated chain dynamics of branch polymers in hyperbranched polyimides based on 2,4,6-triaminopyrimidine and 4,4'-oxydiphthalic anhydride (molar ratio 1:1) cross-linked with ethylene glycol diglycidyl ether by means of broadband dielectric relaxation spectroscopy and thermally stimulated depolarization currents techniques. The secondary γ relaxation increases in magnitude and slows down with increasing degree of cross-linking, whereas the relaxation, associated with the glass transition, becomes faster. These effects were explained in terms of increase of free volume and of constraints to the motion imposed by cross-links.

C.-M. Leu *et al.* [28] prepared dendritic macromolecules with an aromatic ether-imide inner structure and modifiable benzyl ether chain ends is described. The structural component that constitutes the branching regions was derived from 1-(4-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane. The key steps in ether-imide dendron synthesis involve an aromatic nucleophilic displacement of an activated nitro group with phenoxide leading to the ether linkage and cyclocondensation of the amino group with 3-nitrophthalic anhydride, to give rise to the imide ring containing the activated nitro functionality. The dendritic wedges are then coupled to a polyfunctional core to complete the synthesis. The benzyl ether chain ends can be selectively removed by catalytic hydrogenolysis to produce a dendrimer with phenolic chain ends. Further modification of the chain ends is accomplished by etherification of the phenolic groups. Structures of these dendritic poly(ether-imide)s were confirmed by ^1H NMR, ^{13}C NMR and FTIR spectroscopy as well as by mass spectrometry. Properties such as the glass transition temperature and solubility of the dendrimer are greatly affected by the nature of the end groups.

J Borah and N Karak [29] synthesized hyperbranched polyether by a single-step nucleophilic displacement polymerization technique between cyanuric chloride

and the sodium salt of bisphenol-A. The effects of various reaction parameters on the yield, and molecular weight, as measured by the intrinsic viscosity of the polymer, have been studied. The synthesized polymer has been characterized by FT-IR, UV and ^1H NMR spectroscopies, elemental analysis, solubility and viscosity measurements. The polymer is soluble in highly polar solvents such as N,N-dimethylacetamide, N,N-dimethylformamide and dimethyl sulfoxide, partially soluble in dilute aqueous NaOH solution, methanol, ethanol, chloroform, etc., but insoluble in water and non-polar hydrocarbon solvents. The solubility parameter of the hyperbranched polymer has also been measured experimentally.

Craig J. Hawker and J. M. J. Frechet [30] synthesized novel convergent growth approach to topological macromolecules based on dendritic fragments. The polyether dendritic fragments are prepared by starting from what will become the periphery of the molecule and progressing inward. In the first step, 2 mol of a benzylic bromide is condensed with the two phenolic groups of the monomer, 3,5-dihydroxybenzyl alcohol, under phase-transfer conditions. After transformation of the benzylic alcohol functionality of the growing molecule into the corresponding bromide, the procedure is repeated with stepwise addition of the monomer followed again by activation of the benzylic site. After several generations of growth, the resulting dendritic wedges, in their benzylic bromide form, can be coupled to a polyfunctional core such as 1,1,1-tris(4'-hydroxyphenyl)ethane to form the final hyperbranched macromolecule.

Jyotishmoy Borah *et al.* [31] compared hyperbranched and linear polyethers that were prepared by one-pot nucleophilic displacement polymerization technique using cyanuric chloride and aromatic diol as reported earlier. The physical, thermal, dielectric and chemical properties of the hyperbranched polyether and its linear analog have been studied. The amorphous characters of both the polyethers were observed in XRD study. The solubility studies showed that the hyperbranched polyether has relatively higher solubility in different solvents compared to its linear analog. The thermal properties of both polymers have been studied by thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses. The chemical resistance tests indicated that both polyethers are very good chemical resistances except in dilute aqueous alkali solution. The dielectric properties such as

dielectric constant and loss factor for both polyethers have also been studied with respect to changes of frequency (50-500 kHz) and temperature (303-343 K).