CHARACTERIZATION OF HALOGEN-FREE CORE MATERIAL WITH VARIOUS FLAME RETARDANTS

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UNIVERSITI SAINS MALAYSIA

2012

CHARACTERIZATION OF HALOGEN-FREE CORE MATERIAL WITH VARIOUS FLAME RETARDANTS

by

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Thesis submitted in fulfillment of the requirements

for the Degree of

Master of Science

JUNE 2012

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"Characterization of Halogen-Free Core Material with Various Flame Retardants"**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

Saya isytiharkan bahawa kandungan yang dibentangkan di dalam disertasi bertajuk ***"Pencirian Bahan Teras Bebas Halogen Dengan Pelbagai Perencat Nyala"*** *ini adalah hasil kerja saya sendiri dan telah dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya. Disertasi ini juga tidak pernah disertakan untuk ijazah yang lain sebelum ini.*

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ACKNOWLEDGEMENTS

First and foremost, I would like to take this opportunity to pen down my deepest gratitude to God, for providing me the strength and will to complete this thesis. The journey of pursuing lab works, publications and thesis was never easy and requires a lot of mental strength and spiritual support from Him.

I would also like to show my appreciation to my lovely family members; father Raymond Lim Leng Yaw, mother Jeanifer Kong Fon Yeen, and elder brother Philip Lim Wye Kean for the kind understanding in encouraging me to complete my Master's degree studies promptly. Thank you for providing me with such loving and emotional care support.

Next on the list would be the ever supporting, dedicated and inspiring main supervisor, Associate Professor Ir Dr Mariatti Jaafar. Without her consistent effort in directing me to the right path of my Master's studies, I would have had faced many more challenges/problems. Also thank you for having such patience when dealing/discussing my workloads. All the assistances and guidance provided are fully appreciated.

Furthermore, there's Associate Professor Dr Chow Wen Shyang, my co-supervisor for Master's studies. Thank you for the excellent guidance and dedication shown, especially during the writing/analysing process.

I would also like to grab this chance to thank Intel Technology (M) Sdn. Bhd. for acknowledging and rewarding me the Intel Fellowship for year 2009-2011. The allowance provided have definitely spurred me to work harder and relieve my financial constrain. Moreover, I would like to show my gratitude to Mr Mar Kheng

Tat, my Intel sponsor, for acknowledging, appreciating and constantly giving support to my works.

Apart from that, I would like to sow my appreciation to Universiti Sains Malaysia (USM), especially School of Materials and Mineral Resources Engineering (SMMRE) for providing a conducive environment to complete the postgraduate studies. Labs, postgraduate rooms, and equipment were provided willingly to all students. USM had also allocated a postgraduate Research University grant with a grant number of 1001/PBAHAN/8033031, which was used to fund my project. Besides that, I would also grab this chance to thank the Dean of SMMRE, Professor Ahmad Fauzi b. Mohd Noor, all technicians and administrative staffs for the great assistance in ensuring my work progresses steadily.

TABLES OF CONTENTS

CHAPTER 1 - INTRODUCTION

CHAPTER 2 - LITERATURE REVIEW

CHAPTER 3 - EXPERIMENTAL

CHAPTER 4 - RESULTS AND DISCUSSION

CHAPTER 5 – CONCLUSION & SUGGESTIONS FOR FUTURE WORKS

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

APP	Ammonium polyphosphate
AHEW	Amine hydrogen equivalent weight
AlOOH	Aluminium-oxide-hydroxide
$Al(OH)_3$	Aluminium hydroxide
ATH	Aluminium tri-hydroxide
BFR	Brominated flame retardant
CaB	Calcium borate
cm	centimeter
CTE	Coefficient of thermal expansion
DMA	Dynamic mechanical analysis
EEW	Epoxy equivalent weight
EG	Epoxy/Glass fiber
EMC	Epoxy molding compound
EMC_5	Epoxy/Glass fiber/Melamine cyanurate 5%
EMC_{10}	Epoxy/Glass fiber/Melamine cyanurate 10%
EMC_{15}	Epoxy/Glass fiber/Melamine cyanurate 15%
EMC_{20}	Epoxy/Glass fiber/Melamine cyanurate 20%
$EAPP_5$	Epoxy/Glass fiber/Ammonium Polyphosphate 5%
$EAPP_{10}$	Epoxy/Glass fiber/Ammonium Polyphosphate 10%
$EAPP_{15}$	Epoxy/Glass fiber/Ammonium Polyphosphate 15%
$EAPP_{20}$	Epoxy/Glass fiber/Ammonium Polyphosphate 20%
$ECaB_5$	Epoxy/Glass fiber/Calcium borate 5%
$ECaB_{10}$	Epoxy/Glass fiber/Calcium borate 10%

$ECaB_{15}$	Epoxy/Glass fiber/Calcium borate 15%
$ECaB_{20}$	Epoxy/Glass fiber/Calcium borate 20%
EH	Epoxy/Glass fiber/Hybrid flame retardants
EX	Epoxy/Glass fiber/Hybrid flame retardants/metal chelates
FPCB	Flexible printed circuit board
FR	Flame retardant
FTIR	Fourier transform infrared spectroscopy
GPa	Giga pascal (10^9)
h	hour
HRR	Heat release rate
IC	Integrated circuit
I/O	Input/Output
IPDT	Integral procedure decomposition temperature
kHz	kiloHertz
LOI	Limiting oxygen index
M	Molarity
MC	Melamine cyanurate
MDH	Magnesium dihydroxide
ml	mililiter
min	minutes
MPa	Mega pascal (10^6)
mm	milimeter
N	Nitrogen
NR	No- Rating

PBB	Polybrominated biphenyl
PBDE	Polybromodiphenylether
PCB	Printed circuit board
pHRR	Peak heat release rate
RP	Red phosphorus
rpm	revolutions per minute
s	second
SEA	Specific extinction area
T	Temperature
TGA	Thermogravimetric analysis
TGA-MS	Thermogravimetric analysis-Mass spectrometer
TTBA	Tetrabromobisphenol A
UL-94	Underwriter laboratory- 94
UV	Ultraviolet

LIST OF SYMBOLS

^oC	Degree celsius
CO_2	Carbon dioxide
CO	Carbon monoxide
D_{90}	Volume diameter at 90% cumulative volume
D_{10}	Volume diameter at 10% cumulative volume
D_{50}	Volume diameter at 50% cumulative volume
%	Percentage
σ	standard deviation
μm	Micron (10^{-6})
C_F	Final value of oxygen concentration used
C_i	Percent oxygen concentration used during measurement of the last six responses in the NT series
d	Step change in oxygen concentration used
E’	Storage modulus
T_g	Glass transition temperature
T_5	Temperature where 5 wt. % is loss through decomposition
Tan δ	Tan delta

PENCIRIAN BAHAN TERAS BEBAS HALOGEN DENGAN PELBAGAI PERENCAT NYALA

ABSTRAK

Kesan penggunaan tiga perencat nyala bebas halogen yang berbeza, iaitu *intumescent ammonium polyphosphate* (APP), *melamine cyanurate* (MC), dan *calcium borate* (CaB) terhadap komposit epoksi/gentian kaca telah dikaji. Bahan tambah perencat nyala telah digunakan secara tunggal dan hibrid di dalam komposit bagi menyiasat sifat kebolehbakaran, mekanikal dan terma. Secara umumnya, setelah terurai pada suhu 700^{o}C, CaB meninggalkan kuantiti baki yang tertinggi, termasuk arang dan substrat kaca. Ini diikuti dengan APP yang terurai dan membentuk arang dan MC yang terurai kepada gas. Di antara ketiga-tiga perencat nyala, pencapaian APP adalah terbaik dari segi kebolehbakaran, manakala CaB tidak berkesan di dalam komposit ini. Bagi sifat mekanikal komposit, CaB mencatatkan kekuatan lenturan yang tertinggi manakala MC mencatatkan modulus lenturan yang tertinggi. Dari segi sifat terma, perencat nyala telah merendahkan kestabilan terma komposit, tetapi tidak menjejaskan pekali pengembangan terma (CTE) dan suhu peralihan kaca (T_g). Fasa kedua kajian terhadap sistem hibrid mendapati bahawa APP-MC dan APP-CaB yang menggunakan nisbah 80-20, memberikan kesan sinergi terhadap sifat kebolehbakaran komposit. Hibrid komposisi sebegini juga di dapati memberikan kekuatan lentur yang lebih tinggi dengan tidak menjejaskan T_g dan CTE. Penambahan logam *chelates* sebanyak 0.5 *vol.* % ke dalam sistem hibrid perencat nyala di dapati telah tidak memberi kesan yang ketara ke atas sifat kebolehbakaran dari segi LOI. Baki yang di dapati daripada penguraian hibrid perencat nyala juga telah dikurangkan. Sifat kelenturan, T_g dan CTE juga didapati tidak terjejas dengan penambahan logam *chelates*.

CHARACTERIZATION OF HALOGEN-FREE CORE MATERIAL WITH VARIOUS FLAME RETARDANTS

ABSTRACT

The effect of three different types of halogen-free flame retardants, which are the intumescent ammonium polyphosphates (APP), melamine cyanurate (MC) and calcium borate (CaB) on epoxy/glass fiber composites was studied. The single and hybrid flame retardant fillers were used to investigate the composites fire properties, mechanical and thermal properties. In general, after decompose at 700^{o}C, CaB leaves behind the highest residual content, which mainly comprises of chars and glassy substrates. This is followed by APP which decomposes and forms the chars, while MC decomposes mainly into volatile gases. Among the three types, APP performed the best in flame retardancy while CaB is not effective in this composite. As for the mechanical properties of the composites, CaB gives the highest flexural strength while MC provides the highest flexural modulus to the composites. In terms of thermal properties, the flame retardants have lowered the thermal stability of the composites but did not significantly affect the coefficient of thermal expansion (CTE) and glass transition temperature (T_g). The second phase which studied on the hybrid system, found that APP-MC and APP-CaB according to 80-20 ratio gave synergistic effect on the fire properties to the composites. The hybrid compounds remain at V-0 with improved LOI reading. These hybrid's composition also gave higher flexural strength, but was found not to affect the T_g and CTE. On the addition of 0.5 vol. % metal chelates into hybrid-flame retardant system, the fire resistance did not show any improvement in terms of their LOI values. The residual content of the flame retardants after decomposition have also decreased. The flexural properties, T_g and CTE were also not affected by the metal chelates.

CHAPTER 1

INTRODUCTION

1.1 Overview

In line with the development of technology, printed circuit boards (PCB) has gradually transformed over the past decades from being single sided into a now multi-layered circuit board. PCB's soon became a necessary tool to electrically interconnect every electronic component while mechanically supporting them. Meanwhile, the strong demand for lighter weight electronic devices has allowed epoxy polymers to gradually replace the conventional materials used for PCB's such as bakelites and masonites (www.4pcb.com, 2007). Thermosetting epoxy resins are currently heavily used in the electronic industries, especially for electronic packaging applications due to their superior electrical, thermal, and mechanical properties.

Assorted additives and fillers have also been utilized to further improve their properties and reduce the coefficient of thermal efficient (CTE). However, the poor flammability properties exhibited by this combustible organic compound have limited its development and applications in that field due to the high heat involved. With the miniaturisation trend leading the way for electronic devices, the densities and complexities of the PCB's was raise to higher levels, subsequently releasing more heat per unit area (Rakotomalala et al., 2010). This has overall worsen the fire hazard risks and reliability of each electronic devices on the board. To combat this problem, flame retardants were introduced as a compulsory additive for electronic devices that are used at such high temperature.

Flame retardants assist the electronic products in many ways, such as by reducing the content of the combustible organic products, diluting the oxygen content through evolution of other inert gases, and by changing the viscosity of the resulting material (Laoutid et al., 2009). Nevertheless, with the current growing calls to protect the environment coming from most nations, materials that do not conform to the environmental safety regulations were slowly being phased out. Conventional halogenated flame retardant that was commonly employed in the electronic goods has also been replaced due to their toxicity. Most of the current research works were focusing solely on the halogen-free types of flame retardants.

1.2 Problem Statement

Being one of the most crucial additives in today's electronic devices, flame retardants are used in huge quantities for electronic products such as printed circuit boards (PCB). This is due to the overwhelming and rapid spurs in the use of polymers for electronic devices. Although having polymer resins as the base have led to many great benefits such as lighter weight devices, but the flammable organic fractions in polymers had significantly increases the rate and duration of burning in the case of fire. Moreover, for products such as PCB that commonly employs glass fibers for reinforcement purpose, there is a greater risk for the entire device to engulf in flames within shorter period. This is because the glass fibers are known to cause the candlewick effect, whereby the fuels from the flames are transported rapidly through capillary action (Zhao et al., 2008).

Backdated 20 years ago, the popularity of the conventional halogen types of flame retardants reached their prime because of their established effectiveness and role in eliminating fires. Brominated and chlorinated compounds were highly utilized in the electronic applications. It was reported that in 2005, approximately 95% of the FR-4 grade PCBs manufacturers include tetrabromobisphenol A (TTBA) in their formulations to curb any potential fire hazards (Kaprinidis and Fuchs, 2008). Although TTBAs were given clearance by the World Health Organization (WHO) in 1995, this controversial additive had faced numerous market pressures to be replaced. Studies had shown many different halogenated compounds releases toxic dioxins and corrosive gases upon burning, thus subsequently prompted many environmental groups to mount more pressure on PCBs manufacturers. These suspected carcinogenic dioxins were found to be harmful to humans and animals by mutating the living cells upon consuming. This type of flame retardants have also caused problems to the recyclability of the electronic devices because of the high heat involved during recycling and sorting process that could trigger the release of these dioxins. Without undergoing the recycling process, the precious inorganic metal components such as copper and gold in the electronic products will become a waste.

With the on-going global effort to conserve and preserve the natural environment, various types of halogen-free flame retardants were developed. In general, halogen-free flame retardants faced many obstacles in replacing the halogenated compounds such as relatively lower thermal stability, high cost and relatively low efficiency in flame retardation (Wu et al., 2002). Furthermore, for inorganic minerals such as metal hydrates, a huge amount of them are required to function effectively as flame retardants. Thus, this greatly affects their physical and mechanical properties, while escalating the production cost. Comparatively, the halogenated type such as TTBA is cost effective, compatible with circuit board components and required only small loading to be attached with the polymer chain (http://halogenfree.ipc.org, 2005). It was also reported that some of these halogen-free types releases significant amount of water once heated. This could subsequently lead to the ‘pop-corning’ effect and delamination problem on the electronic device. Pop corning is a catastrophic failure caused when a small amount of moisture is heated during the reflow process.

1.3 Objectives

There are three objectives for this research works to be carried out. Among them are:

i. To investigate on the mechanism of each flame retardant in eliminating flames.
ii. To prepare and characterize various types of halogen-free flame retardants with various loadings in epoxy/glass fiber composites.
iii. To prepare and characterize catalyst metal chelates in hybrid flame retardants/epoxy/glass fiber composites.

1.4 Thesis Overview

This thesis covers the entire study on the feasibility of selected halogen-free flame retardants in FR-4 (epoxy/glass fiber) printed circuit boards (PCB). This thesis comprises 5 different chapters. Chapter 1 gives the introduction of flame retardants, current problems faced while using the conventional flame retardants and objectives of this research work. Detailed literature reviews related to PCBs, were presented in Chapter 2. Varieties of halogen-free flame retardants which were used and currently still commercially available were discussed. The mechanisms of each type of flame retardants were also mentioned.

Meanwhile the Chapter 3 shows the materials and methodology applied in this thesis work. Processing parameters/conditions to produce the specific samples and characterizations methods on those composites were discussed. Results were displayed with detailed explanation and discussion in Chapter 4. The results were discussed according to the objectives of the study, which are the effect of different types and loading of flame retardants in epoxy/glass fiber, the hybridization between different flame retardants and the effect of metal chelates in flame retardants. Lastly, Chapter 5 presented the conclusion of the entire research work with the future work in order to improve the current experimental works.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Polymer in Electronic Packaging

In this century, polymer derived goods have distinctively replaced many other types of materials such as metals in various applications. Polymer composite materials gave excellent specific strength, thermal and chemical resistance at cheaper cost of manufacturing. In the electronic industries, polymers such as thermosetting epoxies are well known and vastly used for electronic packaging such as printed circuit boards (PCB), molding compounds, underfill and many others. Their exceptionally strong mechanical properties, good dielectric and excellent corrosion resistance had further promoted their usages in this field.

2.1.1 Flip chip and Underfill

According to Harper (2005), flip chip packaging as shown in Figure 2.1 is the connection of an integrated circuit (IC) to a chip carrier, either a substrate, tape, or printed circuit board with the active surface of the chip facing towards the substrate. Flip chips interconnection is known to have many benefits on top of other types of IC interconnection. The flip chip allows the entire area of the chip to be used to interconnect with the base substrate. Moreover, flip chips provide the shortest possible leads, lowest inductance, highest frequency, best noise control, highest interconnect density compared to another interconnect technology, wire bond. In this flip chip, soldering technology is applied to make electrical and mechanical bonding between the chip bond pad and the carrier bond pad. One of the major issues concerning this flip chip process is the huge difference in coefficient of thermal expansion between the silicon die and the substrate. This generates thermo-mechanical stresses and fatigue in the solder joint during thermal cycling or power cycling which subsequently causes Input/Output (I/O) interconnection failure and reduces the reliability of the electronic devices. However, this problem has been solved with the application of underfill. Underfill material is driven by capillary force to fill the spaces between silicon die and the substrate (Khor et al., 2010). However, the underfilling process is also critical and must be carried out carefully. The underfill flow must be uniform to ensure good wetting around the solder joints without voids (Young, 2003).

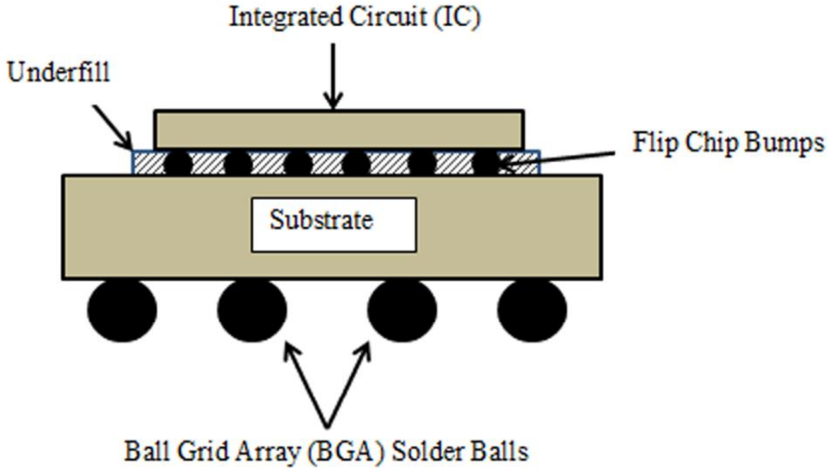

Figure 2.1: Schematic diagram of a flip chip component (Harper, 2005)

2.1.2 Epoxy Molding Compound (EMC)

Epoxy molding compounds (EMC’s) are typically used to protect integrated circuits (IC) from external environmental damage either chemically or mechanically. This is because external factors such as moisture, heat, ultraviolet rays (UV) and impact can badly affect the semiconductor chips performance. Epoxy resin’s high adhesion strength, small shrinkage, superior chemical and mechanical resistance, high heat resistance, and excellent electrical properties are the few reasons being selected as the main resin to be used in the molding compounds. Moreover, in terms of processing, epoxy resins are beneficial in terms of relatively low temperature curing, short curing time, and low melt viscosity before curing. Lu and Wong (2008) commented that phenol novolac resins are commonly employed as hardeners for EMC due to their strong heat resistance, moisture resistance, electrical properties and storage stability. Among the main common problems faced in the production of EMCs are the thermal mismatch of the silicon chips, metal frame and plastic encapsulant that affect the entire package reliability and led to issues such as package cracking, delamination, and package warpage. Other additives used in EMCs include the curing promoter, coupling agents, and flame retardants. The EMC products should satisfy the fire rating of V-0 in the UL-94 standards and to achieve that, halogenated flame retardants with synergist antimony trioxide are commonly used. Due to the generation of toxic gases evolved from the combustion of these compounds, research works have shifted to the halogen-free types. Kim et al., (2003) had investigated feasibility and performance of encapsulated red phosphorus in EMC and found that the encapsulation with resol resin have better fire resistance than melamine or titanium dioxide. Ishii et al., (2006) studied on the usage of calcium borates as flame retardants, coupled with excess phenolic resins in EMCs, and discovered the flammability level improves to satisfy the V-0 rating. Recently, Shi et al., (2011) have also promoted the use of silicon nitride, Si_3N_4 and aluminium hydroxide, $Al(OH)_3$ that can feature a good balance between thermal conductivity and flammability in EMCs.

2.1.3 Printed Circuit Board (PCB)

Printed circuit boards (PCBs), being one of the key building blocks in electronic packaging, comprises a board which specifically holds the electrical components while inter-connecting them using the conductive tracks that were etched from copper sheets. These conductive sheets were laminated on the non-conductive substrate using heat and pressure. PCBs are typically classified into two groups, which are the rigid circuit boards and flexible circuit boards. In recent years, a combination or hybrid between these two types has formed a flex-rigid board.

2.1.3.1 Rigid Circuit Boards

Rigid circuit boards or rigid PCB is the most common type of circuit board and consists of a dielectric substrate with a copper. This dielectric substrate is usually consist of a polymer resin with fibers, and thus will be mechanically capable to support the electronic components that are mounted to it. The rigid PCB may be further sub-classified by the number of wiring layers contained within the substrate, which are single-sided, double-sided and multi-layered PCBs.

A single sided PCB consists of a single layer of conductor interconnection as shown in Figure 2.2. Meanwhile, the dielectric substrate contains multiple layers of prepregs pressed together. Usually, copper cladding is used and applied on the outer layer. Single-sided PCBs are only used for low cost, high volume and low functionality applications.

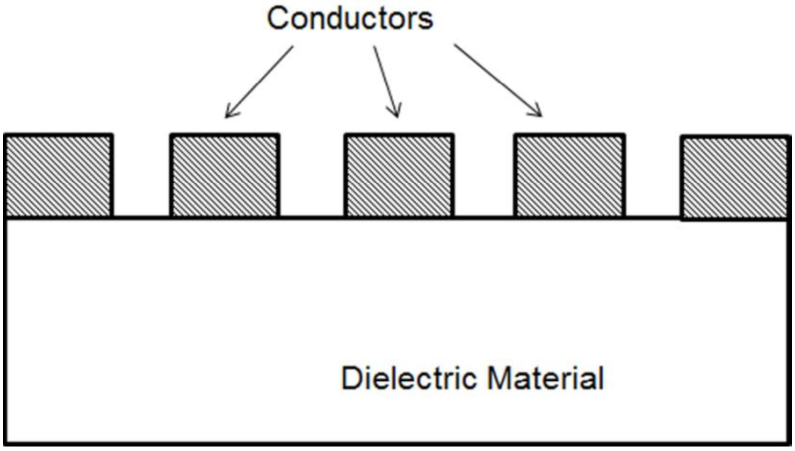

Figure 2.2: Single sided PCB (Harper, 2005).

Figure 2.3 shows the schematic diagram of a double-sided PCB. It is rather similar with the single-sided board, but with the addition of another conductive later on the opposite side. This type of board allows basic x- and y- axis routing of the circuit on both the outer layers which significantly improve the routing efficiency and circuit density.

However, for double-sided and multi-layer PCBs, there is a need for an interconnection between all the conductor patterns. This is accomplished by the drilling method which was also known as ‘plated through hole technology’, whereby holes that are known as ‘vias’ are created through drilling. The normal metallization procedure is to first catalyse these holes with palladium catalyst, followed by electroless copper. The electroless copper will act as a seed layer or conductive material that must be deposited into the vias before electrolytic copper plating can take place (LaDou, 2006).

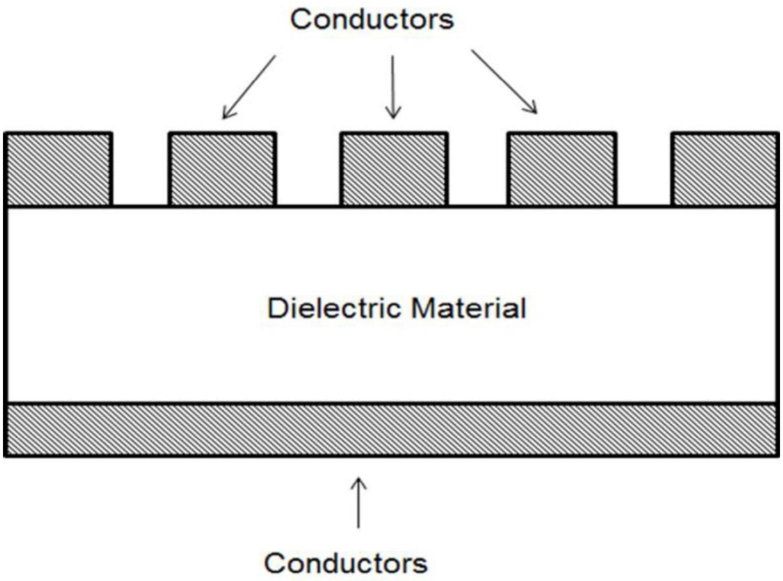

Figure 2.3: Double –sided PCB (Harper, 2005)

Multi-layered PCB is defined as the PCB that contains three or more conductive layers including external pads-only layer. The schematic diagram of a multi-layered PCB can be seen in Figure 2.4. The number of conductive layers included in the PCB varies according to the applications, but modern PCBs typically consist between 4 to 16 layers. Some high density applications might require up to or more than 65 layers.

Some of the multi-layered PCBs also utilized the ‘plated-through-holes’ technique to provide layer to layer interconnection. Nevertheless, many techniques are designed to improve the interconnection wiring density on the conductive layer such as blind, buried, and microvias technique. To utilize these techniques, each layer is fabricated as double sided boards, complete with plated vias.

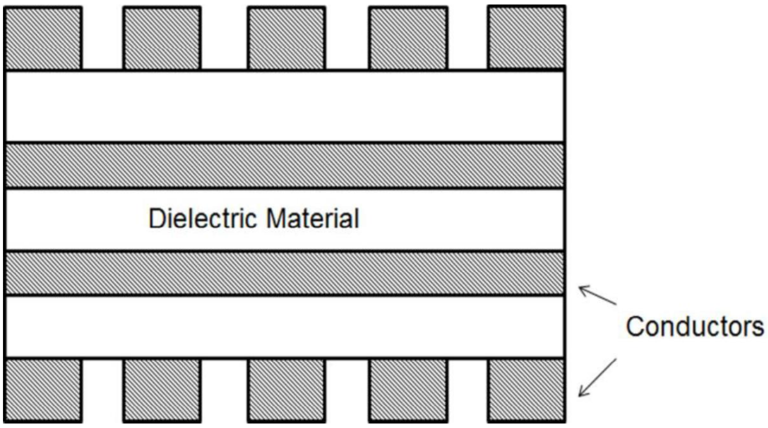

Figure 2.4: Multi-layered PCB (Harper, 2005)

Buried vias as shown in Figure 2.5 are used to connect two adjacent signal layers without affecting routing on other layers. Signal pairs must be routed on opposite sides of the same C-stage component. Usually a non-buried design utilizes a power plane to connect between each signal layer pair but a buried via uses another redundant layer to enable the next signal layer pair onto the same component.

Blind vias as shown in Figure 2.5 are used to connect the surface layer to other internal layers. They are crucially applied in very dense, double-sided surface mount designs where there is interference between input/output (I/O) vias.

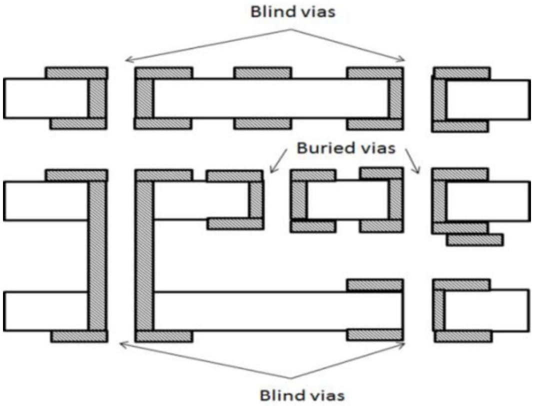

Figure 2.5: Interconnection of six layer multi-layer PCB using buried and blind vias (Harper, 2005).

The conventional method of interconnecting the conductive layers through buried and blind methods are effective to cater for the higher density requirements in PCBs. Nevertheless, this costly mechanical drilling process pushes the invention of another interconnection method called the microvias as seen in Figure 2.6. The microvia concept revolves around producing a very small hole or via through non-mechanical means such as photoresist or etching to connect two layers (Ladou, 2006). By comparing to the mechanical drilling which could not drill vias smaller than 200 µm, microvias can be made as small as 50 µm. With this small-size vias, the density of pads can increase by more than four-folds. There will also be a reduction in the overall board size and layer count which leads to cheaper cost of production (Harper, 2005).

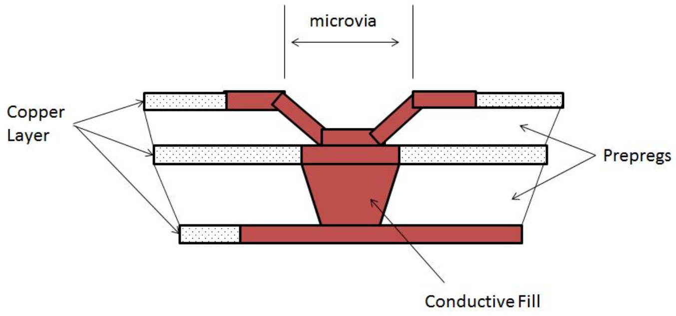

Figure 2.6: Schematic diagram of microvias in PCB (Harper, 2005).

2.1.3.2 Flexible PCB (FPCB)

Flexible printed circuit boards (FPCB) which was highly used in the aerospace and military industry, originated due to the small confinement space between the circuit, cables and connector. The main difference between the flexible and rigid circuit boards is the prepreg used in the substrate. Normally, flexible dielectric materials such as polyesters or polyimide are used in this FPCB. The main reasons for consideration in selecting the appropriate dielectric materials are the cost, thermal properties and dimensional stability. Polyimides, with a thermal stability of over 250°C, can withstand soldering temperature. They are also chemically inert to organic solvents and cannot be fused. Polyesters on the other hand have lower thermal stability of up to 150°C, prompting the usage of mechanical interconnections than soldering process. As for the construction of FPCBs, ductile copper foil is then bonded and etched on the adhesives film. Another layer of adhesive film, which is also known as the cover coat film is then added on top of the formed circuit. The patterns are then transferred to the FPCBs by screen printing of a photoresist and then etching away unnecessary portion of the copper. Upon completing the transfer of pattern, the cover coat film is laminated to the base film using heat and pressure. Basically, FPCB's also has many different grades as with the rigid PCBs such as single-sided, double sided and multi-layer configuration (Harper, 2005).

2.1.3.3 Substrate laminate

As for the insulating portion or substrate, polymer based prepregs are usually used. Pre-pregs are composites whereby the reinforcement materials are pre-impregnated with a resin matrix. Table 2.1 describes the grade name for the base material used for these prepregs. The FR-1 and FR-2 laminates comprises the cellulosed-based paper with phenolic resins. FR-2 offers better moisture and insulation resistance relatively, but both of them are used only for single sided PCB's. FR-3 laminates also consists of paper reinforcement, but with the use of epoxy resin as the base. FR-3 exhibits improved wet-electrical properties and can also be used for some double sided boards. Meanwhile the CEM and CRM grades utilize a combination of two different reinforcement types. These reinforcements had enhanced the physical and mechanical properties such as the impact strength, flexural strength and peel strength. However, the cost has also escalated as a result of this additional reinforcement. In order to have a better balance between the properties and cost, FR-4 which uses woven glass fibers and epoxies were mostly used. The other reasons FR-4 remain the top choice for manufacturers after many so years is because of their capabilities to manipulate the glass transition temperature, T_g by selecting different epoxies system. The T_g can be manipulated up to 170°C for multi-layered and thick circuits. Apart from that, the glass fibers used can also significantly reduce the coefficient of thermal expansion of the entire circuit, which is crucial due to the high densities of electrical components.

Table 2.1: Grades of base materials for prepregs (Coombs, 2001).

Grade	Resin	Reinforcement	Flame Retardant
XXXPC	Phenolic	Cotton Paper	No
FR-1	Phenolic	Cotton Paper	Yes
FR-2	Phenolic	Cotton Paper	Yes
FR-3	Epoxy	Cotton Paper	Yes
FR-4	Epoxy	Woven Glass	Yes
FR-5	Epoxy	Woven Glass	Yes
FR-6	Polyester	Matte Glass	No
G-10	Epoxy	Woven Glass	No
CEM-1	Epoxy	Cotton Paper/Woven Glass	Yes
CEM-2	Epoxy	Cotton Paper/Woven Glass	No
CEM-3	Epoxy	Woven Glass/Matte Glass	Yes
CEM-4	Epoxy	Woven Glass/Matte Glass	No
CRM-5	Polyester	Woven Glass/Matte Glass	Yes
CRM-6	Polyester	Woven Glass/Matte Glass	No
CRM-7	Polyester	Matte Glass/Glass Veil	Yes
CRM-8	Polyester	Matte Glass/Glass Veil	No

Nevertheless, since flammability became a major issue for electronic devices that was addressed since last decade, base materials that do not consist of flame retardants were phased out. Table 2.2 shows the thermal properties for different grades of base materials that have achieved the mandatory V-0 rating in the UL-94 flammability standard. CEM-1 laminates which comprises of the cellulose paper, woven glass and covered with epoxy has excellent mechanical properties and can be cold punched easily. On the other hand, CEM-3 promotes the best electrical properties compared to other epoxy resin base grades, while CRM-5 exhibits good electrical properties in humid conditions and low dielectric constant (Jawitz, 1997).

Table 2.2: Typical thermal properties of various grades of prepregs used in PCBs (Jawitz, 1997)

Base resin grades	**Glass transition temperature, T_g (^{o}C)**	**UL-rating temperature (^{o}C)**	
		Mechanical	**Electrical**
FR-1	75-85	105	105
FR-2	80-100	105	105
FR-3	90-110	105	105
FR-4	125-145	130	140
CEM-1	85-115	140	130
CRM-5	85-115	130	140
CEM-3	95-125	130	130

2.2 Polymer Substrate for PCBs

2.2.1 Epoxy

Epoxy is a thermosetting copolymer that was formed from the chemical reaction of an epoxide resin with the hardener. The resin basically contains a repeating monomer with an epoxide group at either end. There are a few classes of known epoxy resins, such as the aliphatic type, novolac and multifunctional epoxy resins. Most of the aliphatic backbone chain contains –OH groups which can react with epichlorohydrin. The monomers engaged to produce the most common aliphatic epoxy resins, diglycidyl ether of bisphenol A (DGEBA) are bisphenol A and epichlorohydrin. Another common type of epoxy resin used in electronic applications is the novolac epoxy, whereby its chemical structure is seen in Figure 2.7. Novolac epoxy resins are prepared by reacting phenol with formaldehyde. The subsequent resulting product was then reacted with epichlorohydrin to produce the novolac based epoxy resins. This grade of epoxy resins can be cured to a high crosslink density and are used mainly for electronic applications that required very low amount of ionic species such as metal impurities and halogen (Dufton, 2000).

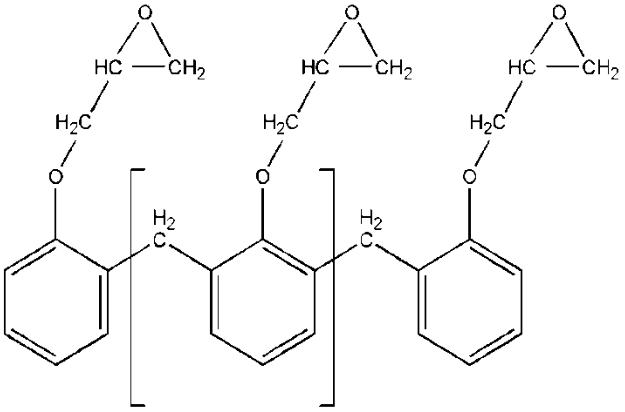

Figure 2.7: A multifunctional epoxy novolac resin (Minges, 1989)

Being the most preferred and utilized resin system for printed circuit boards due to their excellent electrical, thermal, physical and mechanical properties coupled with relatively lower cost , new grades of epoxies were constantly developed to suit the ever increasing demanding applications. Multifunctional epoxy resins, which cater for higher end needs were developed as a result. The multifunctional epoxies contain at least two or more epoxy groups in the same molecule, and are characterized as trifunctional and tetrafunctional epoxy resins. A typical chemical structure of tetrafunctional epoxy group is shown in Figure 2.8 (Kulshreshtha and Vasile, 2002).

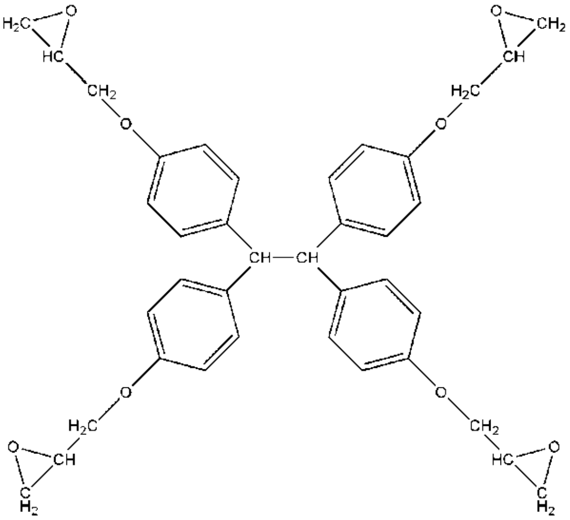

Figure 2.8: Tetrafunctional epoxy resin (Kulshreshtha and Vasile, 2002)

2.2.2 Phenolic Resin

Phenolic resin, also known as phenol formaldehyde resin is a thermosetting resin comprises of phenol and formaldehyde. Their existence and use of more than a century had proven their significant importance in a wide range of applications, from commodity products to high end aerospace industry. This is due to their well-recognized strong mechanical strength, heat resistance and dimensional stability, highly resistance to solvents and water. As for their fire properties, phenolic resins emitted only low smoke count upon incineration, thus allowed its usage in the PCBs as shown earlier in Table 2.1.

However, in terms of many critical engineering fields, phenolic resin could not substitute the epoxy resins or polyimides. The special need to cure at moderately high temperature by a condensation mechanism with the evolution of volatiles had pushed for the compulsory needs of pressure during moulding. This additional step is critical to obtain a void-free component product. Furthermore, the requirement of a catalyst for curing purpose and the limited shelf life of the resin at ambient conditions are among other shortcomings for the phenolic resins (Reghunadhan Nair, 2004).

2.2.3 Polyimides

Polyimides, as aromatic polymers are an important class of high performance polymers, whereby their application ranges from high-end aerospace, microelectronics, photonics, to optics. Among some of their characteristics are excellent thermo-oxidative stability, mechanical strength, electrical properties, high radiation and solvent resistance, low coefficient of thermal expansion, and low dielectric strength (Hasegawa and Horie, 2001; Kirby, 1992). The most widely known type of polyimide is the Kapton H, developed by Dupont in the 1960's, with a chemical structure as shown in Figure 2.9. The high thermal stability of polyimide also has other negative effects such as infusible within the processing temperature and insoluble in organic solvents (Wang et al., 2007). With that, many efforts have been made to increase the solubility of the polyimide such as incorporation of flexible linkages in the backbone chain and introduction of bulky side groups.

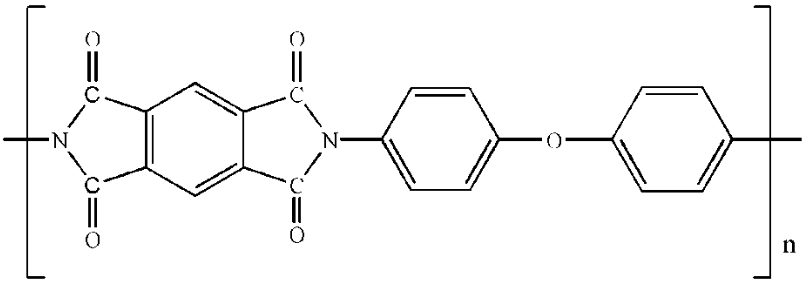

Figure 2.9: Chemical structure of polyimides (Hasegawa and Horie, 2001)

2.3 Fiber Reinforcement

Fibers are in general used to reinforce a polymer resin by enhancing the overall composites mechanical properties. Fibers can be characterized into two different types, organic and inorganic fibers.

2.3.1 Organic Fibers

Organic fibers have once been classified as a low performance material that was used only in the textile industry before aramid fibers were introduced in the 1960's. In current years, the applications for organic fibers have expanded to ballistics, rubber reinforcement, ropes, cables and composites that require high performance.

2.3.1.1 Aramid Fibers

Aramid fibers which is also known as aromatic polyamide fibers consists of a long chain synthetic polyamide where at least 85% of the amide linkages are attached to two aromatic rings. There are basically two types of aramid fibers, namely the para-aramids and meta-aramids. Aramid fibers are attractive organic fibers due to their various benefits such as high stiffness, high fracture strain, and low density. Composites structure reinforced with aramid fibers have also recorded a significant reduction in their weight. However, aramid fibers are known to have poor bonding with most available commercial resins due to their high crystallization, smooth surface and inert chemical structure which prevents interfacial bonding with other resins.

To overcome this deficit, researches have been on-going directed towards the improvement of fiber surface properties by chemical treatments, but this had caused other problems such as the disposal of used drained water and solvents. Therefore, many researchers such as Jia et al., (2011) and Brown et al., (1991) had studied using plasma modification and it was found that the interfacial bonding between aramids and resins had shown vast improvement. However, Liu et al., (2008) mentioned that although these surface modifications had increased the interfacial of the composites through chemically attaching many active functional groups on the surface of aramid, these methods often produce problem to the tensile strength. Thus, the treatment of aramid/epoxy resin composites by ultrasound during winding process was studied and it was proven that this method has also enhanced the wetting between the aramid fibers and epoxy resins.

2.3.2 Inorganic Fibers

Generally, inorganic fibers are more rigid, tougher, have higher melting points and heat resistant compared to the traditional organic fibers. They are also non-flammable fibers and can withstand high temperatures and corrosive environment. Among the many types of inorganic fibers such as boron, silicon carbide, alumina (Al_2O_3), and alumina borosilicate, glass fibers was usually used due to their low cost, excellent chemical resistance and mechanical strength.

2.3.2.1 Glass Fibers

Being one of the strongest and versatile of materials, glass fibers were mostly used as reinforcement especially for polymeric composite materials. Its application ranges from fabrics, electrical and thermal insulation up to filtration purposes. There are basically many grades of glass produced globally with different formulations and Table 2.3 shows the chemical composition of each glass grade. Grade-C is used mainly due to their strong chemical resistance and grade-S for their superior strength and stiffness. Grade-D glass has good dielectric properties that are suitable for aircraft to minimize the impact of lightning strikes. Grade-E glass which is also known as electric glass, are often used for epoxy pre-pregs or as fabric due to their good properties at low cost (Baker et al., 2004)

Table 2.3: Chemical formulations for various grades of glass (Coombs, 2001).

Compositions	**Grades of Glass**				
	A	**C**	**D**	**E**	**S**
SiO_2 (%)	72	65-66	73-74	52-56	64.2
Al_2O_3 (%)	0.6	4-5	-	12-16	24.8
CaO (%)	10	13-14	0.2-0.3	15-25	0.01
MgO (%)	2.5	2-3	0.2-0.3	0.5	10.27
B_2O_3 (%)	-	5-5.5	22-23	5-11	0.01
F (%)	-	-	-	0-0.7	-
Fe_2O_3 (%)	-	-	0.1-0.2	0.05-0.5	0.21
Na_2O (%)	14.2	8-8.5	1.3	0.25-1	0.27
K_2O (%)	-	≤0.5	1.5	0.25-1	-
BaO_2 (%)	-	-	-	-	0.2
TiO_2 (%)	-	-	-	0-1	-

2.3.2.2 Carbon Fibers

Utilized since 1960’s, the production and use of carbon fibers have increased drastically since the last decade. Carbon fibers are predominantly used with polymers as to form advanced composite materials due to their high strength and modulus in relative to other reinforcing fibers (Fitzer and Manocha, 1998). These composites are usually applied in high-end applications such as aerospace, automobiles, and sports utilities. Basically, carbon fibers are produced from rayon, pitch and polyacrylonitrile (PAN) precursor fibers. However, PAN precursor dominated the market due to their cheaper cost and simpler processes involved (Chung, 1994).

2.4 Overview of Polymer Combustion

Owing to the organic chemical structure which mainly consists of carbon and hydrogen groups, polymers are highly susceptible to flames and combustion (Troev, 2006). When the polymers are exposed to high temperatures and heat, the organic resin decomposes and release heat, smoke, soot, and other volatile fractions. These volatile compounds diffuse into the air and produces combustible gases. Subsequently, these gases can auto-ignite when the temperature approaches the activation energy for combustion or ignite with the assistance of an external source of energy such as sparks and flames. Ignition however depends on several parameters, typically the oxygen concentration.

Various reactions take place during the combustion process. Among them is polymer depolymerisation that happens through the chain scission reaction. The main reactions are the end or random chain scissions that subsequently generate radical species. At the meantime, chain stripping also takes place. During this process, part of the functional groups or moiety that was not attached to the polymer backbone chain was also stripped away. Lastly, for the flame retardants that react in the condensed phase, cross-linking between the radicals that was produced during the chain-scission leads to a new thermally stable substance called the char (Rakotomalala et al., 2010).

2.4.1 Flame retardants

Flame retardants are basically added into polymer system to stop the polymer combustion process by cooling the polymer physically or by chemically interfering with the combustion process to stop the flame. Flame retardants can be incorporated into the polymer by either through physically or chemically addition.

2.4.1.1 Physical mode

In general, there are two types of mechanism of action which are condensed phase and vapour phase. The mode of action is classified as vapour phase if the species produced interfere with the flame propagation mechanism, while condensed phase revolves when the interaction before vaporization changes the nature of the products/residues of combustion and degradation (Atkinson et al., 2000). The physical mode of flame retardants usually revolved around the condensed phase. This includes materials that decompose in endothermic reaction that reduces the surrounding temperature by heat consumption. Some flame retardants such as the metal hydrates liberates water vapour causes a heat sink, while some releases inert gases such as ammonia and carbon dioxide gases that can dilute the concentration of reagents, specifically oxygen gases. Moreover, there are others which assist in forming a protective solid or gaseous layer that limits the transfer of combustible volatile gases to the oxygen. The separation of these volatile gases from the oxygen can then stop or slower the combustion process.

2.4.1.2 Chemical mode

As for the flame retardants that react chemically in the combustion process, this takes place either in the vapour or condensed phase. In the vapour phase, the release of free radicals (halogenated Cl*or Br*) interacting with the reactive species (H* or OH*) can form less reactive or inert molecules. The modification of the combustion reaction process will give a significantly decrease in the exothermic reaction, thus heading to a lower temperature produced. Alternatively, for the flame retardants that react in a condensed phase, the flame retardants can chemically transform the degrading polymer chains into chars or carbonized vitreous layer at the