DEVELOPMENT OF CORE LAYER MATERIALS USING PARTICULATE FILLED EPOXY COMPOSITES

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2008

DEVELOPMENT OF CORE LAYER MATERIALS USING PARTICULATE FILLED EPOXY COMPOSITES

by

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Thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

April 2008

ACKNOWLEDGEMENTS

First, I would like to express my heartiest appreciation and deep gratitude to my main-supervisor, Dr Mariatti Jaafar for her supervision, advice, assistance, encouragement and constant dedication during my period of study. Sincere thanks are accorded to my co-supervisor, Dr Hazizan Md. Akil for spending his time and effort to evaluate my research papers. Your willingness in revising of the thesis prior to submission will always be appreciated.

I am grateful to the Dean and all the staff in the School of Materials and Mineral Resources Engineering, USM for their co-operation and helps. I would also like to forward my gratitude to technical staff namely Mr. Segar, Mr. Mohd Zandar, Mr. Mohd. Hassan, Mr. Faizal, Mr. Rokman, Mr. Sharul Ami Zainal Abidin, Mr. Mohtar and Mr. Suhaimi for their guidance and co-operation in laboratory works.

Special thanks are acknowledged to Intel Technology Sdn. Bhd. for the fellowship and research grants that have made this research possible.

Finally, I would like to send my sincere gratitude to my husband, parents, brothers, and sister for your patient support, motivation and encouragement.

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LIST OF SYMBOLS

		Page
ppm/°C	Part per million per degree celsius	1
GPa	Giga pascal	3
°C	Degree celsius	10
%	Percentage	13
SiO_2	Silicon dioxide	21
Si-O-Si	Siloxane group	21
$Mg_3Si_4O_{10}(OH)_2$	Magnesium silicate	22
$Al_3O_3.2SiO_2.2H_2O$	Kaolinite	24
Al_2O_3	Aluminum oxide	25
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	Cordierite	26
NaOH	Sodium hydroxide	28
H_2O	Water	32
g/cm^3	Gram per cubic centimeter	34

cP	Centipoise	34
μm	Micron	37
g/mol	Grams per mole	38
vol%	Volume percent	39
wt%	Weight percent	40
mm	Millimeter	44
°C/ min	Degree Celsius per minute	44
ε'	Dielectric constant	48
MPa	Mega pascal	57
K_{1C}	Fracture toughness	58
E'	Dynamic flexural storage modulus	60
$tan\ \delta$	Tangent delta	60
T_g	Glass transition temperature	61
Mol/m^3	Mole per cubic meter	87
kHz	Kilo hertz	97
MHz	Mega hertz	97
cps	Counts per second	102

LIST OF ABBREVIATION

		Page
IC	Integrated circuit	1
CTE	Coefficients of thermal expansion	1
EMI	Electromagnetic interference	5
C4	Control collapse chip connection	7
PTH	Plated through hole	11
RTM	Resin transfer molding	19
LLDPE	Linear low-density polyethylene	28
DCP	Dicumyl peroxide	28
PHR	Parts per hundred	39
GP	Glass powder	39
FS	Fused silica	39
MS	Mineral silica	39
RPM	Revolutions per minute	40
A	Epoxy cured with Jeffamine	40

AE	Epoxy cured with Ethacure	40
END	Epoxy with non-diluent system	41
ED	Epoxy with diluent system	41
C	Cordierite	42
C-TA	Cordierite surface treatment with (3-aminopropyl)trimethoxysilane	42
C-TP	Cordierite surface treatment with (3-glycidyloxypropyl)trimethoxysilane	42
TMA	Thermal mechanical analyzer	44
DMA	Dynamic mechanical analyzer	45
TGA	Thermo gravimetric analyzer	45
SEN-T	Single-edge notched - tensile	46
XRD	X-ray diffraction	47

LIST OF PUBLICATIONS & SEMINARS

1. Teh, P.L., Jaafar, M., Akil, H.M., Seetharamu, K.N., Wagiman, A.N.R. and Beh, K.S. (2004). Thermal properties of fused silica and glass powder filled epoxy resin. In: *Proceedings of 6th Electronic Materials And Packaging Conference* 5 - 7 December.

2. Teh, P.L., Jaafar, M., Akil, H.M., Seetharamu, K.N., Wagiman, A.N.R. and Beh, K.S. (2005). Thermal expansion and flexural properties of particulate fillers filled epoxy composites. In: *Proceedings of 5th National Symposium of Polymer Materials*. 23-24 August.

3. Teh, P.L., Mariatti, M., Akil, H.M., Yeoh, C.K., Seetharamu, K.N., Wagiman, A.N.R. and Beh, K.S. The properties of epoxy resin coated silica fillers composites. *Materials Letters*, **61(11-12):** 2156-2158.

4. Teh, P.L., Mariatti, M., Akil, H.M., Seetharamu, K.N., Wagiman, A.N.R. and Beh, K.S. (2006). High filled epoxy composites for electronic packaging application. In: *31st International Electronics Manufacturing Technology Conference (IEMT),* 9-10 November.

5. Teh, P.L., Mariatti, M., Akil, H.M., Seetharamu, K.N., Wagiman, A.N.R. and Beh, K.S. (2006). Improved tg of mineral silica filled epoxy composites. In: *Proceedings of National Symposium of Polymeric Material (NSPM) 2006*. 19-20 December.

6. Teh, P.L., Mariatti, M., Akil, H.M., Wagiman, A.N.R. and Beh, K.S. (2006). The effect of curing agent on the properties of mineral silica filled epoxy composites. *Polymer Composites*, **26(1)**: 27-36.

7. Teh, P.L., Mariatti, M., Akil, H.M., Seetharamu, K.N., Wagiman, A.N.R. and Beh, K.S. (2006). Effect of ethanol as diluent on the properties of mineral silica filled epoxy composites. *Journal of Composite Materials,* **42(2)**: 129-142.

PEMBANGUNAN BAHAN LAPISAN TERAS MENGGUNAKAN KOMPOSIT EPOKSI TERISI PARTIKULAT

ABSTRAK

Kajian ke atas epoksi terisi pengisi partikulat ini adalah terdiri daripada enam peringkat. Bahagian pertama kajian ini melibatkan pengkajian mengenai kesan pengisi-pengisi partikulat: silika terlakur, serbuk kaca dan silika mineral, terhadap sifat-sifat fizikal, haba dan mekanikal komposit epoksi. Tiga jenis pengisi partikulat ini telah disebatikan dengan resin epoksi jenis 'Bisphenol A' yang dimatangkan dengan agen pematang alifatik ("Jeffamine') dengan menggunakan teknik pencampuran mekanikal. Kandungan pengisi telah diubah dari 0 hingga 40% isipadu. Nilai kekuatan pelenturan, kekakuan dan keliatan meningkat dengan pertambahan pengisi-pengisi di dalam semua sistem komposit epoksi. Mikroskopi penskanan elektron (SEM) telah menunjukkan interaksi pengisi-matrik yang tidak baik wujud di dalam komposit epoksi terisi serbuk kaca pada 40% isipadu. Selain daripada itu, didapati nilai modulus pelenturan yang tinggi diperolehi di dalam komposit terisi silika mineral pada 40% isipadu. Pengisi didapati meningkatkan sifat kestabilan haba and mekanikal terma dinamik dan mengurangkan pekali haba pengembangan (CTE) epoksi. Nilai CTE terendah diperhatikan di dalam komposit epoksi terisi 40% isipadu silika terlakur, ini adalah disebabkan oleh nilai CTE semulajadi yang rendah bagi pengisi tersebut. Kajian bahagian kedua dijalankan untuk membandingkan dua jenis agen pematang yang berlainan, iaitu alifatik dan aromatik ('Ethacure') agen pematang jenis kumpulan berfungsi amina dalam komposit epoksi terisi silika mineral. Didapati bahawa sifat-sifat mekanikal dan haba resin epoksi adalah bergantung kepada jenis agen pematang. Morfologi dalam kedua-dua sistem epoksi-pematangan ini adalah berlainan. Ketumpatan sambung-silang yang diukur melalui ujian pembengkakan menunjukkan kumpulan berfungsi amina aromatik memberikan ketumpatan sambung-silang yang tinggi, oleh itu ia meningkatkan sifat-sifat mekanikal dan haba. Bahagian ketiga dalam kajian terdiri daripada penggunaan etanol sebagai

pencair dalam komposit epoksi terisi silika mineral. Etanol dengan 10% berat telah digunakan sebagai pencair dalam sistem epoksi untuk menurunkan kelikatan sistem tersebut. Secara umumnya, didapati bahawa sifat-sifat komposit epoksi adalah dipengaruhi oleh kandungan pengisi dan penambahan pencair etanol. Penambahan pencair dalam epoksi membolehkan kandungan pengisi yang lebih tinggi ditambah dalam sistem komposit epoksi, iaitu pada 60% isipadu, jika dibandingkan dengan sistem tanpa pencair iaitu 40% isipadu. Kehadiran kandungan pengisi yang tinggi telah menghasilkan nilai kekakuan yang tinggi dan nilai CTE yang rendah seperti yang diperlukan dalam aplikasi pembungkusan elektronik. Bahagian keempat kajian ialah menghasilkan komposit silika mineral disaluti resin epoksi dengan kandungan pengisi yang tinggi, iaitu dari 80 hingga 95% isipadu yang terupaya dihasilkan dengan teknik pencampuran yang baru. Bahan ini telah menunjukkan nilai CTE yang rendah, dengan nilai serendah 25 ppm/°C, dan modulus kelenturan yang tinggi sekitar 20 GPa ke atas. Secara umumnya, SEM telah menunjukkan bahawa pengisi gagal disaluti oleh resin spoksi dengan sempurna pada kandungan pengisi yang lebih daripada 80% isipadu. Kordierit telah disintesiskan dalam bahagian kelima kajian ini untuk digunakan dalam resin epoksi. Di sini kordierit telah dipilih kerana ia mempunyai sifat-sifat CTE yang rendah dan kekuatan yang tinggi. Komposit kordierit disaluti epoksi telah dihasilkan pada kandungan pengisi dari 80 hingga 95% isipadu untuk dijadikan perbandingan dengan komposit silika mineral disaluti epoksi. Komposit kordierit disaluti epoksi tersebut menunjukkan lenturan yang baik dan sifat-sifat mekanikal, haba dan pemalar dielektrik yang setara jika dibandingkan dengan komposit silika mineral disaluti epoksi. Bahagian keenam kajian ini melibatkan penggunaan dua jenis agen pengkupel silana, iaitu (3-aminopropil) trimetoksisilana’ dan (3-glisidiloksipropl) trimetoksisilana, dalam komposit kordierit disaluti epoksi dengan kandungan pengisi yang optimum iaitu pada 80% isipadu. Sistem ini telah menunjukkan peningkatan dalam sifat-sifat mekanikal di samping mengekalkan sifat-sifat haba dan pemalar dielektrik.

DEVELOPMENT OF CORE LAYER MATERIALS USING PARTICULATE FILLED EPOXY COMPOSITES

ABSTRACT

The research on epoxy filled with particulate fillers composites consist of six parts. The first part of the study is to investigate the effect of types particulate fillers: fused silica, glass powder and mineral silica, on the physical, thermal and mechanical properties of epoxy composites. These three types of particulate fillers were compounded with Bisphenol A epoxy resin cured by aliphatic curing agent (Jeffamine) using mechanical mixing technique. The fillers content were varied from 0 to 40 vol%. Flexural strength, stiffness and toughness values were improved with incorporation of fillers for all filled epoxy composites systems. Scanning electron microscopy (SEM) showed poor filler-matrix interaction in glass powder filled epoxy composites at 40 vol%. On the other hand, the highest flexural modulus was observed in mineral silica filled epoxy composites at 40vol%. It was found that fillers increase the thermal stability and dynamic thermal mechanical properties and reduces the coefficient of thermal expansion (CTE) of the epoxy. The lowest CTE value was observed in 40 vol% of fused silica filled epoxy composites, which was traced to the effect of its nature of low intrinsic CTE value of the fillers. The second part of the research was carried out to compare two different types of curing agents, i.e. aliphatic and aromatic (Ethacure) amine functional curing agents in mineral silica filled epoxy composite. It was found that the mechanical and thermal properties of epoxy resins are strongly depended on the types of curing agent. Morphology changed differently in these two epoxy-curing systems. Crosslink density measured from the swelling test showed that aromatic amine functionality group gives higher crosslink density and thus increase mechanical and thermal properties. The third part of the research involves the use of ethanol as diluent in mineral silica filled epoxy composites. Ethanol at 10 wt% was used as diluent in the epoxy system to reduce the viscosity of the entire system. In general, it was

found that the properties of epoxy composites are governed by the filler loading and the addition of ethanol as diluent. The addition of the diluent in epoxy permits higher amount of filler content that can be incorporated in the epoxy composites system, i.e. 60 vol%, compared to that of non-diluent system which is at 40 vol%. The presence of higher filler loading presents in diluent system resulted in higher stiffness and low CTE as required in the electronic packaging application. The fourth part of study is to produce epoxy resin coated mineral silica composites with high percentage of filler loading, i.e. from 80 to 95 vol% are able to be produced by a new mixing technique. Apparently, the materials exhibited low CTE, i.e. as low as below 25 ppm/°C, and high flexural modulus of above 20 GPa. In general, SEM revealed that at high filler content i.e. above 80 vol%, the epoxy resin was insufficient to coat the filler well. Cordierite was synthesized in fifth part of the study to be applied in epoxy resin. Cordierite was chosen here due to its low CTE and high strength properties. Epoxy coated cordierite composites were produced at the filler content of 80 to 95 vol% in order to do comparison with epoxy coated mineral silica composites. The epoxy coated cordierite composites showed better flexural strength and comparable properties in mechanical, thermal and dielectric constant properties than the epoxy coated mineral silica composites. The sixth part of study involves the use of two types of silane coupling agents, i.e. (3-aminopropyl)trimethoxysilane and (3-glycidyloxypropyl)trimethoxysilane, in epoxy coated cordierite composite filled at 80vol% of optimum filler content. This system showed improvement in mechanical properties while maintaining the thermal and dielectric constant properties.

CHAPTER 1
INTRODUCTION

Recent advances in increasing the packaging density and number of transistor in integrated circuit (IC) has resulted in a need for substrate materials with low coefficients of thermal expansion (CTE) in order to minimize thermal stresses that can cause solder joint failure. This thesis attempts to overcome the CTE problem by investigating few possible materials to replace the existing organic substrate materials. This thesis is emphasized on the second level packages, particular on the core or base layer of the organic substrates materials by looking in the thermal mismatch issues.

1.1 Problem statement

Electronic packaging industry has continuous increasing in circuit density and functionality in unit area or space. Therefore, the interconnection technology in materials, equipment and process development has eventually become important in optimizing the package reliability. As the result, flip chip technology has been replacing the old technology for the best overall performance.

Organic substrate materials have been introduced into the electronic packaging industry to meet the requirements of low cost, high interconnect and better reliability. However, it is previously observed that organic substrate based on polymeric materials generates warpage during thermal cycling test (Raj et al., 2001). Warpage is caused by the lack of dimension control. Another issue is the large different of CTE between the substrate and silicon die. CTE of epoxy is normally at above 80 ppm/°C, and it is relatively high compared to that of silicon chips (2-3 ppm/°C). Therefore, when thermal mismatch occurred, the package will be generated shrinkage and expansion under the continuous temperature cycle. Figure 1.1 shows the condition of package during thermal cycling. In this condition, the solder balls, which are located in between the gap

of the die and substrate, are stressed under the continuous temperature cycling. This subsequently will cause failure to the solder balls due to thermo-mechanical fatigue. The common failure modes of this defect are normally balls cracking and delamination of balls.

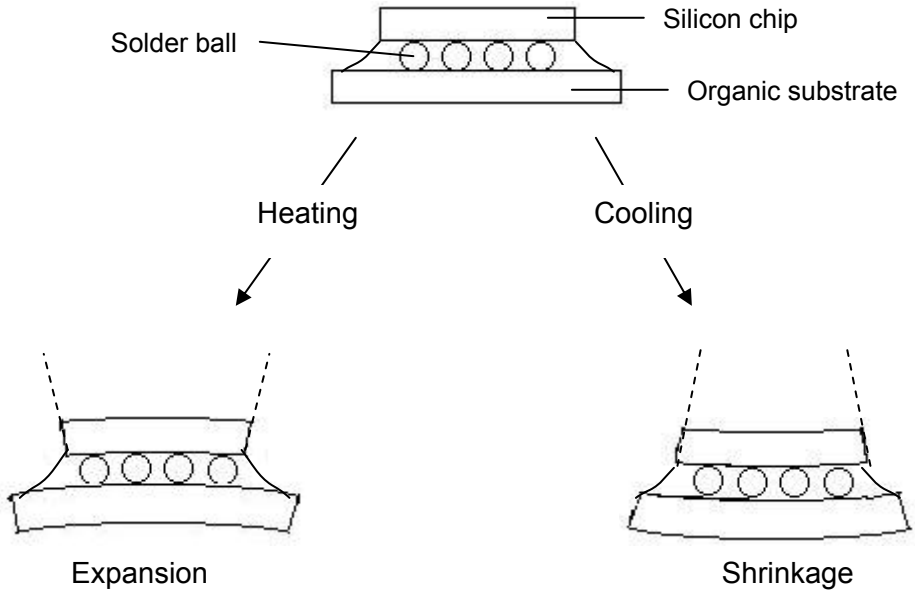


Figure 1.1: Thermal cycling of package.

To overcome this CTE problem, an organic material called underfill has been used in industry to fill up the gap in between the silicon chip and organic substrate. Basically, this underfill material will act as the mechanical inter-locking materials to minimize the package failure. However, there are many aspects to be concerned of using this material, this includes: fast curing and rheology behaviors, thermal stability, good adhesive stress, high toughness, minimum moisture absorption, optimum CTE and cost effective. Therefore, for the ultimate substrate materials, a thermal expansion matched to that of the silicon chips would be desirable to improve reliability particularly as chips size continuously decreased in size.

Beside thermal expansion properties, dielectric constant is also one of the major factors affecting the performance of the package. It is because dielectric

constant plays an important role in determining the circuit speed. As known that the signal transmissions from the silicon chip to the board is governed by the dielectric constant of the substrate. If the total resistance is low, the signal will be propagated with the speed of light. On the other hand, if the resistance is high and eventually the signal transmission is slow. Thus, dielectric constant property is also considered for this application.

Another solution to improve the package performance and reliability is to utilize an ultra high modulus organic substrate material. Note that high stiffness substrate materials are favored to achieve fine pitch interconnect reliability and minimized the warpage. The existing substrate materials, FR-4 (Flame Retardant-4) is one type of layered woven glass fiber reinforced epoxy composites which have fulfilled the high modulus properties which is at 20GPa (Banerji et al., 2002). However, this woven fiber reinforced materials have limitations on the anisotropic properties. Properties of these materials, such as mechanical and thermal are differed in different direction. According to Ehrler (2002), a typical FR-4 material has CTE in *z*- direction at 58-86 ppm/°C and 20-30 ppm/°C in *x, y*- directions for temperature at below glass transition temperature. Therefore, particulate fillers in epoxy resin are applied here in order to obtain the isotropic properties and hence improved the warp and solder joint reliability of the package.

1.2 Objective of the research

This thesis attempts to develop suitable core layer materials in organic or polymer substrate material. Thus, the objectives of this thesis are summarized as follow:

(a) To study the effect of different particulate fillers on the properties of epoxy based composites.

(b) To study the effect of curing agents on the properties of mineral silica filled epoxy composites.

(c) To study the effect of ethanol as diluent on the properties of mineral silica filled epoxy composites.

(d) To study the properties of epoxy coated mineral silica composites.

(e) To synthesize the cordierite and to study the properties of epoxy coated cordierite composites.

(f) To study the effect of silane coupling agent on the properties of epoxy coated cordierite composites.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction to electronic packaging

2.1.1 Overview

The increased usage of computers and electronic components in all respects in our lives, increasing performance of electronic packaging configurations without increasing the cost is becoming a major thrust in electronic industry (National Research Council, 1990).

According to Pecht et al. (1999) electronic packaging is referred to the technology of packaging electronic equipment, which includes six major categories:

(1) the packaging of the integrated circuit chips (dies)

(2) the interconnections for signal transmission, power and ground

(3) the encapsulation for protecting the chips and interconnections from moistures, chlorides and other element in the environment

(4) the heat sinks and other cooling devices needed to remove heat from the chips

(5) the power supply

(6) the housing for electromagnetic interference (EMI)

Electronic packaging is involving in multi level interconnection. Basically, the chip level or zero level packaging includes chip metallization, and provisions for chip-package interconnection as shown in Figure 2.1. The first level interconnection is referring to the attachment of the chips to the substrate to form a single or a multiple chip module. The substrate materials are normally consisting of organic or ceramic package. While second level packaging is the assembly of chips modules and other

components on the printed circuit boards (PCBs) and the third level packaging is involved in plugging the PCBs into the motherboard.

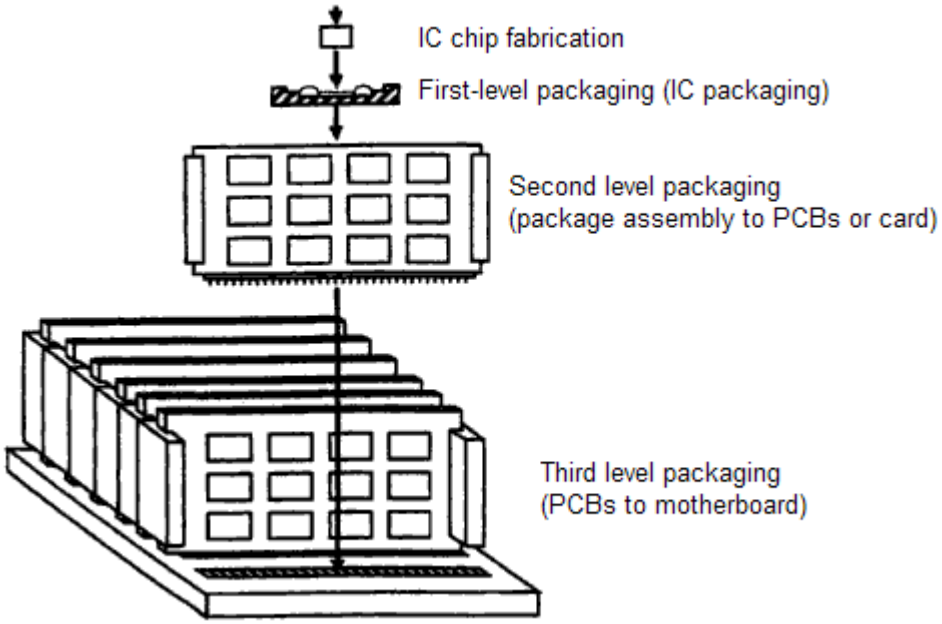


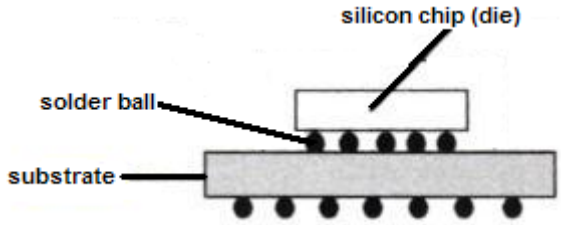
Figure 2.1: Typical hierarchy showing different levels of packaging (Datta et al., 2004).

Recently, attention was directed from first level to second and third levels. The rapid miniaturization during the last 20 years has resulted large increases in packing density, heat generated by chip and amount of interconnections. The challenge is to design the chips and interconnections in a compact way that permits for sufficient heat removal, which allows the electronics to operate at high speed and enable to withstand the thermal cycling during applications.

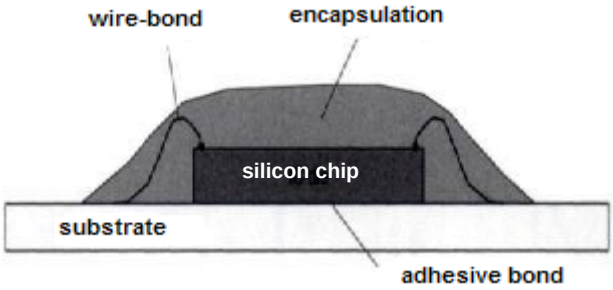
2.1.2 Flip chip technology

Various packaging technologies such as flip chip, chip on board, tape automated bonding, ball grid array and multi chip module technology, have been introduced in the market to improve the interconnection performance and reliability. One of the significant developments to improve cost, reliability and productivity in the electronic packaging industry has been flip chip technology.

Flip chip is the new technology which replacing wire-bond technology in current electronic industry. Wire bond technology has been used for many years because high speed wire bonders meet most of the needs for interconnections. The past decade witnessed an explosive growth in the research and developed the solder ball flip chip technology. For flip chip package, as shown in Figure 2.2(a), the bare die is mounted directly to the substrate. The electrical connection of face-down electronic components onto substrates by solder balls. In contrast, for wire bonding package, as shown in Figure 2.2(b), uses face-up chips with a wire connection to each pad. According to Harper (2002a), the wires are typical 90-100 μm in length and 25-35 μm in diameter and the wires are usually gold and aluminum.



(a)



(b)

Figure 2.2: A typical (a) flip chip and (b) wire bond packages.

Flip chip technology was originally invented by IBM in 1962 (Blackwell, 2000; Tummala, 2001). At that time, they are focused on solid logic technology with silicon transistors mounted on a thick film ceramic substrate. Several years later, the concept of control collapse chip connection (C4) technology was introduced. Till now, the

concept of flip chip is extended to house high I/O count semiconductor chips. Flip chip technology is considered to be an advance form of surface mount technology where a bare semiconductor chip processed with solder balls on its surface is turn up side down and bonded directly to the chips. According to Lau & Lee (1999), the advantages of flip chip technology are as follow:

- High package density without the need of a lead frame
- Smaller size; Eliminating packages and bond wires reduces the required board area by up to 95%, and requires far less height. Weight can be less than 5% of packaged device weight. Flip chip is the simplest minimal package, smaller than Chip Scale Packages (CSP's) because it is chip size.
- Achieves a high I/Os; Flip chip gives the greatest I/Os connection flexibility. Wire bond connections are limited to the perimeter of the die, driving die sizes up as the number of connections increases. Flip chip connections can use the whole area of the die, accommodating many more connections on a smaller die.
- Enhance electrical performance as the result of short distance between the chip and the substrate; includes minimal propagation delay and minimal transmission losses at high frequency
- Noise control and lower cost

2.2 Overview of substrate materials used in flip chip technology

2.2.1 Introduction

A substrate is also known as chip carrier. It is a sheet on which one or more chips are attached as shown in Figure 2.3. Materials used for substrate materials in flip chip technology must satisfy a number of requirements. The three major criteria of the materials include high modulus, low dielectric constant and low coefficient of thermal

expansion. The combination of the fiber, whicker and particulate reinforcement with the variety of existing matrices such as metal, polymer and ceramic, provides a virtually limitless array of potential new materials. Today, the substrate used in electronic industry can be broadly classified into three types: ceramic (alumina), insulated metal (insulated copper) and organic (polymer). Each technology has its distinct advantages.

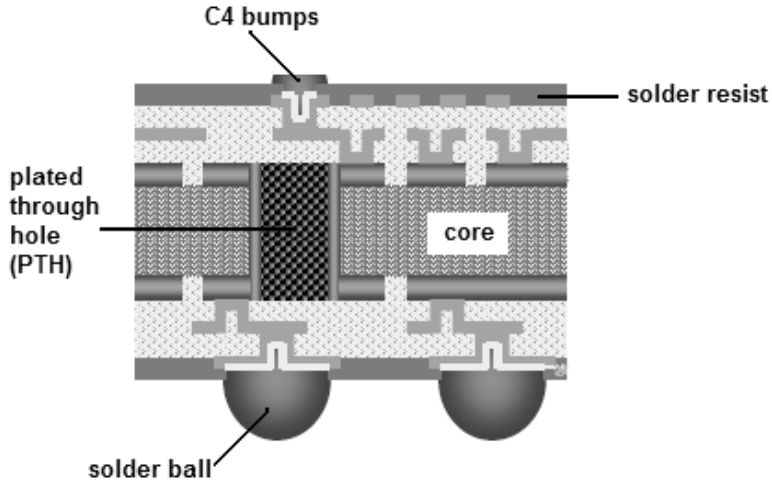


Figure 2.3: A typical substrate material.

According to Levinson (1987), the first ceramic substrate materials were made in the mid 1950s from steatite that fires in the range of 1200 to 1350°C. These particular substrate was used for capacitors, conductors etc. The steatite was then replaced by aluminum oxide or alumina (Seraphim et al., 1989). Alumina processes the advantage of high electrical resistivity of the order of 10^{12} ohm-cm and gives excellent insulation criteria. The CTE of 96 percent alumina in market is 6.3ppm/°C, which is closely, matches to that of silicon. This close match prevents differential stresses that lead to mechanical failure. However, the thermal conductivity of this material is about 15 W/m-°C which compares unfavorably with that copper (209.3 W/m-°C). Hence, alumina can not be used in high-power application. The ceramic substrate material is less mature and currently has higher associated materials and manufacturing costs.

Metal substrates include steel, copper and aluminum and it is insulated with a dielectric layer on which the circuitry is built. Similar to those other substrates, it can be explored as an alternative to ceramic and organic substrates. The substrate offers some advantages in thermal management. Also the metal substrates offer certain geometry advantages due to the ductile mature of the material. However, a key of issue is the development of all the required electronic circuit materials system compatible with metal substrate. According to Chang (2002), the silicon carbide filled aluminum composites with multilevel chips metal substrate exhibited low thermal expansion and high thermal conductivity. This brings to the high reliability of the package, which can be matched, with the thermal expansion of that ceramic substrate.

Organic substrate package technology started in year 1970s and 1980s. Injection molded plastic package was the first batch package technology and it has been used until now due to the low cost and vast infrastructure base. This material also offers the significant advantages of higher circuit density than that any other substrate materials. Viswanadham & Singh (1998) have found that the substrate materials have been changing from inorganic (ceramic) to organic (polymer), for example polyimide or epoxy glass (FR-4). Nowadays, the FR-4 is the most wisely used organic substrate materials. One to concern is organic substrate can not withstand the same solder balls high reflow temperature as ceramic substrate, which is at 200-240°C (Ho et al., 1999), so low temperature flip chip process has been introduced by many vendors.

2.2.2 Components in organic substrate

Organic substrate materials are constructed by many components, as shown in Figure 2.3 in Section 2.2.1. It can be seen that different components played different role in substrate application, this includes:

(a) Core - Commercial core layer material is made up of multi layer glass fiber reinforced resin. The specifications of fiber dimensions and layer count can be changed accordingly to the application. The resin used can be specified into many types, such the common used epoxy and bismalemide resins. These core layer materials are normally attached with copper foils, a layer of conductive metal.

(b) PTH - PTH is known as plated through hole. It provides electrical connection through core layer of the substrate. PTH is produced through drilling process. This process can be either using mechanical or laser drilling. Parameter such as drilling speed is critical in this process.

(c) C4 balls- C4 balls are the micro solder balls which are attached on the substrate materials to provide thermal, electrical and mechanical connection with the chips. The high lead solder ball material has been replaced by eutectic material for safety precaution purpose.

(d) Solder ball - Solder ball is the sphere ball under the substrate which is formed during the solder joint or reflow soldering. A typical solder ball has maximum of 50 micron (Prasad, 1997) in size and it provides mechanical and electrical interconnection with the motherboard. Electrical short can occur when the solder ball are loosen from the interconnection.

(e) Solder resist – Solder resist or mask is applied on the substrate and it is in green color. The solder resist is made from organic coating materials such as epoxies, melamines, polystyrenes, polyimides, polyurethanes or silicones (Manko, 1995). The function of this

material is to prevent from the solder wet or adhere to the substrate.

2.3 Organic substrate materials

2.3.1 Advantages and disadvantages of organic substrate materials

One of the major factors why industry has moved from ceramic to organic substrate materials is the cost saving aspect. It is believed that in term of volume production, organic materials are cheaper as compared to that of ceramic materials. Beside that, organic materials also own the excellent electrical properties due to the nature of low dielectric constant, ε' (Pant et al., 2006).

However, using organic materials in flip chip technology have generated many problems and solutions. One of the main concern factors is the large different thermal mismatch or CTE between the silicon chip and organic substrate. As the result, the underfill materials have been introduced into the market to act as the mechanical locking materials in between the silicon chips and organic substrate to reduce the shear stress of solder ball during thermal cycling. However, regarding to this issue, there are still many critical defects occurred such as warpage. Another issue is regarding to the reflow temperature of solder ball. High Pb content in Sn-Pb solder have been replaced by eutectic Sn-Pb solder due to its high processing temperature at above 300°C (Whitney & Corbin, 2006; Yang et al., 2006).

2.3.2 Properties of organic substrate materials

Recently, wisely used organic substrate materials in market are based on laminate structure. It can be divided into rigid, flexible, rigid-flexible and molded. Furthermore, they can be single-sided, double sided or multi layer substrate. The laminate composites are made up of reinforcements and resins. The resin provides

protection to the reinforcement, thus allow load transfer from resin to reinforcement. The reinforcement is the backbone of the structure that resists damage. Commercial reinforcements used in market are such as E-glass, A-glass and C-glass (Kumosa et al., 2005).

Rigid substrate is fabricated from epoxy-glass cloth laminate. The common used rigid substrate is FR-4 (Siebert, 2006). It is a designation of Electronic Industry Association for fire retardant epoxy/ E-glass cloth laminate. E-glass fibers are predominantly used reinforcement in this industry. They are easy to handle and form a good bond with the resin. The typical processing of laminate can be divided into three main steps, this includes fiber drawing process, producing a woven or non-woven fiber, and applied resin to form prepreg, then finally the numerous of prepreg are stacked and pressed together to form laminate. The chemical composition of E-glass fiber is shown in Table 2.1 (Douthit et al., 2002). Beside that, glass fibers are normally treated with silane coupling agent in manufacturing before sent for processing. This treatment process is to provide a good bonding of fiber with resin (Lau, 1995). Beside FR-4, there are many other alternative substrate materials to meet some specific requirements, such as polyimide and Bismaleimide-triazene polymers (Waris et al., 2005). These polymers also provide excellent heat resistance and high temperature performance.

Table 2.1: Typical chemical composition of E-glass fiber (Douthit et al., 2002).

Compositions	Weight (%)
Silicon dioxide (SiO_2)	52-56
Aluminium oxide (Al_2O_3)	12-16
Calcium oxide (CaO)	16-25
Magnesium oxide (MgO)	0-5
Boron trioxide (Br_2O_3)	5-10
Ferrie oxide (Fe_2O_3)	0.05-0.4
Sodium oxide (Na_2O)	0-2
Potassium oxide (K_2O)	0-2
Flourine (F_2)	0-1
Titanium oxide (TiO_2)	0-0.08

Flexible substrate materials have been established used in market especially for disk drives application. Flexible substrate materials are thin and compliant, making them suitable for used as chip carrier in certain applications. Materials utilized for flexible substrate are normally polyimides, polyesters, nylon and non-woven fiber reinforced composites (Aschenbrenner et al., 1997; Waris et al., 2005). Flexibility of the materials is one of the important factors in material selection. It is important to ensure that the materials are able to withstand thousand of flexures without catastrophic failure over a long period of time (Kear, 1987). Beside that, it is also necessary to ensure that the flexible substrate are also will not extend or shrink in the machine direction during application.

Several researcher have conducted studies on the organic substrate materials. Calmidi (2005) have investigated on a new type of thin core and high density substrate in FR-4 system. He has reported that the performance of the thin core substrate materials is influenced by the parameters such as die size, core via in the substrate and assembly condition. Eng et al. (2006) have studied that the flexural and thermal expansion properties are related to the linear density or fiber content and the number of woven fabric stacking in the woven glass fabric reinforced epoxy. Advance package technology has caused the decreasing in die size. Therefore, there are many aspects have to be taken into account in optimizing the chip carrier performance, this includes: tighten the core via pitches, finer signal lines, to have more wiring layers and the most important is the cost of the package (Audet et al., 2004).

In this study, the possibility of using particulate fillers instead of woven fabric in epoxy composites was investigated. Next section will discuss on few parameters which might influence the properties of particulate filler filled thermoset composites, such as types of resin, types of particulate fillers and surface treatment of fillers.

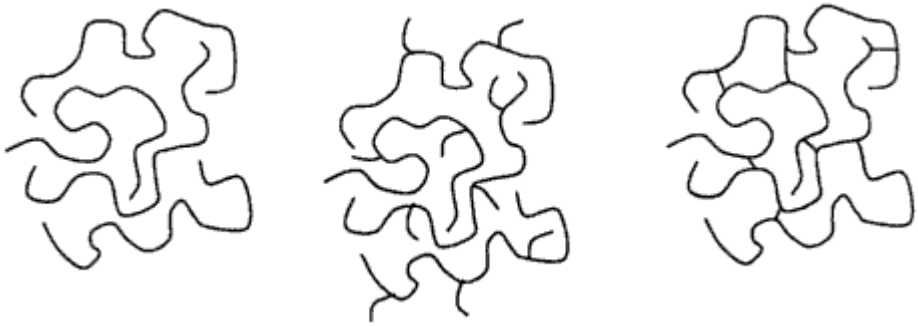
2.4 Factors influencing particulate fillers filled thermoset materials

2.4.1 Types of thermoset resin

2.4.1(a) Introduction

In general, based on intermolecular bonding, plastic can be classified into two major categories: thermoplastics and thermosetting plastics. According to Harper (2002b), thermoplastic is a high molecular weight polymer with either linear or branched structures and it is not crosslinked. Weak secondary bonds hold the linear or branched chains together. It is soften when heating and harden when cooling and it is a reversible process. There is no chemical reaction in structure occurs during the heating or cooling cycles. The heating and cooling cycles can be repeating any number of times to obtain the desirable shapes.

On the other hand, thermoset is chemically joined together by crosslinking, forming rigid and three-dimensional networks. Once the network chains are formed during polymerization, the thermoset polymers can not be melted or reshaped. Therefore, these thermoset polymers are widely used in electronic packaging industry. It is because the non-reversible property is able to fulfill the performance over the wide range of temperature during thermal cycling. Figure 2.4 shows different types of structures of thermoplastic and thermoset polymers.



(a) (b) (c)

Figure 2.4: Types of polymer structures: (a) linear, (b) branched and (c) crosslinked (Astrom, 1997).

2.4.1(b) Thermoset resin

Thermosetting resins are usually low viscosity liquids or low molecular weight solids that are formulated with suitable additives known as cross-linking agents to induce curing, and with fillers or fibrous reinforcements to enhance properties as well as thermal and dimensional stability.

Epoxy

In general, epoxy resins are all based on epoxide group, which consists of three-membered carbon, carbon, oxygen ring structure as shown in Figure 2.5. Epoxy resin are wisely used as composites matrix, this is because cured epoxy resin combine good mechanical performance and easy in processing. They have low viscosity, low shrinkage, good electric properties, resistance to thermal and mechanical shock and good adhesion properties.

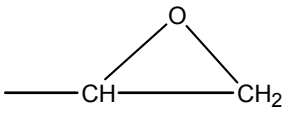
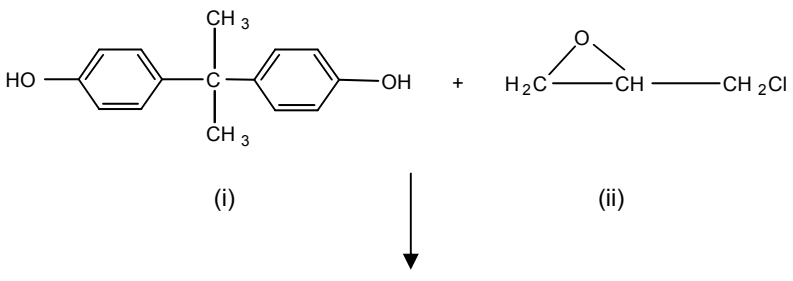
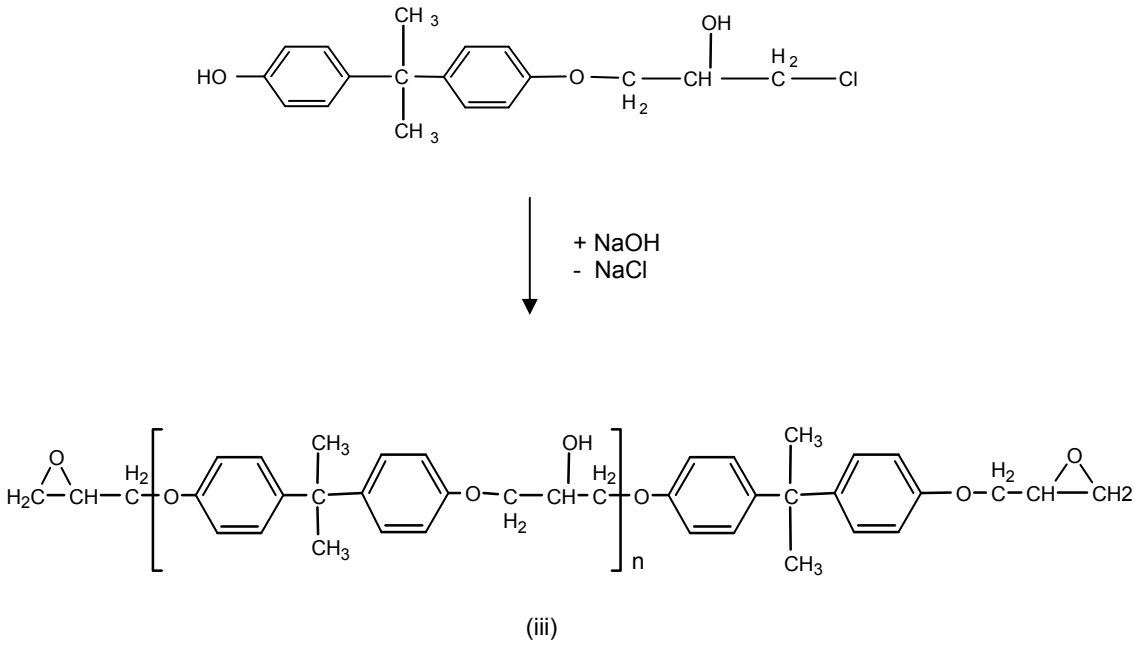


Figure 2.5: Epoxide group of epoxy resin.

The common epoxy resins are made by reacting epichlorohydrin (i) with bisphenol A (ii), in the presence of an alkali, to give the diglycidyl ether of bisphenol A (iii-DGEBA) as shown in Figure 2.6. Liquid epoxy resin has *n* value less than 1, for solid types *n* value is generally more than 1. Higher resins (*n*>1) are less useful in electronic packaging application due to its relatively high reaction temperature which is at 160- 200°C, moreover selection of suitable catalysts are important in order to avoid side reaction such as branching or gelation occurred.





(iii)

Figure 2.6: Reaction of epichlorohydrin and bisphenol A.

Epoxy resins are cured with hardener or curing agent to form crosslinked network. There are many categories of curing agents, such as aliphatic amines, cycloaliphatic amines, aromatic amines, acid anhydrides, novolacs and catalytic curing agents. The curing agent molecule is chemically bond into the epoxy resin for crosslinking. There are two types of crosslinking process. One type is referred to heteropolymerization and another is homo-polymerization. Homopolymerization is the process where the curing agent behaves as catalyst and thus encouraging self-polymerization. There are many factors concerning in selecting the correct curing agent, this includes: the aim of processing, the properties required of the cured material, limitation on cure speed or temperature, and the cost of curing agents. Table 2.2 shows the advantages and disadvantages of various types of curing agents.

Table 2.2: The advantages and disadvantages of various types of curing agents (Goosey, 1999).

Types of curing agents	Advantages	Disadvantages
Aliphatic amines	Low viscosity, low cost room temperature curing, and good chemical resistance.	Low T_g.
Cycloaliphatic amines	High T_g than aliphatic amines	Poor thermal stabilities.
Aromatic amines	High T_g, longer pot life, high chemical resistance, enhanced electrical properties.	High curing temperature.
Anhydrides	High heat stability, long pot lives, not skin-sensitizing agents.	Long and high temperature curing, required accelerator in curing.
Novolacs	High T_g, high thermal resistance.	Accelerators needed for curing, high temperature curing.
Catalytic	High heat and chemical resistance, brittleness.	Poor adhesion properties, may caused corrosion with certain metal or sensitive devices.

Bismalemide

Bismaleimide resins are one type of polyimide resin. The common polyimide group resins have phthalimide grouping in the repeating unit, as shown in Figure 2.7. The monomer and pre-polymer of bismaleimide resin are prepared via the reaction of maleic anhydride and diamines. It is becoming increasingly important in the manufacture of high temperature composite like bismaleimide resin. Properties like high regularity and stiffness of the backbone, able to crosslink, and high crosslink density of the formed network among others, contribute to high temperature performance after cured. Thus, composite materials produced with bismaleimides can be used in highly demanding environments, particularly in the field of aerospace engineering.

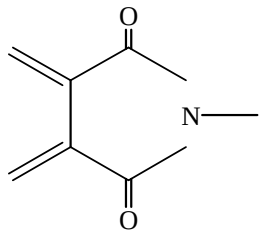


Figure 2.7: Phthalimide group in polyimide.

This material is very reactive and can be homo polymerized or co-polymerized to produce a wide variety of thermoset resin. It can be operated in the range of 200-232°C as compared to that epoxy in the range of 150°C. These materials are wisely used in printed wiring board substrate, which needs higher operating temperature.

However, two important aspects of bismaleimide resin systems limit their more widespread use. The first problem relates to the ease of processing of these systems. Bismaleimides generally possess a high melting point and high crystallinity that makes them difficult to dissolve in common diluents and the resulting solution easily recrystallizes. As a result, it cannot be effectively used in low cost processing such as low temperature resin transfer molding (RTM). The second obstacle is that the high molecular rigidity and crosslink density result in very low fracture toughness of the fully cured resin. Moreover, there are four to five times more expensive than epoxy resin.

Phenolic

Phenolic resins are produced by the condensation of phenols with formaldehyde by step-growth polymerization, this involve two processes. The reaction of phenols and formaldehyde can lead to either a heat reactive resole or a stable novolac. It is dependent upon the type of catalysis and molar ratio of phenols to formaldehyde. The possible reaction occurred between phenol and formaldehyde is exhibited in Figure 2.8 (Carley, 1994; Wittcoff et al., 2004). Resole resins are produced under alkaline catalysed with excess formaldehyde. It can undergo further thermal

reaction to eliminate water and produce high crosslinked system. This involves high degree of branching. More linkages between aromatic rings methylene (CH_2) groups through some ether (CH_2O) linkages. On the other hand, novolac resins are produced under acid catalysed with excess phenol. Novolac resins are linear polymer that has no free methylene groups for crosslinking. Therefore, it requires addition curing agent to form addition methylene groups and crosslinking.

According to Gradziella et al. (2000), phenolic are commonly used in fiber reinforced composites, laminates or molding compound due to its excellent heat, adhesive ability and dimensional stability. However, there are limitations of phenolic. They have low insulation resistance, high water adsorption and sensitivity of electric properties to humid environments.

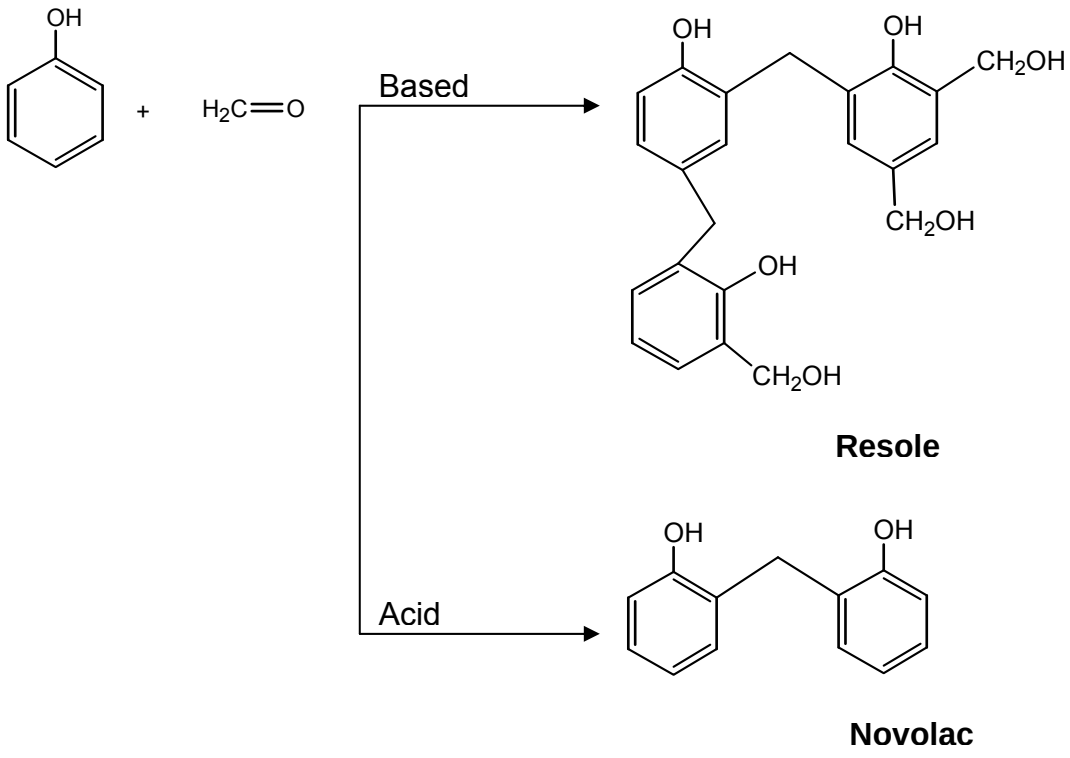


Figure 2.8: Reaction occurred between phenol and formaldehyde.

2.4.2 Types of particulate fillers

Polymeric materials can be reinforced with either organic or inorganic particulate fillers in industrial applications. Fillers are normally added to reduce cost but may also have the effect of improving some aspect of the mechanical, thermal stability or ease of processing (ASM International & Library., 1997).

2.4.2(a) Inorganic fillers

Silica

Silica is also as identified as silicon dioxide with chemical formula SiO_2. It is described as a continuous network of SiO_4 tetrahedron. This tetrahedron are linked to one another by shared corner, where each oxygen atoms forms a bridge between two silicon atoms, as shown in Figure 2.9. At the surface of silica, the structure terminates with siloxane groups, Si-O-Si.

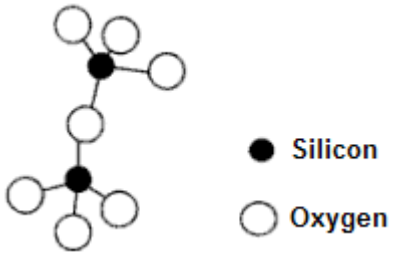


Figure 2.9: The basic structure unit of SiO_2 (Asthana et al., 2006).

In electronic industry, silicon dioxide is used to produce silicon for silicon chips application. This involves reaction between silicon dioxide and coke, a poor grade of graphite, using high temperature and electronic arc (Carraher & Seymour, 2003) (Equation 2.1).

$$SiO_2 + C \rightarrow Si + CO_2 \qquad (2.1)$$

Another common used silicon dioxide in electronic industry is fused silica. Fused silica is high purity crystalline quartz that is produced under a very high temperature in an arc furnace. Fused silica is commonly used as reinforcement filler in underfill application due to its low thermal expansion coefficient.

Talc

Talc is a hydrated magnesium silicate with the chemical formula of $Mg_3Si_4O_{10}(OH)_2$. As shown in Figure 2.10, the element sheet is composed of a layer of magnesium-oxygen or hydroxyl octahedron, which is sandwiched between two layers of tetrahedral silica. The elementary sheets are stacked on top of one another, like flaky pastry, and because the binding forces (known as Van de Waal's forces) linking one elementary sheet to its neighbors are very weak, the platelets slide apart at the slightest touch, giving talc its characteristic softness. The size of an individual talc platelet i.e. a few thousand elementary sheets, can vary from approximately 1 micron to over 100 microns depending on the conditions of formation of the deposit. It is this individual platelet size that determines talc's lamellar. Highly lamellar talc will have large individual platelets whereas microcrystalline talc will have small platelets.

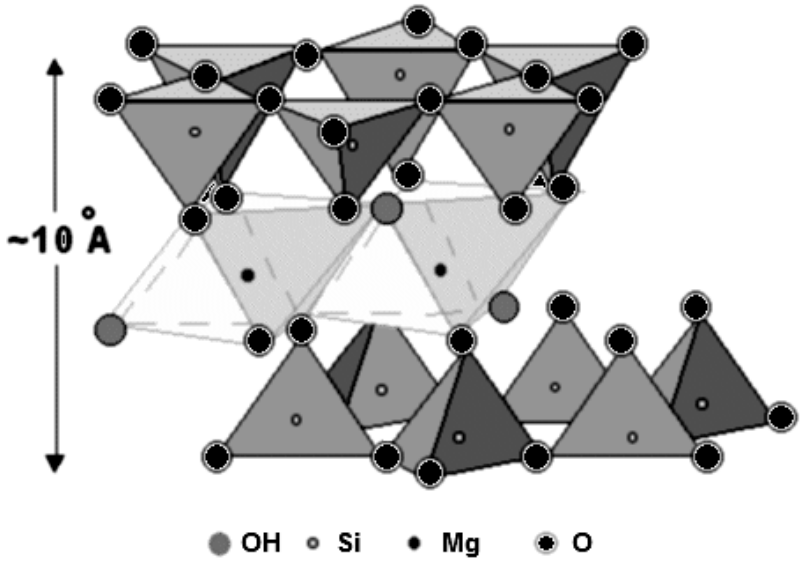


Figure 2.10: The element sheet of talc (Xanthos, 2005).

Talc is odorless. It is insoluble in water, weak acids and alkalis. Although talc has a marked affinity for certain organic chemicals, it generally has very little chemical reactivity. It is neither explosive nor flammable. Above 900°C, talc progressively loses its hydroxyl groups and above 1050°C, it re-crystallizes into different forms of anhydrous magnesium silicate. Talc's melting point is at 1500°C (Milewski & Katz, 1987).

Talc can acts as effective filler in polymer composites. Talc filled composites have low gas permeability and high permittivity because of the plate-like nature of the talc particle. Beside that, talc is organophilic in nature. In the case of talc's affinity for polypropylene, a likely explanation is that the position of the oxygen atoms on the surface of the talc platelet corresponds to the carbon bonds on the surface of the polypropylene crystal. These organophilic properties are used to great benefit in a number of applications: for instance, it helps polypropylene to crystallise. In papermaking, the talc particles attract the undesirable resin droplets (i.e. organic chemicals) in the pulp onto their surface. This is known as pitch control. In body powder applications, perfume is adsorbed onto the talc surface and retained.

Denac et al. (2005) have found that homogeneously incorporated talc crystals accommodated mostly plane parallel in the isotactic polypropylene copolymer (iPP) matrix, can affects the crystallization of polypropylene composites and the orientation of iPP lamellae and thus give better mechanical properties. This is proven using polarization and SEM micrographs; they have found that Talc crystals are partially or completely encapsulated by iPP matrix and formed core-shell morphology. Beside that, according to Clerc et al. (2005), when talc is employed in ethylene vinyl acetate (EVA) copolymer, it helps to increase the thermal stability and flame retardant of the composites. It was observed that the increasing of talc lamellar index and specific surface area has led to better fire resistance.

Kaolin

Kaolin is a soft, white material composed of the clay mineral kaolinite with the composition of $Al_3O_3.2SiO_2.2H_2O$. Structurally, kaolinite consists of an alumina octahedral sheet bound on one side to a tetrahedral silica sheet, stacked alternately. The two sheets of kaolinite form a tight fit, with the oxygen atoms forming the link between the two layers as shown in Figure 2.11. Pure kaolin having melting point at 1260°C, but it is difficult to shape due to its poor ductility (Hummel, 2004).

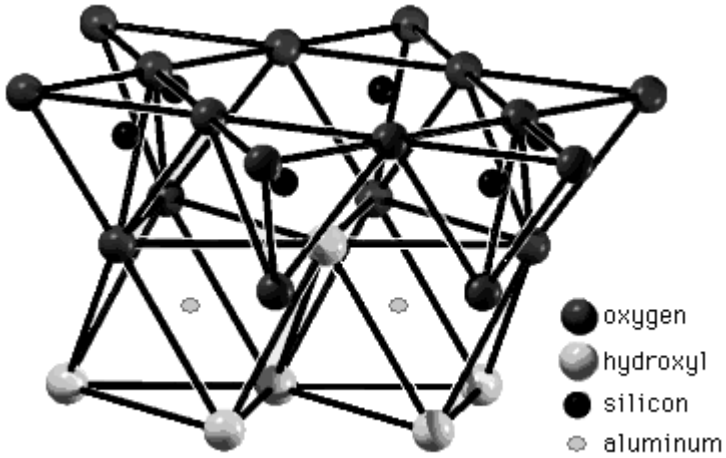


Figure 2.11: Structure of 1:1 layer silicate (kaolinite) illustrating the connection between tetrahedral and octahedral sheets (Xanthos, 2005).

Kaolin is used in plastics to provide smooth surfaces, dimensional stability and resistance to chemical attack, to conceal fiber reinforcement patterns and to reduce shrinkage and cracking during polymer compounding and shape forming. It is also used as a rheological modifier and functional filler, in which capacity it is used to improve mechanical, electrical and thermal properties (Moudgil et al., 2003). A major application is in PVC cables where its main function is to improve electrical properties. Other important applications include specialty films where they impart anti-blocking or infrared absorption characteristics. Chemically treated, calcined kaolin is one of the major additives used in the manufacture of automotive parts based on engineering thermoplastics