CHAPTER TWO

LITERATURE REVIEW
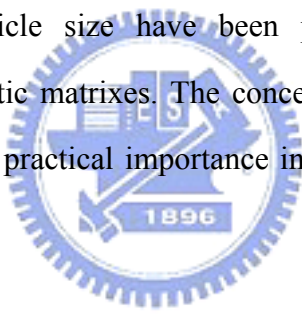
Summary

In this chapter, the research activities in the field of organic/inorganic nanocomposite materials and general background of the sol-gel chemistry are first given. Based on the fundamental understanding of these researches, this chapter goes to present the synthesis, structure-property response, and potential applications of the metal-containing polyimides. Finally, the motivation of this research is described.

2.1 Synthesis and Applications of Organic/Inorganic Nanocomposites

A new range of material properties can be produced by combining the features of the inorganic sol-gel alkoxide moieties with those of oligomeric/polymeric species. The resulting composites can vary from soft and flexible to brittle and hard materials depending on the chemical structure of the organic components and the overall composition ratio of organic to inorganic. Organic/inorganic hybrid materials prepared by the sol-gel process can be generated using different synthetic techniques by incorporating various starting inorganic and organic components with varied molecular structure:

1. Hybrid networks can be synthesized by using low molecular weight organoalkoxysilanes as one or more of the precursors for the sol-gel reaction in which organic groups are introduced within an inorganic network through the $\equiv$Si$-$C$-$ bond [1-2].
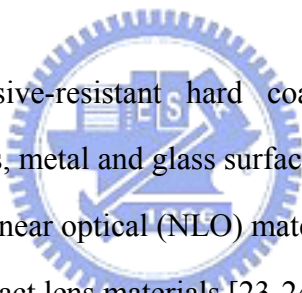
2. Organic/inorganic hybrid network materials can also be formed via the co-condensation of functionalized oligomers or polymers with metal alkoxides in which chemical bonding is established between inorganic and organic phases [3-4].

3. A hybrid material can also be synthesized through the in situ formation of inorganic species within a polymer matrix. Specifically, inorganic species, generally in the form particles with a characteristic size of a few hundred angstroms, can be generated in situ within the polymers by first swelling cross-linked, ionomeric or crystalline polymeric host with a compatible solution containing metal alkoxides followed by the promotion of the sol-gel reaction of the inorganics. Various inorganic particles with extremely homogeneous particle size have been prepared in this manner within elastomeric or plastic matrixes. The concept of such "in situ" generation of fillers is novel and practical importance in terms of elastomer reinforcement [5-6].

4. Starting from the opposite direction of (3), organic/inorganic composites can be obtained by either the infiltration of previously formed oxide gels with polymerizable organic monomers or the mixing of polymers with a single or mixture of metal alkoxides in a common solvent. In the first approach, the impregnation of porous oxide gels with organics is followed by an in situ polymerization initiated by thermal or irradiation methods. In the second approach, polymers can be trapped within the oxides gel network if the hydrolysis and condensation of metal alkoxide are carried out in the presence of preformed polymers. Optically transparent composite materials can be obtained if there is no macro- or microphase separation during both the gel forming and drying process [7-9].

5. Similar to approach (4), organics can also be simply impregnated or entrapped as a guest within inorganic gel matrixes (as a host). This approach has been extensively used in the incorporation of enzymes, proteins, and various organic dyes such as luminescent dyes, photochromic dyes, and nonlinear optical (NLO) dyes into an inorganic network. The main driving force behind the intensive research activity in preparation of these types of materials is the development of new optical and bioactive materials in the application of photophysical, electrical, biotechnical and nonlinear optical (NLO) devices [10-13].

6. Hybrid networks can also be formed by interpenetrating networks and simultaneous formation of inorganic and organic phases. By using triethoxysilane R'Si(OR)$_3$ as the precursor with R' being a polymerizable group such as an epoxy group, an organic network can be formed within the inorganic network by either photochemical or thermal curing of such groups, as Schmidt has demonstrated in 1984. Novak and Grubbs also developed an interesting convenient method to form inorganic/organic simultaneous interpenetrating network (SPINs), where both inorganic glass and polymer formation occur concurrently. These transparent composites are synthesized through a synchronous application of the aqueous ring-opening metathesis polymerization (aqueous ROMP) of cyclic alkenyl monomers and the hydrolysis and condensation of metal alkoxides [14-16].

The preparation of organic/inorganic hybrid materials by sol-gel process makes it possible to optimize selected properties independently. Specifically, the introduction of inorganic moieties into an organic matrix leads to new structure-property variation, thereby promoting new potential applications for the resulting composite materials. As examples:

- Flexibility can be introduced by the incorporation of organic/oligomeric/ polymeric materials into the inorganic networks.

- New electronic properties, such as conductivity, redox properties, etc., can be achieved by introducing conductive polymers along with transition-metal alkoxides.

- By incorporating organic dyes or π-conjugated polymers into the inorganic network, the optical properties can be systematically altered in both the linear as well as nonlinear optical properties (NLO).

To date, the number of commercial sol-gel hybrid products is still comparatively small, but the promise of new technological uses remains. Some potential applications for these materials are as follows:

- Scratch and abrasive-resistant hard coatings and special coatings for polymeric materials, metal and glass surfaces [17-20].

- Electrical and nonlinear optical (NLO) materials [21-22].

- Adhesives and contact lens materials [23-24].

- Reinforcement of elastomers and plastics [25-27].

- Catalyst, porous supports and adsorbents [28-29].

- Tunable solid-state lasers and chemical/biomedical sensors [30-31].

2.2 General Background of Sol-Gel Chemistry

Considering the key role of the sol-gel reaction in the preparation of organic/ inorganic hybrid materials, it is difficult to understand their preparation without a basic knowledge of the sol-gel process. Over the past two decades numerous studies have been carried out in the field of sol-gel chemistry and great progress has been made in understanding the reaction mechanism although many questions remain. As stated earlier, the sol-gel reaction is a method to prepare pure ceramic

precursors and inorganic glasses at relatively low temperatures [32-34]. The reaction is generally divided into two steps: hydrolysis of metal alkoxides to produce hydroxyl groups, followed by polycondensation of the hydroxyl groups and residual alkoxyl groups to form a three-dimensional network. The general scheme can be represented in Figure 2.1.

The sol-gel process generally starts with alcoholic or other low molecular weight organic solutions of monomeric, metal or semimetal alkoxide precursors $M(OR)_n$, where M represents a network-forming element such as Si, Ti, Zr, Al, B, etc., and R is typically an alkyl group (C_xH_{2x+1}) and water. Generally, both the hydrolysis and condensation reactions occur simultaneously once the hydrolysis reaction has been initiated. As can be seen from Figure 2.1, both the hydrolysis and condensation steps generate low molecular weight byproducts such as alcohol and water. These small molecules must be removed from the system, and such removal would lead, in the limit, to a tetrahedral SiO_2 network if the species were silicon. The removal of these byproducts also contributes to the high shrinkage that occurs during the classical sol-gel process.
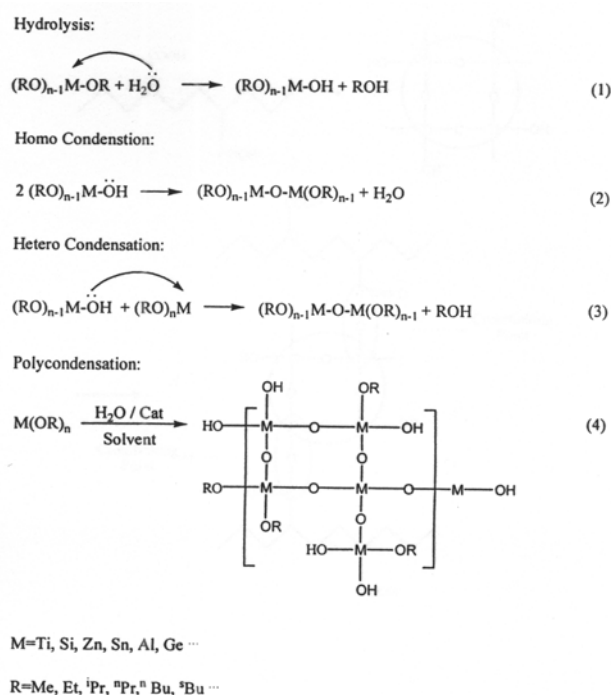
Hydrolysis:

$$(RO)_{n-1}M\text{-}OR + H_2\ddot{O} \longrightarrow (RO)_{n-1}M\text{-}OH + ROH \qquad (1)$$

Homo Condenstion:

$$2\,(RO)_{n-1}M\text{-}\ddot{O}H \longrightarrow (RO)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + H_2O \qquad (2)$$

Hetero Condensation:

$$(RO)_{n-1}M\text{-}\ddot{O}H + (RO)_nM \longrightarrow (RO)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + ROH \qquad (3)$$

Polycondensation:

$$M(OR)_n \xrightarrow[\text{Solvent}]{H_2O\,/\,Cat} \qquad (4)$$

M=Ti, Si, Zn, Sn, Al, Ge ⋯

R=Me, Et, ^{i}Pr, ^{n}Pr, ^{n}Bu, ^{s}Bu ⋯

Figure 2.1 The sol-gel reaction of a metal alkoxide.

Both hydrolysis and condensation occur by nucleophilic substitution (S_N) mechanisms which involve three steps: nucleophilic addition (A_N), proton transfer within the transition states and removal of the protonated species as either alcohol or water. For non-silicate metal alkoxides, generally no catalyst is needed for hydrolysis and condensation because they are very reactive. In the case of silicon based metal alkoxides, the hydrolysis and condensation reactions typically proceed with either an acid or base as catalyst.

Metal alkoxides are also of great interest because of the potential properties and applications they provide. However, a simple mixing of metal alkoxide and polymer matrix results in gelation and phase separation due to the relatively fast hydrolysis rate of metal alkoxides. Therefore, the control of the reactivity of metal alkoxides is necessary in order to be able to tailor the structure of the resulting materials. The hydrolysis and condensation reactions in the sol-gel process generally start with the nucleophilic addition of hydroxylated groups onto the electrophilic metal atoms which results in an increase of the coordination number of the metal atom in the transition state. As described by Sanchez and Ribot, the degree of reactivity of a given metal or semi-metal atom of an alkoxide is not due only to the electrophilic nature but rather is more a function of degree of unsaturation. The extent of unsaturation is given as (*N-Z*), where *N* is the coordination number of the atom in the stable oxide network and *Z* is the oxidation state. Table 2.1 lists the electronegativity and the degree of metal unsaturation for a few metal alkoxides. It is noted that silicon has a low electrophilicity and zero degree of unsaturation. Therefore, silicon alkoxides are less reactive. On the other hand, non-silicate metal alkoxides, including elements such as Ti, Zr, Al and B with higher unsaturation, all have much higher reactivity than silicon. They are so sensitive to moisture, even in the absence of a catalyst, that precipitation of the oxide will generally occur as soon as water is present. For example, the hydrolysis

and condensation rates of titanium butoxide are much faster than that of tetraethoxysilane (TEOS). The sequence of reactivity is expressed as follows [35-36]:

$$Zr(OR)_4, Al(OR)_3 > Ti(OR)_4 > Sn(OR)_4 >> Si(OR)_4$$

Table 2.1 Electronegativity (χ), coordination number (N), and degree of unsaturation (N-Z) for some metals.

Alkoxides	χ	N	Z	N-Z
Si(OPr^i)$_4$	1.90	4	4	0
Sn(OPr^i)$_4$	1.96	6	4	2
Ti(OPr^i)$_4$	1.54	6	4	2
Zr(OPr^i)$_4$	1.33	7	4	3
Ce(OPr^i)$_4$	1.12	8	4	4
Al(OPr^i)$_3$	1.61	6	3	3

In order to prevent phase separation or gelation, methods must be taken to slow down the hydrolysis and condensation reactions of metal alkoxides. So far, as reported in the literatures, there are several ways to control the reactivity of metal alkoxides to avoid unnecessary phase separation. Chemical additives, such as glycols, organic acid (acetic acid) and β-diketones have often been used as chelating ligands to slow the reaction rates of metal alkoxides or mixed-metal alkoxide systems [37-39]. After forming a complex with the chelating ligand, the species between metal and chelating agent is less easy to hydrolyze.

■ **Reactions with Glycol**s

Many alkoxides (B, Al, Si, Ge, Sn, Se, Te, Sb, Fe^{III}, Ti, Zr, Nb, Ta and U) are reacted with glycols to form glycolate or mixed alkoxide glycolate derivatives according to the reaction:

$$M(OR)_x + n \; \underset{OH}{\overset{OH}{\diagdown}} G \rightarrow (RO)_{x-2n} \; M(\underset{O}{\overset{O}{\diagup}} G \;)_n + 2n \; ROH$$
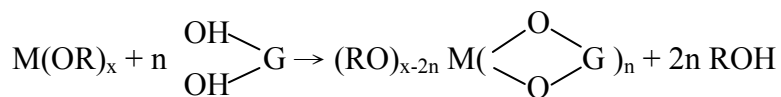
where G = alkyl or alkylene group

These compounds favor high molecular association affording, in some cases, species more resistant to hydrolysis than the parent alkoxides. These features have been used by Guizard et al. to prepare multicomponent systems having zirconia as a major component. Zirconium alkoxides hydrolyze with facility so that it is necessary to control the reaction in order to avoid the precipitation of hydrated products. These authors proved that the reaction with ethylene glycol affords zirconium glycoxides succeeding in the achievement of a transparent gel.

■ **Reactions with Organic Acids**

Metal alkoxides react with organic acid according to the reaction:

$$M(OR)_n + x \; RCOOH \rightarrow M(OR)_{n-x}(OOCR)_x + x \; ROH$$

This reaction was used by Doeuff et al. and Sanchez et al. to modify $Ti(OBu^n)_4$ by acetic acid and to stabilize it against precipitation. They showed that acetate groups, behaving as bidentate ligands, are not easily removed by water which first attacks the alkoxy ligands. This enables the control of both the hydrolysis and condensation processes.

■ **Reactions with β-Diketones and β-Ketoesters**

β-diketones exhibit keto-enol tautomerism.

keto form   enol form
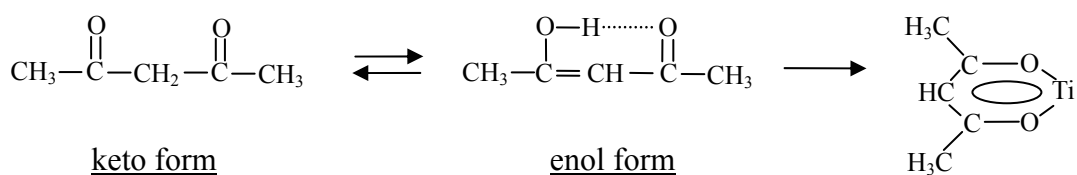
The enol form, containing a reactive hydroxyl group, reacts very readily with metal alkoxides giving structures where the enol form of the β-diketones is stabilized by chelating to the metal ion. The same behavior can be extended to β-ketoesters, R'COCH$_2$COOR''. Acetylacetone is one of the most often used β-diketones in the sol-gel process. It has been used to stabilize alkoxides of aluminum, zirconium and titanium. Indeed, complexes may be considered inert versus hydrolysis and, in general, versus substitution reactions. This fact is conceivable taking into account the peculiar stability of the six-member ring and electronic charge distribution in moiety. Example of the alkoxide precursor modified by the reaction with β-diketones is the acetylacetinate titanium alkoxide used by La Course and Kim to prepare TiO$_2$ and TiO$_2$/SiO$_2$ monolithic gels and fibers.

2.3 Synthesis and Properties of Metal-containing Polyimides

Nowadays, organic/inorganic hybrid materials have become a popular topic in material science because of their unique properties. Polyimides, which can be prepared from a variety of starting materials by a variety of synthesis routes and possess high thermal stability, high chemical resistance and excellent mechanical properties, are a promising candidate type for the matrix of hybrid materials.

Metal-containing polyimides are first reported by Angelo [40], who adds organometallic complexes to several types of polyimides and reports the metallic contents, dielectrics and volume resistivity for the copper-containing polyimides. Polyimide films containing metal/metal oxide particles generated in situ have been studied extensively by Taylor with several collaborative teams in an attempt to synthesize materials with unique electrical, magnetic, thermal, or adhesive properties [41-48]. They have incorporated directly more than twenty metallic salts and organometallic complexes such as Al(acac)$_3$, AlCl$_3$, SnCl$_2$ and CoAc$_2$ etc. in

poly(amic acid) followed by thermal conversion. The incorporation of SnCl$_2$·2H$_2$O exhibited the best electrical properties. It is believed that lowered electrical surface resistivity appear to be correlative with the presence of surface tin oxide on the hybrid film surface. However, several experimental problems have arisen with this procedure, limiting the preparation of good quality hybrid films. These problems include:

- The poor solubility of the metal complexes in most common organic solvents.
- Gelation of the polymer may occur upon interaction with the metal.
- Poly(amide aicd) precipitation takes place when the metal complex is added.
- The metals are prone to aggregate into large particles during imidization process.
- The metal content in the hybrid films is limited.
- The metal promotes thermo-oxidative degradation of the polymer hybrid film during curing process.
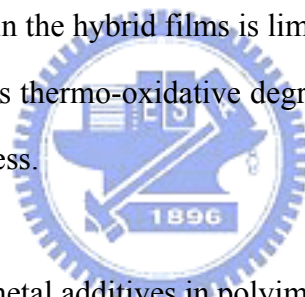
Table 2.2 The types of metal additives in polyimide system.

Types of metal additives	Example	Problem
Inorganic salts	AlCl$_3$; SnCl$_2$	ionic residual
Metal alkoxide	Ti(OCH$_3$)$_4$; Sn(OC$_2$H$_5$)$_4$	gelation occur
Organometallic complexes	Fe(acac)$_3$; Al(acac)$_3$	poor solubility in organic solvents

2.4 Motivation

For solving the above problems due to simple mixing of poly(amic acid) and the metal additives (metal salts and organometallic), metal alkoxide incorporated by sol-gel method is developed. However, when metal alkoxides is added into polyimide matrix, the gelation and phase separation easily occur due to the relatively fast hydrolysis rate of metal alkoxides. Therefore, the use of chelating

agent is necessary in order to be able to control the reactivity of metal alkoxides and to tailor the structure of the resulting hybrid materials. Due to the expected properties of TiO_2 (high-refractive-index, catalytic etc.), we devotes to incorporate titanium alkoxide into polyimide matrix. Besides, the poly(amic acid) transforms into polyimide at a curing temperature that is compatible with the TiO_2 formation temperature. In this study, we manage to demonstrate a simpler process to prepare good quality and well-dispersed polyimide/titania hybrid film with relatively high titania content. The expectation is that the inorganic phase, formed via sol-gel process, would uniformly disperse in polyimide matrix and result in a tailored effect of the hybrid films without compromising other essential properties of polyimide.

2.5 References

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