# SYNTHESIS AND CHARACTERIZATION OF SILICA NANOPARTICLES AND THEIR APPLICATION AS FILLERS IN SILICA-BISMALEIMIDE NANOCOMPOSITE

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by

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## LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

(Sample notations or abbreviations are given in Chapter 3)

| Symbols | Descriptions |
|---|---|
| [MI] | Concentration of maleimide double bonds |
| $[MI]_{homopolym}$ | [MI] consumed for homopolymerization cross-linking reaction |
| [PA] | Concentration of primary amine |
| [SA] | Concentration of secondary amine |
| [TA] | Concentration of tertiary amine |
| AD | Alcohol dehydration |
| $\alpha_{OH}$ | Silanol number |
| APTS | 3-aminopropyltrimethoxysilane |
| AS1 | Si-O-Si asymmetrical stretching |
| BMI | Bismaleimide or 1,1'-(Methylenedi-4,1-phenelene)bismaleimide |
| BMI/DDM or BD | Bismaleimide/4, 4'-diaminodiphenylmethane |
| CTE | Coefficient of thermal expansion |
| $\alpha_1$ | CTE below $T_g$ |
| $\alpha_2$ | CTE above $T_g$ |
| CVC | Chemical vapor condensation |
| d | Average diameter of particles |
| $\delta$ | Bending vibration |
| $D_a$ | Apparent density |
| DABPA | O',O-diallyl bisphenol A |
| DCM | Dichloromethane |
| DCP | Dicumylperoxide |
| DDM | 4, 4'-diaminodiphenylmethane |
| $\Delta H$ | Enthalpy |
| DLMCA | Diffusion limited monomer-cluster aggregation |
| DMA | Dynamic mechanical analysis |
| $\delta_{OH}$ | Silanol concentration |
| $D_p$ | Pore size |
| $D_t$ | True density |
| $\varepsilon$ | Paramagnetic defect sites |

| Symbols | Descriptions |
|---|---|
| E’ | Storage modulus |
| EDL | Electrical double layer |
| EDX | Energy dispersive X-ray |
| eV | Electron volt |
| FD | Freeze drying |
| FTIR | Fourier transform infrared |
| GPTS | 3-glycidyloxypropyltrimethoxysilane |
| **K** | Ionic conductivity measured in μS (micro Siemens) |
| **t’** | Time where **K** become constant |
| LM | Light microscope |
| $\lambda_{max}$ | Lambda maximum |
| MA | Magnetic agitation |
| MCA | Monomer-cluster aggregation |
| $\nu$ | Stretching vibration |
| $N_A$ | Avogadro number ($6.022 \times 10^{23}$) |
| $\nu_{as}$ | Asymmetric stretching vibration |
| $NH_4X$ | Ammonium salts |
| NMR | Nuclear magnetic resonance |
| NPM | *N*-phenyl maleimide |
| OD | Oven drying |
| ODC | Oxygen deficient centers |
| **P** | Probability of finding agglomerates in silica powder |
| PAAM | Polyacrylamide |
| phr | Part per hundred resin |
| PL | Photoluminescence |
| PMC | Polymer matrix composite |
| PSD | Particle size distributions |
| $\theta$ | Si-O-Si bond angle |
| QBSD | Backscattering mode |
| R | $[H_2O]/[TEOS]$ ratio |
| *R*’ | Organo-functional groups |
| RLMCA | Reaction limited monomer-cluster aggregation |
| RM | Reverse microemulsion |

| Symbols | Descriptions |
|---|---|
| $R_s$ | $SSA_{BET}/SSA_{Theoretical}$ |
| $\sigma$ | Standard deviation of particle size |
| SAXS | Small angle X-ray scattering |
| SBN | Silica-Bismaleimide Nanocomposite |
| SE | Secondary electron mode |
| SEM | Scanning electron microscopy |
| $Si(OR)_3R'$ | Silane coupling agent |
| SSA | Specific surface area |
| $SSA_{BET}$ | BET specific surface area |
| $SSA_{Theoretical}$ | Theoretical specific surface area |
| STE | Self-trapped exciton |
| T | Temperature (°C) |
| tan $\delta$ | Damping behavior |
| $T_d$ | Decomposition temperature |
| TEM | Transmission electron microscopy |
| TEOS | Tetraethylorthosilicate |
| $T_g$ | Glass transition temperature |
| $T_\beta$ | Beta transition temperature |
| TGA | Thermogravimetric analysis |
| TMA | Thermomechanical analysis |
| US | Ultrasonic |
| UV-Vis | Ultraviolet-visible |
| $V_{mp}$ | Micropore volume |
| $V_p$ | Pore volume |

**SINTESIS DAN PENCIRIAN SILIKA NANOZARAH DAN PENGGUNAANYA SEBAGAI PENGISI DI DALAM NANOKOMPOSIT SILIKA-BISMALEIMIDA**

## ABSTRAK

Penyelidikan yang dijalankan adalah untuk mengkaji pembentukan, pertumbuhan dan kaedah pengawalan saiz zarah silika melalui proses sol-gel dengan menggunakan tetraetoksilikat (TEOS) sebagai pemula dalam keadaan bes. Pembentukan dan pertumbuhan zarah silika didapati sangat dipengaruhi oleh kepekatan $NH_3$ (mangkin). Sol yang stabil telah terbentuk pada kepekatan $NH_3$ yang rendah manakala kepekatan yang tinggi telah menghasilkan zarah yang besar dan berbentuk sfera dengan saiz dalam julat 90 – 700 nm. Pendekatan pertama secara penambahan sedikit garam ammonium ($NH_4X$) telah menghasilkan silika nanozarah yang tersebar dengan saiz 20.5 hingga 34.1 nm. Ini bergantung kepada saiz dan kepekatan anion yang hadir di dalam sistem. Pendekatan kedua telah digunakan untuk mengurangkan lagi saiz zarah silika melalui pengoptimuman parameter tindak balas seperti kepekatan TEOS, nilai R (nisbah kepekatan air terhadap TEOS), kadar penambahan $NH_3$ dan suhu tindak balas. Zarah silika yang sangat halus dan tersebar dengan saiz 7.1 ± 1.9 nm yang berada di dalam julat zarah asas telah berjaya dihasilkan pada keadaan optimum. Silika nanozarah yang dihasilkan kemudianya disebar dan dikeringkan dengan menggunakan kaedah penyahidratan-alkohol (AD). Kaedah ini merupakan suatu kaedah pengeringan yang baru, mudah dan rendah kosnya serta mampu menggurangkan penggumpalan dan meningkatkan sebaran silika nanozarah berbanding kaedah pengeringan beku (FD) and pengeringan ketuhar (OD). Silika nanozarah yang telah diproses mempunyai beberapa sifat menarik yang bergantung kepada saiz. Peningkatan luas permukaan spesifik (SSA) and kepekatan silanol ($\delta_{OH}$) yang nyata serta peningkatan ketumpatan ketara ($D_a$) yang

beransur telah diperhatikan apabila saiz zarah dikurangkan daripada 400 kepada 7 nm. Selain itu, pengurangan nombor silanol ($\alpha_{OH}$) dan sudut ikatan Si-O-Si serta kewujudan kecacatan aktif-optik pada saiz zarah yang lebih kecil mencadangkan bahawa perubahan ketara berlaku pada struktur nanosilika. Pengubahsuaian permukaan silika secara kimia telah dijalankan dengan mencantum kumpulan epoksida and maleimida. Kumpulan epoksida telah dicantum dengan menggunakan 3-glisidiloksipropiltrimetoksisilana (GPTS) manakala kumpulan maleimida telah dicantum melalui tindak balas 1,1'-(Metilenadi-4,1-fenilena)bismaleimida (BMI) kepada silika nanozarah yang terlebih dahulu dicantumkan dengan kumpulan amina menggunakan 3-aminopropiltrimetoksisilana (APTS). Kedua-dua kumpulan epoksida dan maleimida yang didapati terikat secara kovalen pada permukaan silika adalah reaktif. Muatan kumpulan berfungsi didapati meningkat dengan pengurangan saiz zarah, sebagai contoh 130 nm (1.09 mmol/g) < 20 nm (1.70 mmol/g) < 7 nm (2.04 mmol/g) bagi kumpulan epoksida. Matriks untuk nanokomposit silika-bismaleimida (SBN) telah disediakan daripada formulasi yang mengandungi BMI and 4,4'-diaminodifenilmetana (DDM) pada nisbah 2:1 (BMI/DDM) dengan 0.1 % berat dikumilperoksida (DCP) sebagai pemecut pematangan. Formulasi tersebut menghasilkan komposit dengan masa-gel yang panjang (208 s/g) dan masa pasca-pematangan yang singkat (2 jam) berbanding dengan formulasi lain. Zarah nanosilika (7, 20 dan 130 nm) telah dicampurkan ke dalam matriks BMI/DDM secara kaedah gabungan yang melibatkan pra-rawatan serbuk silika dengan BMI dan adunan-lebur. Silika nanozarah yang tulen didapati berinteraksi dengan matriks polimer melalui ikatan hidrogen manakala zarah silika dengan permukaan yang diubahsuai telah menghasilkan interaksi pengisi-matriks yang kuat melalui ikatan kovalen. Justeru, zarah silika dengan permukaan yang diubahsuai telah menyebabkan peningkatan sifat

mekanik terma SBN seperti E', $T_g$ dan $T_d$ yang ketara dengan penurunan CTE. Peningkatan sifat-sifat tersebut didapati bergantung kepada kepekatan pengisi, kumpulan berfungsi pada permukaan dan saiz zarah. Secara keseluruhan, sifat mekanik terma yang terbaik bagi SBN telah diperoleh dengan zarah silika bersaiz 7 nm (dicantum dengan kumpulan epoksida) pada kepekatan 10.0 % berat, iaitu E': 14.1 GPa (pada 30 °C), $T_g$: 300 °C, $\alpha_1$: 28.8 ppm/°C dan $T_{d\ (onset)}$: 451 °C.

**SYNTHESIS AND CHARACTERIZATION OF SILICA NANOPARTICLES AND THEIR APPLICATION AS FILLERS IN SILICA-BISMALEIMIDE NANOCOMPOSITE**

## ABSTRACT

A series of investigations were carried out to study the formation, growth and methods to control the size of silica particles via sol-gel process using tetraethylorthosilicate (TEOS) as the precursor in basic condition. The formation and growth of silica particles were significantly affected by the $NH_3$ (catalyst) concentration. Lower $NH_3$ concentrations lead to the formation of stable sols while higher $NH_3$ concentrations resulted in bigger, spherical silica particles with sizes varying from 90 - 700 nm. In the first approach, the addition of small amount of ammonium salts ($NH_4X$) produced monodispersed silica particles ranging from 20.5 to 34.1 nm depending on the size and concentration of the anion present in the system. The second approach was conducted to further reduce the silica size by optimizing the reaction parameters such as concentration of TEOS, R (water to TEOS concentration ratio) value, $NH_3$ feed rate and reaction temperature. The optimal reaction conditions successfully produced highly dispersed ultrafine silica nanoparticles with particle size of 7.1 ± 1.9 nm which falls in the primary size range. The freshly synthesized silica nanoparticles was dispersed and dried using a relatively new, simple and cost effective alcohol-dehydration (AD) technique which was able to suppress the agglomeration and improve the dispersion of silica compared to freeze drying (FD) and oven drying (OD) techniques. The processed silica nanoparticles exhibited some interesting size-dependent properties. Significant increase in the specific surface area (SSA) and silanol concentration ($\delta_{OH}$) and a more gradual increase in the apparent density ($D_a$) were observed as the particle size was reduced from around 400 to 7 nm. In addition, the decrease in the silanol number ($\alpha_{OH}$)

and Si-O-Si bond angle and the presence of optically active defect sites at smaller particle sizes suggest that the silica structure has been significantly altered at the nanoscale. Chemical modification of silica surface was conducted by grafting epoxide and maleimide groups. The epoxide groups were grafted using 3-glycidyloxypropyltrimethoxysilane (GPTS) while the maleimide groups were grafted by reacting 1,1'-(Methylenedi-4,1-phenelene)bismaleimide (BMI) with silica nanoparticles pre-grafted with amino groups using 3-aminopropyltrimethoxysilane (APTS). Both epoxide and maleimide groups were found covalently bonded to the silica surface and reactive. The loading of functional groups increased with the decrease in the particle size: e.g. 130 nm (1.09 mmol/g) < 20 nm (1.70 mmol/g) < 7 nm (2.04 mmol/g) for the epoxide groups. The matrix for the silica-bismaleimide nanocomposite (SBN) was prepared using a formulation containing BMI and 4,4'-diaminodiphenylmethane (DDM) at 2:1 (BMI/DDM) mol ratio with 0.1 wt.% of dicumylperoxide (DCP) as the curing accelerator. The specified formulation exhibited longer gel-time (208 sec/g) and shorter post-curing time (2 hours) compared to other formulations. The silica nanoparticles (7, 20 and 130 nm) were incorporated into the BMI/DDM matrix using a combination of procedures involving pre-treatments of silica powder in presence of BMI and melt-mixing. The pure silica nanoparticles interacted with the polymer matrix through hydrogen bonding while the surface modified nanoparticles exhibited strong filler-matrix interaction via covalent bonding. Therefore, the surface modified nanoparticles resulted in significant improvements in thermal mechanical properties of SBN such as E', $T_g$ and $T_d$ and also reduction in CTE. The property enhancements were found dependent on the filler concentration, surface functional group and particle size. Overall, the best thermal mechanical properties were

obtained for SBN containing 7 nm silica particles (grafted with epoxide groups) at 10.0 wt.%, i.e., E': 14.1 GPa (at 30 °C), $T_g$: 300 °C, $\alpha_1$: 28.8 ppm/°C and $T_{d\ (onset)}$: 451 °C.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Nanotechnology

On December 29, 1959, Richard Feynman in his famous talk entitled "There's Plenty of Room at the Bottom" has described the possibility of maneuvering things atom by atom in the future [1]. Now, his prediction seems to be realized with the rapid development in nanotechnology. Nanotechnology is rapidly sweeping through all vital fields of science and technology such as electronics and pharmaceuticals with tremendous supports from researchers from both academic and industrial sectors. This is an emerging technology of the 21st century. In the year 2005 alone, US$ 9.6 billion worth of fund had been dedicated to nanotech research by the governments, corporations and venture capitalists throughout the world [2]. In the same year, US$ 32 billion worth of goods incorporated with nanotechnology were sold, ranging from General Motors vehicles that includes parts made of polymer-nanoclay composites, to antimicrobial bandages that contains nanosilver particles [2]. Thus, nanotechnology does not only open more room for research and developments but also promises good revenues through commercialization of nanomaterial incorporated products.

The term nanotechnology can be briefly defined as the science and engineering involved in the design, synthesis, characterization, and application of materials and devices on the nanometer scale or one billionth of a meter [3]. In materials where strong bond is present, delocalization of valence electron is extensive and the extent of delocalization depends and varies with the size of the system [4]. This in turn, affects the properties of the material such as chemical properties, magnetic

properties, optical properties, thermal properties and surface reactivity [4]. As a result, nanomaterials often exhibit unique and improved properties compared to the bulk counterparts. Therefore, it provides opportunity to develop new classes of advanced materials which can meet the demands from high-tech industries such as electronics, aerospace, defense and pharmaceutical.

## 1.2 Nanoceramics

Development of ceramic particles in nano dimension with improved properties has been studied with much success in several areas such as synthesis, surface science and texturology [4]. Ceramic is defined as non-metallic and inorganic, thus all the metal oxides, nitrides and carbides falls in this category [5]. Examples of ceramic are silicon dioxide (silica), aluminum oxide (alumina), titanium dioxide (titania), silicon nitride, and etc. The ceramic materials have been reported to exhibit unique surface chemistry in the nano dimension [6]. Therefore, nanoceramics such as silica nanoparticles have been intensively studied in recent years due to its prospect of application in various commercial fields.

### 1.2.1 Silica Nanoparticles

Advancement in nanotechnology has lead to the production of nano-sized silica, $SiO_2$, which has been widely used in both scientific research and engineering development [7]. Generally, materials with the particle size in the range of 1 – 100 nm are defined as nanomaterials [4, 8-10]. Natural silica is found in plants such as barley, rice husk and bamboo and also in mineral forms of quartz and flint. The silica particles extracted from these natural resources contains metal impurities and not favorable for advanced scientific and industrial applications. Thus, focus is given to synthetic silica

(colloidal silica, silica gels, pyrogenic silica and precipitated silica), which is pure and produced mostly in amorphous powder forms compared to natural mineral silica (quartz, tridymite, cristobalite) which are in crystalline forms [11]. As shown in Figure 1.1, the various methods that have been used to obtain nanomaterials can be categorized into two main approaches: top-down and bottom-up [4, 12]. Top-down is characterized by reducing the dimension of the original size by utilizing special size reduction techniques. Bottom-up approach which involves synthesis of nanomaterials from atomic or molecular scale is the common route used to produce silica nanoparticles. Some of the widely used methods to synthesize silica nanoparticles are sol-gel process, reverse microemulsion and flame synthesis.

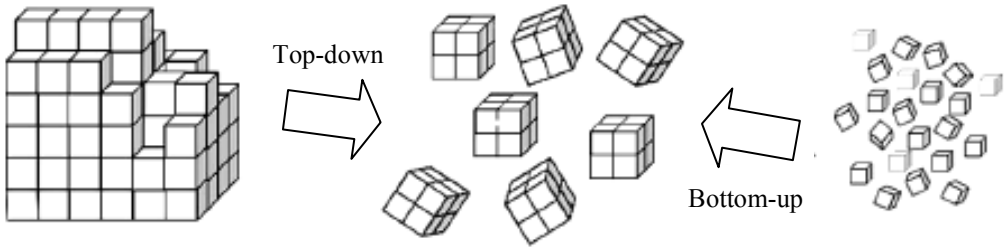


**Figure 1.1**: Top-down and bottom-up approaches to produce nanomaterials [4, 12].

#### 1.2.1.1 Sol-Gel Process

The sol-gel process is widely applied to produce ceramic materials due to its ability to form pure and homogenous products at mild conditions. The process involves hydrolysis and condensation of metal alkoxides [5, 13] such as tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$) or inorganic salts [13] such as sodium silicate ($Na_2SiO_3$). Silicate particles mostly synthesized in the presence of mineral acid (e.g. HCl) or base (e.g. $NH_3$) as catalyst. Flow chart of a typical sol-gel process which leads to the production silica nanoparticles using silicon alkoxides ($Si(OR)_4$), is shown in Figure 1.2.

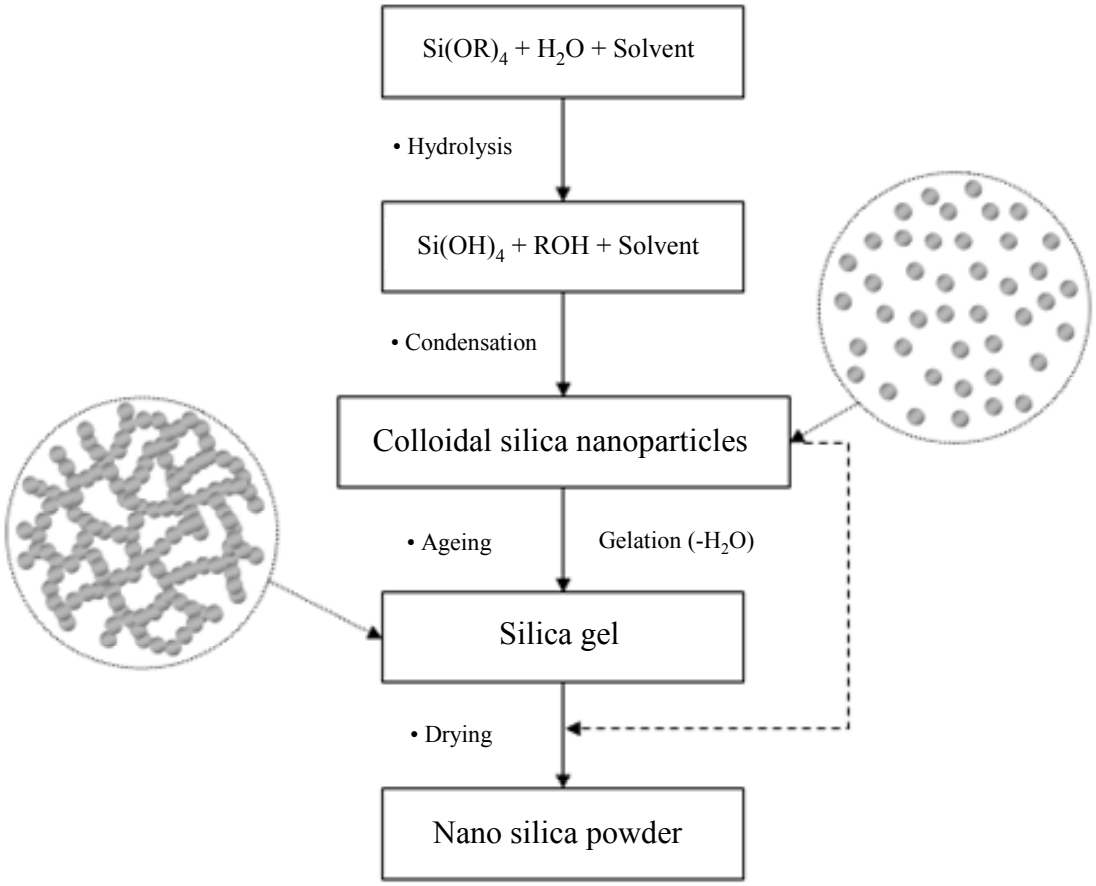


**Figure 1.2**: Flow chart of a typical sol-gel process for preparing nanosilica powder [6].

Condensation of hydroxide molecules by elimination of water leads to the formation of sol (colloidal silica). After a prolonged ageing process, the colloidal particles will link together to form network structure, resulting in a porous gel. Removal of solvent from the sol or gel will produce silica powder. Since the sol-gel process starts with the nanosized hydroxide units, and undergoes reaction on the nanometer scale, it results in the formation of nanometer silica particles [4]. Optimizing the reaction conditions of sol-gel process such as concentration of reactants, concentration of catalyst and reaction temperature [14, 15] and addition of electrolytes (metal salts) [16] are some of the recent attempts made by the researchers to reduce the silica size using the sol-gel

platform. The smallest possible silica nanoparticles with average diameter of 14 to 20 nm, in colloidal form have been produced using these approaches [14-16].

#### 1.2.1.2 Reverse Microemulsion

Reverse microemulsion (RM) is an efficient method to synthesis monodispersed nanoparticles [17]. In a typical RM system, the surfactants molecules dissolved in organic solvents forms spherical micelles. As illustrated in Figure 1.3, in the presence of water, the polar head groups organize themselves to form microcavities containing water, which is often called as reverse micelles [18]. Synthesis of silica nanoparticles inside the microcavities can be achieved by controlled addition of silicon alkoxides and catalyst into the medium containing reverse micelles. The surfactant stabilized microcavities (in nanometer size) provides a cage-like effect that limits particle nucleation, growth and agglomeration [19, 20], leading to the formation of homogenous silica nanoparticles. Major drawbacks of the RM approach are the high cost and difficulties in the removal of surfactants after the synthesis [21].

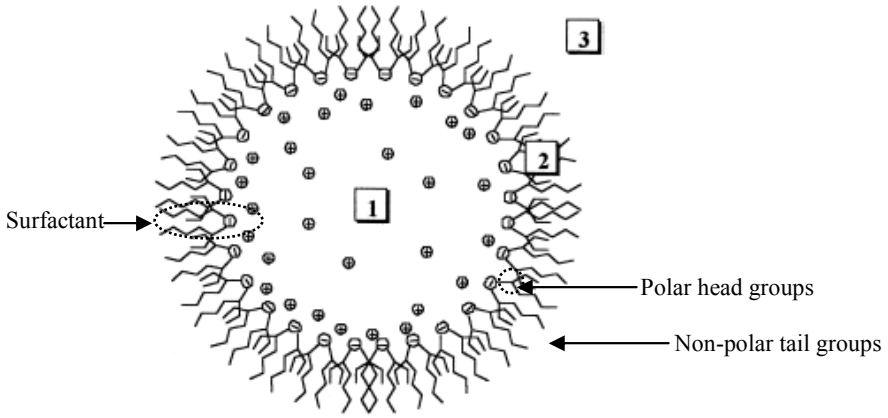


**Figure 1.3**: Schematic representation of reverse micelles, showing the different regions of a micellar solution: (1) water pool; (2) interface; and (3) organic phase [18].

#### 1.2.1.3 Flame Synthesis

Silica nanoparticles also can be produced through high temperature flame decomposition of metal-organic precursors. This process also referred as chemical vapor condensation (CVC) [3]. In a typical CVC process, silica nanoparticles are produced by burning silicon tetrachloride, $SiCl_4$ with hydrogen and oxygen [11]. Difficulty in controlling the particle size, morphology and phase composition is the main disadvantages of the flame synthesis [4]. Nevertheless, this is the prominent method that has been used to commercially produce silica nanoparticles in powder form.

### 1.2.2 Applications of Silica Nanoparticles

Silica nanoparticles are widely used in high-tech applications owing to their many attractive properties such as excellent physical, chemical, mechanical and sintering properties [4]. At present, silica nanoparticles are extensively studied for their prospective as photonic crystals [22, 23], chemical sensors [24], biosensors [25], nanofillers for advanced composite materials [26-28], markers for bioimaging [29], substrate for quantum dots [30, 31] and catalysts [32, 33], and etc. Optical absorption and emission properties, concentration of silanol groups, specific surface area and density are some of the key parameters that govern the utilization of silica nanoparticles in the contemporary research works. However, literatures describing the size-dependent properties and contemporary application of silica nanoparticles are still lacking at the moment.

### 1.2.3 Agglomeration and Aggregation Problems in Silica Nanoparticles

The extents of agglomeration and aggregation in silica nanoparticles are important parameters that govern their utility in various types of application. Agglomeration is the sharing of a plane or side between two particles, while aggregation indicates one-point linking of particles [11]. The presence of agglomerates and aggregates will readily affect the physical properties such as surface area. Therefore, agglomeration and aggregation-free nanoparticles are essential in ceramics, composites and electronics applications [34]. It has been reported that the agglomeration can be reduced by appropriate drying of the sol or gel that carries the nanoparticles [35]. On the other hand, chemical modification of silica surface has been proven to effectively reduce the aggregation phenomena [11].

## 1.3 Silica-Polymer Nanocomposites

In principle, the incorporation of inorganic moieties (fillers) with organic polymeric materials (matrix) results in the formation of composite materials [8]. Once, one of the dimensions of the filler material is of the order of a nanometer scale or more definitively in the range of 1 - 100 nm, it is termed as nanocomposite [4, 8-10]. The final product does not have to be in nanoscale, but can be micro- or macroscopic in size [36]. The resulting inorganic-organic hybrid materials, which is also often called as the polymer matrix composite (PMC), have been proven to exhibit excellent properties in terms of thermal, mechanical, electrical and magnetic behaviors compared to the pure organic polymer due to the synergism between the properties of the components [8]. Exceptionally low coefficient of thermal expansion (CTE) of silica caused by the high Si-O bond energy has made the silica filled PMCs widely studied, especially for the applications at elevated temperatures such as in semiconductor packaging [7].

The application of silica nanoparticles as fillers in the preparation of advance PMC has drawn much attention in recent years. This is due to the increased demand for new materials with improved thermal, mechanical, physical and chemical properties, especially for the application in semiconductor packaging, aerospace and defense related industries. Recent developments in the synthesis of monodispersed, narrow size distributed silica nanoparticles are realized to provide significant boost to the development of silica-polymer nanocomposites. Silica nanoparticles which exhibit significantly higher specific surface area and silanol concentration compared to the bulk silica [4] is expected to drastically alter the properties of polymer composite with respect to macroscopic composites that are made of the same components. In the case of particle filled composite system, the surface area per unit volume is inversely proportional to the material's diameter. Thus, greater surface area per unit volume (*A/V* ratio) is achieved with smaller particle size [37, 38]. Higher *A/V* ratio results in increased interaction between the nanoparticles and polymer matrix, leading to various property enhancements.

Generally, three types of nanocomposite can be prepared by varying the type of chemical interaction between the inorganic-organic components in PMC, i.e., (i) strongly bonded (via covalent, coordination, ionic interactions); (ii) weakly bonded (van der Waals, hydrogen-bonding interactions); and (iii) without chemical interactions [39, 40]. A critical challenge in the design of these hybrid inorganic–organic systems is the ability to control the mixing between the two dissimilar components or phases [8]. Homogenous mixing of the inorganic-organic components can be achieved by surface modification of silica nanoparticles.

### 1.3.1 Surface Modification of Silica Nanoparticles

Physical mixtures of organic polymers and preformed silica nanoparticles may lead to phase separation, resulting in poor mechanical, thermal, optical and etc. properties [8]. The hydrophilic nature of silica surface shows restricted affinity towards the polymer matrix [7]. In addition, silica nanoparticles tend to form aggregates during the formation of nanocomposite due to the inter-particle interactions. According to Kickelbick [8], there are five possibilities to overcome the phase separation in hybrid particulate systems, i.e., (i) the use of a polymer which weakly interacts (secondary bondings) with the nanoparticles; (ii) the covalent attachment of an inert organic layer on the surface of the particle to serve as a compatibilizer at the particle/polymer interface; (iii) the encapsulation of the particles through emulsion polymerization; (iv) the attachment of functional groups which allow a covalent linkage with the polymer; and (v) the attachment of initiation groups for grafting of polymer chains from the particle surface. Among the five different methods, attachment of functional groups which could form covalent bonding with the polymer matrix is relatively popular and used by many researchers to impart strong interfacial bonding in the nanocomposite.

In the case of silica based nanocomposites, silane coupling agents, $Si(OR)_3R'$ are widely used to functionalize the hydrophilic silica surface [41-43], where the functional groups, *R'*, introduced to the silica surface via condensation of silanol groups (≡Si-OH) with the alkoxy groups, -O*R*. The selection of desirable functional group (*R*') depends on the subject of application.

### 1.3.2 Selection of Polymer Matrix

In order to exploit the full potential of the technological applications of the nanomaterials, it is very important to endow them with good processability which has ultimately guided scientists to use conventional polymers as one component of the nanocomposites [44]. The conventional polymer matrixes used in the preparation of composite materials can be classified into two main categories: thermoplastics and thermosets. A thermoplastic is a plastic that melts to a liquid when heated and freezes to a glassy state when cooled sufficiently. Thermoplastics often have only very weak intermolecular forces between non-oriented chain segments [45]. Examples of thermoplastics are acrylic, acetate, nylon, polyethylene, polystyrene and etc. On the other hand, thermosetting plastics or thermosets are polymer materials that irreversibly cure, to a stronger form [46]. Upon curing, the thermoset will form permanent network structures through formation intermolecular cross-links (covalent bonds) between the polymer chains [45, 46]. Thus, it exhibits good dimensional stability and resist viscous flow at elevated temperature compared to the thermoplastics. Therefore, thermosets are often used as the matrix for the preparation of advanced composite materials that can meet common engineering needs of high temperature applications such as in aerospace, defense and semiconductor packaging industries. Epoxies, poly(arylene ethers), polyurethanes, polybenzimidazoles, bismaleimides, organofluoro polymers, certain silicones and liquid crystalline polyesters are some of the common commercially available thermosets.

#### 1.3.2.1 Epoxies

At present, epoxy resins such as diglycidyl ether of Bisphenol A (DGEBA) are widely used as the matrix for the preparation of silica-polymer nanocomposite. The main advantages of epoxies are they are easy to handle and show good processability. However, the silica-epoxy nanocomposites are not favorable for applications above 250 °C due to their low $T_g$, i.e., 165 – 240 °C [47, 48]. In addition, the incorporation of silica nanoparticles has been reported to decrease the $T_g$ of the neat epoxy polymer by 7 to 12 °C with the increase in the filler loading from 15 to 50 wt.% [47, 48]. Thus, it is necessary to find new classes of silica-thermoset nanocomposites which can withstand high temperature with minimal loss in the thermal mechanical properties as compared to the conventional epoxies. Thermosetting polyimide resins such as bismaleimides and nadimides are being favorably considered as replacements for epoxy resins in certain commercial and military applications [49].

#### 1.3.2.2 Bismaleimide

The bismaleimide (BMI) systems dominate over the other thermosetting polymer matrices primarily due to their high performance-to-cost ratio and relatively high temperature resistance (e.g. high $T_g$ and $T_d$ and low CTE) [50]. Besides, BMI also offers superior thermal and oxidative stability, low susceptibility for moisture absorption and good flame retardance. The main advantage of BMI is that it can withstand high stress at high temperatures at which typical epoxies, phenolics and most of the high performance plastics are unstable [51]. One disadvantage of BMI is that it relatively brittle due to their aromatic nature and high cross-linking density. Therefore, many BMI resins have been modified through various chain extension reactions to enhance their fracture toughness. Co-polymerizing the maleimide double bond with

aromatic diamine such as 4, 4'-diaminodiphenylmethane (DDM) is one of the most efficient and cost-effective method to achieve this objective [52-54]. Some of the reported inorganic-BMI composites are carbon-BMI [55-57], clay-BMI [58] and potassium titanate-BMI [59] hybrids. However, works on silica nanoparticles-BMI composites have not been reported in the literatures, thus the oppurtunitiy to develop such material is still open.

## 1.4 Problem Statements

The research developments addressed in the above sections would have given some brief pictures on the synthesis and applications of silica nanoparticles. Following are some of the challenges and opportunities that exist in the contemporary research in silica nanoparticles:

(a) At present, the synthesis of monodispersed and narrow size distributed silica nanoparticles significantly below 10 nm, in powder form via sol-gel process is not much reported in the literatures. Most of the reported works focused on the synthesis of colloidal silica nanoparticles. Preparation of silica nanoparticles in powder form would benefit many applications which require solvent free nanoparticle systems that are easy to handle and store;

(b) To date, metods to control the agglomeration of the sol-gel derived silica nanoparticles is not much reported in the literatures. Effective drying techniques could reduce the agglomeration of silica nanoparticles;

(c) Literatures on size-dependent properties of silica nanoparticles are still lacking due difficulty in producing silica nanoparticles in well defined size ranges and from the same origin.

(d) As described earlier, the incorporation of silica nanoparticles into BMI polymer matrix would yield potentially a new class of nanocomposite, which is not much reported. Chemical modification of silica surface with BMI compatible organo-functional groups and preparation of BMI polymer matrix are two important steps that have to be passed prior to the preparation of silica-BMI nanocomposite.

## 1.5 Research Objectives

The main objectives of this study are;

(a) To establish effective method(s) to synthesize monodispersed and narrow size distributed silica nanoparticles especially below 10 nm by;
   (i) Studying the effect of electrolytes (ammonium salts) on the formation of silica nanoparticles in the sol-gel process, and;
   (ii) Investigating the important experimental parameters that govern the growth and size of the silica particles in the sol-gel process.

(b) To study the effect of drying technique(s) on the morphology of silica nanoparticles;

(c) To determine the size-dependent properties of silica nanoparticles;

(d) To conduct chemical modification of silica surface by grafting organo-functional group(s);

(e) To develop a bismaleimide-diamine polymer matrix with optimal formulation and curing conditions, and;

(f) To explore the potential of silica nanoparticles prepared in this study as fillers in silica-bismaleimide nanocomposite system.

## 1.6 Scope of the Study

This study emphasizes on the synthesis, characterization and chemical modification of ultrafine silica nanoparticles and evaluates its potential application as fillers in a potentially novel PMC, i.e., silica-bismaleimide nanocomposite. The works conducted in this research can be categorized into three parts, i.e., (i) inorganic, (ii) organic, and (iii) inorganic-organic hybrid. The inorganic part involves the synthesis, characterization and surface modification of silica nanoparticles while the organic part includes the preparation of BMI/DDM polymer matrix. On the other hand, the hybrid part entails the preparation and characterization of silica-bismaleimide nanocomposites.

In the first part, two approaches are used to produce smallest possible silica nanoparticles via sol-gel process, i.e., via (i) addition of electrolytes (ammonium salts) and (ii) optimization of reaction parameters (reagents and conditions). The efficiency of the synthesis routes are evaluated based on the resulting particle size, morphology and yield. This followed by an investigation on drying techniques, aimed to reduce the agglomeration of silica nanoparticles in powder form. Focus is given to develop a new and cost effective drying technique based on alcohol dehydration to remove the liquid phase from the suspension that contains the silica nanoparticles. Next, the size dependent properties of silica nanoparticles are studied using various solid state characterization techniques. The study centers on the determination of some important physical, chemical and optical properties of silica nanoparticles. Subsequently, chemical modifications of silica surface are conducted to graft some selected organo-functional groups, i.e., epoxide and maleimide groups onto the silica surface. Characterization of the modified silica surfaces and determination of the functional

groups' reactivity are the main emphasis of this fraction of study. The second part focused on the preparation of BMI/DDM polymer matrix with optimal formulation and curing conditions. Finally, the third part involves the preparation and characterization of silica-bismaleimide nanocomposites. In this part, the effects of filler concentration, surface functional groups and particle size on the resulting thermal mechanical properties of silica-bismaleimide nanocomposites are studied. In addition, the effect of fillers on the curing profile of BMI/DDM polymer matrix and chemical interaction between the fillers and polymer matrix are also investigated.

## 1.7 Thesis layout

This thesis is composed of 11 chapters. Chapter 1 provides a brief introduction to highlight current state of research on silica nanoparticles and the objectives of the study. Chapter 2 consists of literature studies, mainly on the synthesis of silica nanoparticles via sol-gel process, agglomeration of silica nanoparticles, the size-dependent properties, silica-polymer nanocomposites, chemical modification of silica surface and bismaleimide polymer matrix. The experimental procedures which are compilation of experimental methods for Chapter 4 to 10 are described in Chapter 3. Chapters 4 to 10 are actually results and discussion chapters which serve the research objectives listed in Section 1.5, in a similar order. Chapter 4 and 5 describes the synthesis of silica nanoparticles in the presence of electrolytes and under optimized reaction conditions of sol-gel process, respectively. Chapter 6 elaborates the effects of drying techniques on the morphology of silica nanoparticles while Chapter 7 reports the size-dependent properties of silica nanoparticles. Chapter 8 conveys the chemical modification of silica surface using various organo-functional groups. The preparation and characterization of BMI/DDM polymer matrix and silica-bismaleimide

nanocomposite are discussed in Chapter 9 and 10, respectively. Finally, the thesis ends with conclusion and recommendation for future research in Chapter 11.

## References


1. Drexler, K. E. (1986). *Engines of Creation: The coming era of nanotechnology*. Doubleday/Anchor Press, New York.

2. Nordan, M. M. (2006). Nanotechnology's impact today - and how to make sense of it (Business Spotlight). *Advanced Materials and Processes*. **August Issue**: 37.

3. Silva, G. A. (2004). Introduction to nanotechnology and its applications to medicine. *Surgical Neurology* **61**: 216.

4. Klabunde, K. J. (2001). *Nanoscale materials in chemistry*. Wiley-Interscience, New York.

5. Brinker, C. J. and Scherer, G. W. (1990) *Sol-Gel Science: The physics and chemistry of sol- gel processing*. Academic Press Inc., San Diego.

6. Klabunde, K. J., Stark, J. V., Koper, O., Mohs, C., Park, D. G., Decker, S., Jiang, Y., Lagadic, I., and Zhang, D. (1996). Nanocrystals as stoichiometric reagents with unique surface chemistry. *J. Phys. Chem.* **100**: 12142.

7. Sun, Y., Zhang, Z. and Wong, C. P. (2005). Study on mono-dispersed nano-size silica by surface modification for underfill applications. *J. Colloid Inter. Sci.* **292**: 436.

8. Kickelbick, G. (2003). Concepts for the incorporation of inorganic building blocks into organic polymers on a nanoscale. *Prog. Polym. Sci.* **28**: 83.

9. Zeng, Q. H., Wang, D. Z. Yu, A. B. and Lu, G. Q. (2003). Synthesis of polymer-montmorillonite nanocomposites by in situ intercalative polymerization. *Nanotechnology* **13**: 549.

10. Wang, Z. and Pinnavaia, J. T. (1998). Nanolayer reinforcement of elastomeric polyurethane. *Chem. Mater*. **10**: 1820.

11. Vansant, E. F., Voort, P. V. D. and Vrancken, K. C. (1995). *Characterization and chemical modification of the silica surface*, Elsevier Science, New York.

12. Reverchon, E. and Adami, R. (2006). Nanomaterials and supercritical fluids. *J. Supercritical Fluids* **37**: 1.

13. Iller, R. K. (1979). *The chemistry of silica and silicates*, Wiley, New York.

14. Park, S. K., Kim, K. D. and Kim, H. T. (2002). Preparation of silica nanoparticles: determination of the optimal synthesis conditions for small and uniform particles, *Colloids Surf. A*. **197**: 7.

15. Rao, K. S., Hami, K. E., Kodaki, T., Matsushige, K. and Makino, K. (2005). A novel method for synthesis of silica nanoparticles. *J. Colloid Inter. Sci*. **289**: 125.

16. Kim, S. S., Kim, H. S., Kim, S. G. and Kim, W. S. (2004). Effect of electrolyte additives on sol-precipitated nano silica particles. *Ceramics Inter*. **30**: 171.

17. Petit, C., Lixon, P. and Pileni, M. P. (1990). Synthesis of cadmium sulfide in situ in reverse micelles. 2. Influence of the interface on the growth of the particles. *J. Phys. Chem.* **94**: 1598.

18. Silber, J. J., Biasutti, A., Abuin, E. and Lissi, E. (1999). Interactions of small molecules with reverse micelles. *Adv. Colloid Inter. Sci*. **82**: 189.

19. Leung, R., Hou, M. J. and Shah, D. O. in: Wasan, D. T., Ginn, M. E. and Shah D. O. (Eds.) (1988), *Surfactant Science Series*, *vol. 28*, Marcel Dekker, New York.

20. Pillai, V. and Shah, D. O. in: Soalns, C and Kunieda H. (Eds.) (1997) *Industrial Application of Microemulsion*, Marcel Dekker, New York.

21. Buining, P. A., Liz-Marza´n, L. M., and Philipsea, A. P. (1996). Simple preparation of small, smooth silica spheres in a seed alcosol for Stöber synthesis. *J. Colloid Interface Sci.* **179**: 318.

22. Chiappini, A., Armellini, C., Chiasera, A., Ferrari, M., Jestin, Y., Mattarelli, M., Montagna, M., Moser, E., Conti, G. N., Pelli, S., Righini, G. C., Gonçalves, M. C. and Almeida, R. M. (2007). Design of photonic structures by sol–gel-derived silica nanospheres. *J. Non-Cryst. Solids* **353**: 674.

23. Pallavidino, L., Razo, D. S., Geobaldo, F., Balestreri, A., Bajoni, D., Galli, M., Andreani, L. C., Ricciardi, C., Celasco, E., Quaglio, M. and Giorgis, F. (2006). Synthesis, characterization and modeling of silicon based opals. *J. Non-Cryst. Solids* **352**: 1425.

24. Wang, C. T., Wu, C. L., Chen, I. C. and Huang, Y. H. (2005). Humidity sensors based on silica nanoparticle aerogel thin films. *Sens. Actuators B.* **107**: 402.

25. Grant, S. A., Weilbaecher, C. and Lichlyter, D. (2007). Development of a protease biosensor utilizing silica nanobeads. *Sens. Actuators B.* **121**: 482.

26. Wang, H., Bai. Y., Liu, S., Wu, J. and Wong, C. P. (2002). Combined effects of silica filler and its interface in epoxy resin. *Acta Mater.* **50**: 4369.

27. Zhang, H., Zhang, Z., Friedrich, K. and Eger, C. (2006). Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content. *Acta Mater.* **54**: 1833.

28. Kwon, S. C., Adachi, T., Araki, W. and Yamaji, A. (2006). Thermo-viscoelastic properties of silica particulate-reinforced epoxy composites: Considered in terms of the particle packing model. *Acta Mater.* **54**: 3369.

29. Sharma P., Brown S., Walter G., Santra, S. and Moudgil, B. (2006). Nanoparticles for bioimaging. *Adv. Colloid Interface Sci.* **123**: 471.

30. Jiang, L., Wang, W., Wu, D., Zhan, J., Wang, Q., Wu, Z. and Jin, R. (2007) Preparation of silver quantum dots embedded water-soluble silica/PAAc hybrid nanoparticles and their bactericidal activity. *Mater. Chem. Phys*. **104**: 230.

31. Lai, C. Y., Wu, C. W., Radu, D. R., Trewyn, B. G. and Lin, V. S. Y. (2007). Reversible binding and fluorescence energy transfer between surface-derivatized CdS nanoparticles and multi-functionalized fluorescent mesoporous silica nanospheres. *Stud. Surf. Sci. Catal.* **170**: 1827.

32. Neri, G., Rizzo, G., Crisafulli, C., Luca, L. D., Donato, A., Musolino, M. G. and Pietropaolo, R. (2005). Isomerization of α-pinene oxide to campholenic aldehyde over Lewis acids supported on silica and titania nanoparticles. *Appl. Catal. A* **295**: 116.

33. Gole, J. L., Burda, C., Wang, Z. L. and White, M. (2005). Unusual properties and reactivity at the nanoscale. *J. Phys. Chem. Solids* **66**: 546.

34. Pratsinis, S.E. (1998). Flame aerosol synthesis of ceramic powders. *Prog. Energy Combust. Sci*. **24**: 197.

35. Kwon, S. and Messing, G. L. (1997). The effect of particle solubility on the strength of nanocrystalline agglomerates: Boehmite, *NanoStruc. Mater*. **8**: 399.

36. Hussain, F., Hojjati, M., Okamoto, M. and Gorga, R. E. (2006). Polymer-matrix nanocomposites, processing, manufacturing, and application: An overview. *J. Composite Materials* **40**: 1511.

37. Luo, J. J. and Daniel, I. M. (2003). Characterization and modeling of mechanical behavior of polymer/clay nanocomposites. *J. Compos. Sci. Technol*. **63:**1607.

38. Thostenson, E., Li, C. and Chou, T. (2005). Review nanocomposites in context. *J. Compos. Sci. Technol*. **65**: 491.

39. Judeinstein, P. and Sanchez, C. (1996). Hybrid organic–inorganic materials: a land of multidisciplinarity. *J. Mater. Chem.* **6**: 511.

40. Schubert, U. and Husing, N. (2000). *Synthesis of inorganic materials*. Wiley–VCH, Weinheim.

41. Jesionowski, T. and Krysztafkiewicz, A. (2002). Preparation of the hydrophilic/hydrophobic silica particles. *Colloids Surfaces A*. **207**: 49.

42. Fonseca, M. G., Oliveira, A. S. and Airoldi, C. (2001). Silylating agents grafted onto silica derived from leached chrysotile. *J. Colloid Interface Sci.* **240**: 533.

43. Yu, Y. Y., Chen, C. Y. and Chen, W. C. (2003). Synthesis and characterization of organic–inorganic hybrid thin films from poly(acrylic) and monodispersed colloidal silica. *Polymer* **44**: 593.

44. Gangopadhyay, A. and De, A. (2000). Conducting polymer nanocomposites: A brief overview. *Chem. Mater.* **12**: 608.

45. Elias, H. G. (1996). *An introduction to polymer sc*ience. VCH Publishers, New York.

46. Pascault, J. P., Sautereau, H., Verdu, J. and Williams, R. J. J. (2002). *Thermosetting polymer*. Marcel Dekker, Inc. New York.

47. Ragosta, G., Abbate, M., Musto, P., Scarinzi, G. and Mascia, L. (2005). Epoxy-silica particulate nanocomposites: Chemical interactions, reinforcement and fracture toughness. *Polymer* **46**: 10506.

48. Liu, Y. L., Hsu, C.Y., Wei, W. L. and Jeng, R. J. (2003). Preparation and thermal properties of epoxy-silica nanocomposites from nanoscale colloidal silica. *Polymer* **44**: 5159.

49. Torrecillas, R., Regnier, N and Mortaigne, B. (1996). Thermal degradation of bismaleimide and bisnadimide networks-products of thermal degradation and type of crosslinking points. *Polym. Degrade. Stab*. **51**: 307.

50. Lin S. C. and Pearce, E M. (1993). *High performance thermoset: Chemistry, properties and applications*, Hanser, Munich.

51. Kumar, K. S. S., Nair, C. P. R., Sadhana, R. and Ninan K. N. (2007). Benzoxazine–bismaleimide blends: Curing and thermal properties. *Euro. Polym. J*. **43**: 5084.

52. Guilio, C. D., Gautier, M. and Jasse, B. (1984). Fourier transform infrared spectroscopic characterization of aromatic bismaleimide resin cure states. *J. App. Polym. Sci*. **29**: 1771.

53. Loustalot, M. F. G. and Cunha, L. D. (1997). Study of molten-state polymerization of bismaleimide monomers by solid-state $^{13}C$ n.m.r. and FTi.r. *Polymer* **39**: 1833.

54. Wu, W., Wnag, D. and Ye, C. (1998). Preparation and characterization of bismaleimide-diamine prepolymers and their thermal-curing behavior. *J. App. Polym. Sci*. **70**: 2471.

55. Bao, L. R. and Yee, A. F. (2002). Effect of temperature on moisture absorption in a bismaleimide resin and its carbon fiber composites. *Polymer* **43**: 3987.

56. Bao, L. R. and Yee, A. F. (2002). Moisture diffusion and hygrothermal aging in bismaleimide matrix carbon fiber composites: part II—woven and hybrid composites. *Compos. Sci. Technol*. **62**: 2111.

57. Parka, J. M., Kim, J. W. and Yoon, D. J. (2002). Interfacial evaluation and microfailure mechanisms of single carbon fiber/bismaleimide (BMI) composites by tensile and compressive fragmentation tests and acoustic emission. *Compos. Sci. Technol*. **62**: 743.

58. Meng, J. and Hu, X. (2004). Synthesis and exfoliation of bismaleimide–organoclay nanocomposites. *Polymer* **45**: 9011.

59. Liang, G., Hu, X. and Lu, T. (2005). Inorganic whiskers reinforced bismaleimide composites (Part II). *J. Mater. Sci*. **40**: 1743.

# CHAPTER TWO

# LITERATURE REVIEWS

## 2.1 Sol-Gel Process

Interest in sol-gel processing of inorganic ceramics materials began in the mid-1800s with the initial works reported by Ebelmen [1] and Graham [2] on silica gels. Their works dealt with hydrolysis of tetraethylorthosilicate (TEOS), $Si(OC_2H_5)_4$, under acidic conditions which eventually produced 'glass like' silica materials. In the period of 1950 to 1960, Roy and co-workers used the sol-gel method to produce various types of novel ceramics containing Al, Si, Zr, Ti, etc. [3-5]. In the same period, Iller's prominent works in silica chemistry [6] made significant impact on further development of sol-gel process. Iller's contributions led to the first commercial production of colloidal silica nanoparticles called Ludox®, by Du Pont Chemicals Company [7].

The sol-gel process is widely used to produce homogenous and pure silica particles under mild conditions. It provides many advantages such as the ability to control the particle size, size distribution and morphology of silica compared to other techniques like flame synthesis and microemulsion route. The general reactions of TEOS that leads to the formation of silica particles in the sol-gel process can be written as [7-10]:

$$Si(OC_2H_5)_4 + H_2O \xrightarrow{\text{hydrolysis}} Si(OC_2H_5)_3OH + C_2H_5OH \quad (2.1)$$

$$\equiv Si\text{-}O\text{-}H + H\text{-}O\text{-}Si\equiv \xrightarrow{\text{water condensation}} \equiv Si\text{-}O\text{-}Si\equiv + H_2O \quad (2.2)$$

$$\equiv Si\text{-}OC_2H_5 + H\text{-}O\text{-}Si\equiv \xrightarrow{\text{alcohol condensation}} \equiv Si\text{-}O\text{-}Si\equiv + C_2H_5OH \quad (2.3)$$

The hydrolysis of TEOS molecules forms silanol groups. The polycondensation between the silanol groups or between silanol groups and ethoxy groups creates siloxane bridges (Si-O-Si) that forms the entire silica structure [10]. The polycondensation reaction also often referred as polymerization [6]. The polymerization rate depends on reaction conditions which might result in the formation of either a three dimensional network or single monodispersed particles [11]. According to Iller [6], the polymerization occurs in three stages i.e., (i) polymerization of monomers to form primary particles, (ii) growth of the particles, and (iii) linking of particles into chains and then networks which forms the gel structure. In addition, he also stated that the condensation reactions takes place in such a fashion as to maximize the number of Si-O-Si bonds and minimize the terminal hydroxyl (silanol) groups through internal condensation [6]. In general, the formation of silica particles can be divided into two stages: nucleation and growth. Figure 2.1 shows the polymerization behavior of aqueous silica, given by Iller [6]. As shown in the figure, in basic condition (B), the particles grow in size and decrease in number through Oswald ripening mechanism [10]. By contrast, in acidic condition (A) or in presence of flocculating salts the particles aggregates into three-dimensional networks and form gels.

Two models, monomer addition [12, 13] and controlled aggregation [9, 14] have been proposed to describe the growth mechanism of silica. The monomer addition model describes that after an initial burst of nucleation the particle growth occurs through the addition of hydrolyzed monomers onto the (primary) particle surface. By

contrast, the aggregation model elaborates that the nucleation occurs continuously throughout the reaction and the resulting nuclei (primary particles) will aggregate together to form larger particles (secondary particles).

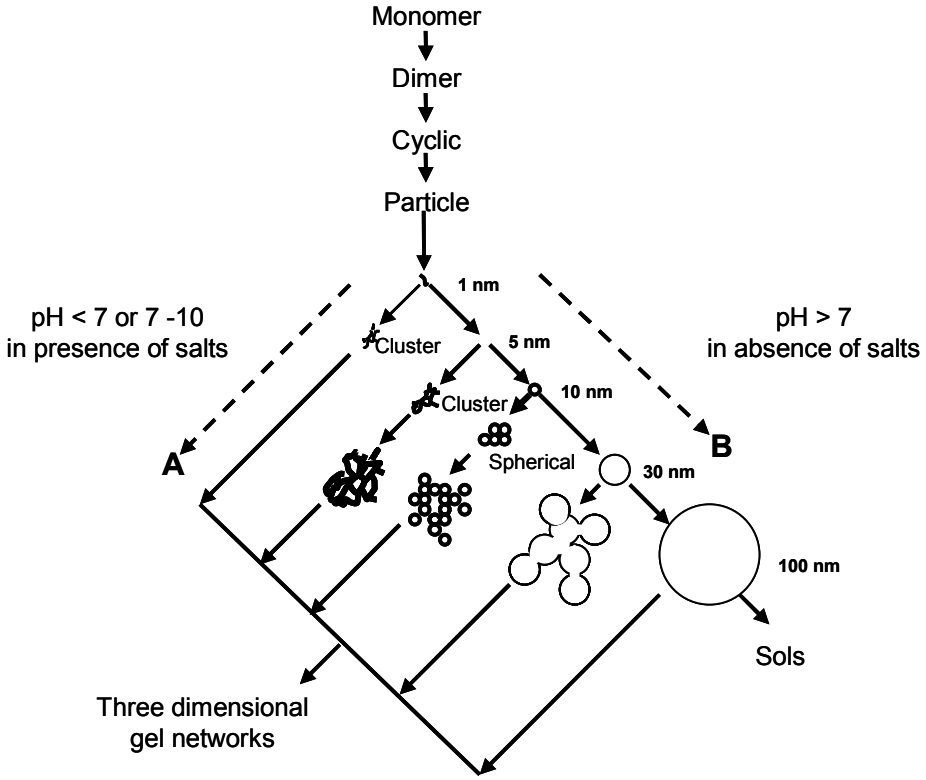


**Figure 2.1**: Polymerization behavior of aqueous silica [6].

According to Brinker and Scherer [10], in basic conditions the particle growth occur predominantly by monomer addition or monomer-cluster aggregation (MCA) kinetic model. This model is further divided into diffusion limited monomer-cluster aggregation (DLMCA) and reaction limited monomer-cluster aggregation (RLMCA) mechanisms. According to DLCMA, monomers ($Si(OH)_4$) travel by random walks and stick irreversibly (condensation reaction) at first contact with the growing cluster. Opposite to the DLMCA, RLMCA provides that condensation between monomer and