

**DEVELOPMENT OF A NEW CLASS OF LIQUID CRYSTALLINE EPOXY RESIN
CURED BY MESOGENIC DIOLS**

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**UNIVERSITI SAINS MALAYSIA
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**Thesis yang diserahkan untuk memenuhi
keperluan bagi Ijazah Sarjana Sains**

MEI 2008

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LIST OF ABBREVIATION

LCER	Liquid crystalline epoxy resin
MC-PLC	Main chain polymer liquid crystal
SC-PLC	Side chain polymer liquid crystal
BP1	4,4'-Di(2,3-epoxypropoxy)biphenyl
BP2	4,4'-Biphenyl-di[4-(2,3-epoxypropoxy)benzoate]
DDS	Diaminodiphenylsulfone
DDE	Diaminodiphenylester
¹ H-NMR	Proton nuclear magnetic resonance
DSC	Differential scanning calorimeter
DMA	Dynamic mechanical thermal analyzer
DGEBP-F	Diglycidyl ether of bisphenol F
DGE-DHBP	Diglycidyl ether of 4,4'-dihydroxybiphenol
MTHPA	Methyltetrahydrophthalic
FT-IR	Fourier transfer infrared spectroscopy
DDM	4,4'-diaminodiphenylmethane
PDA	1,4-phenylenediamine
DGEBA	Diglycidyl ether of bisphenol-A
DGETA	Diglycidyl ether of terephthalylidene-bis-(<i>p</i> -aminophenol)
IBd	Bis(2-{4-[(2,3-epoxypropoxy)phenyliminomethylidene]benzoyloxy}-ethyl)ether
IBt	1,2-Bis({4-[(2,3-epoxypropoxy)phenyliminomethylidene]benzoyloxy}-ethoxy)ethane

IIAd	Bis{2-[4-(2,3-epoxypropoxybenzoyliminomethylidene)phenoxy]-ethyl}ether
IIAt	1,2-Bis(4-[(2,3-epoxypropoxybenzoyliminomethylidene]phenoxy}-ethoxy)ethane
DAT	2,4-diaminotoluene
NA2	4-aminoacetophenone azine
CAA	4,4'-bis(ω -carboxyalkoxy)azoxybenzenes
DGEBA	4,4'-bis(2,3-epoxypropoxy)bisphenol A
EPTB	4,4'-bis(2,3-epoxypropoxy)-3,3',5,5'-tetramethylbiphenyl
HDT	Heat distortion temperature
PLM	Polarized Light Microscope
Cr	Crystal stage
N	Nematic stage
I	Isotropic stage
T_m	Melting point temperature
T_i	Isotropic temperature
T_g	Glass transition temperature

**PEMBANGUNAN KELAS BARU HABLUR CECAIR RESIN EPOKSI
TERMATANG OLEH MESOGENIK DIOL**

ABSTRAK

Dalam kajian yang telah dijalankan, kelas baru hablur cecair resin epoksi telah dihasilkan dengan menindakbalaskan resin epoksi berasaskan bisphenol A (DGEBA) dengan dua azomethina mesogenik diol yang berbeza yang bertindak sebagai agen pematangan bagi menggantikan amina. Dalam resin epoksi konvensional, amina bertindak sebagai agen pematangan tetapi disini ia hanya bertindak sebagai pemangkin kepada tindakbalas pematangan. Tiga nisbah yang berbeza telah digunakan bagi mengkaji kesan nisbah tersebut kepada sifat-sifat hablur cecair resin epoksi. Nisbah DGEBA kepada azomethina mesogenik diol yang digunakan adalah 1:1, 1:2 dan 2:1. Monomer dan polimer yang dihasilkan di cirikan melalui penggunaan spektrometri infra merah (FT-IR) dan nuklear magnetic resonans ($^1\text{H-NMR}$). Mikroskop berpolar (POM) dan imbasan berskala kalorimetri (DSC) telah digunakan untuk menentukan kehadiran fasa hablur cecair dalam azomethina mesogenik diol yang telah dihasilkan dan juga semasa proses pematangan. Daripada keputusan yang telah diperolehi, kehadiran fasa hablur cecair telah dicatatkan semasa proses pematangan dan suhunya bergantung kepada nisbah tadi. Dengan ini, proses pematangan telah berjaya dilakukan dan produk yang telah termatang diuji kekuatan termal dan mekanikalnya. Kestabilan termal telah dikaji menggunakan analisis termal gravimetric (TGA) dan resin yang termatang mempunyai sifat kestabilan termal dan fleksibel yang tinggi beserta dengan kekuatan lekatan yang baik.

DEVELOPMENT OF A NEW CLASS OF LIQUID CRYSTALLINE EPOXY RESIN CURED BY MESOGENIC DIOLS

ABSTRACT

In this study, a new class of liquid crystalline epoxy resins were developed by reacting the diglycidylether of bisphenol A (DGEBA) with two new mesogenic diols that acted as curing agent to replace amines. Instead of its role as curing agent in conventional epoxy resin, amine here is used as a catalyst in the curing process. Three different ratios are used to study the effect of the ratio to the properties of liquid crystalline epoxy resin. The ratio of DGEBA to the azomethine mesogenic diols used are 1:1, 1:2 and 2:1. The monomers and polymers were characterized by using Fourier Transformed Infra-Red (FT-IR) and Nuclear Magnetic Resonance ($^1\text{H-NMR}$). Polarized Microscope (POM) and Differential Scanning Calorimetry (DSC) were used to investigate the liquid crystalline phase of the synthesized azomethine mesogenic diols and during curing process as well. From the results obtained, it is confirmed that there is a liquid crystalline phase occurred during curing process and the temperature is varied depending on the ratio. The curing process had been successfully conducted and the cured product then tested for their thermal and mechanical properties. Thermal stability was investigated by using Thermal Gravimetric Analysis (TGA) and the cured resins were found to exhibit high thermal stability, high flexibility and good adhesion properties.

CHAPTER 1

INTRODUCTION

1.1 Epoxy Resin

Epoxy resin can be differentiated from other resin by the presence of epoxide functional group called oxirane group in its polymer chain. The oxirane group is capable to react with compound containing hydrogen active atoms for example amines, amides, carboxylic acid, phenol and mercaptan. Figure 1.1 shows the structure of the oxirane group that play an important role in the epoxy resin curing process (Mija et al., 1996).

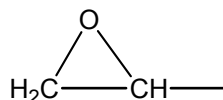


Figure 1.1 Oxirane group

1.2 History and Development of Epoxy Resin

The history of Epoxy resin starts when I.G Farben patented his findings about liquid polyepoxides in the German Patent in 1939. P. Castan then patented his finding in 1943, about the hardening of epoxy resin with dibasic acids in U.S. Patent (Brydson, 1969). In 1945, a polymer called epoxy resin based on Bisphenol A which is the diglycidyl ether of Bisphenol A (DGEBA) had been successfully synthesized from condensation reaction between 2-chloromethyl-oxirane (epichlorohydrin) (Figure 1.2) and 2,2-bis(4'-hydroxyphenyl)propane (Bisphenol A) (Figure 1.3) had marked the starting point for the development and the technology of epoxy resin. Scheme 1.1 (page 3) illustrates the reaction between epichlorohydrin and Bisphenol

A to produce epoxy resin based on Bisphenol A. According to Kaynak et al. (2002) epoxy resin was first commercialized in 1946 and used in industries. Apart from epoxy resin based on Bisphenol A and epichlorohydrin which is firstly commercialized, there are also a few types of epoxy resin that had been introduced in the late 1950's and early 1960's.

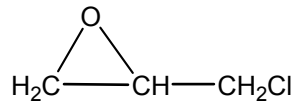


Figure 1.2 2-chloromethyl-oxirane (epichlorohydrin)

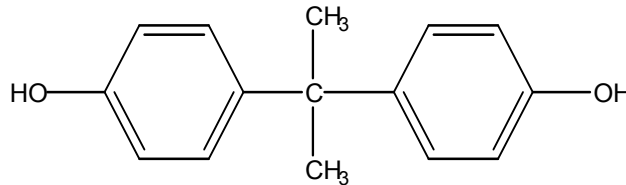
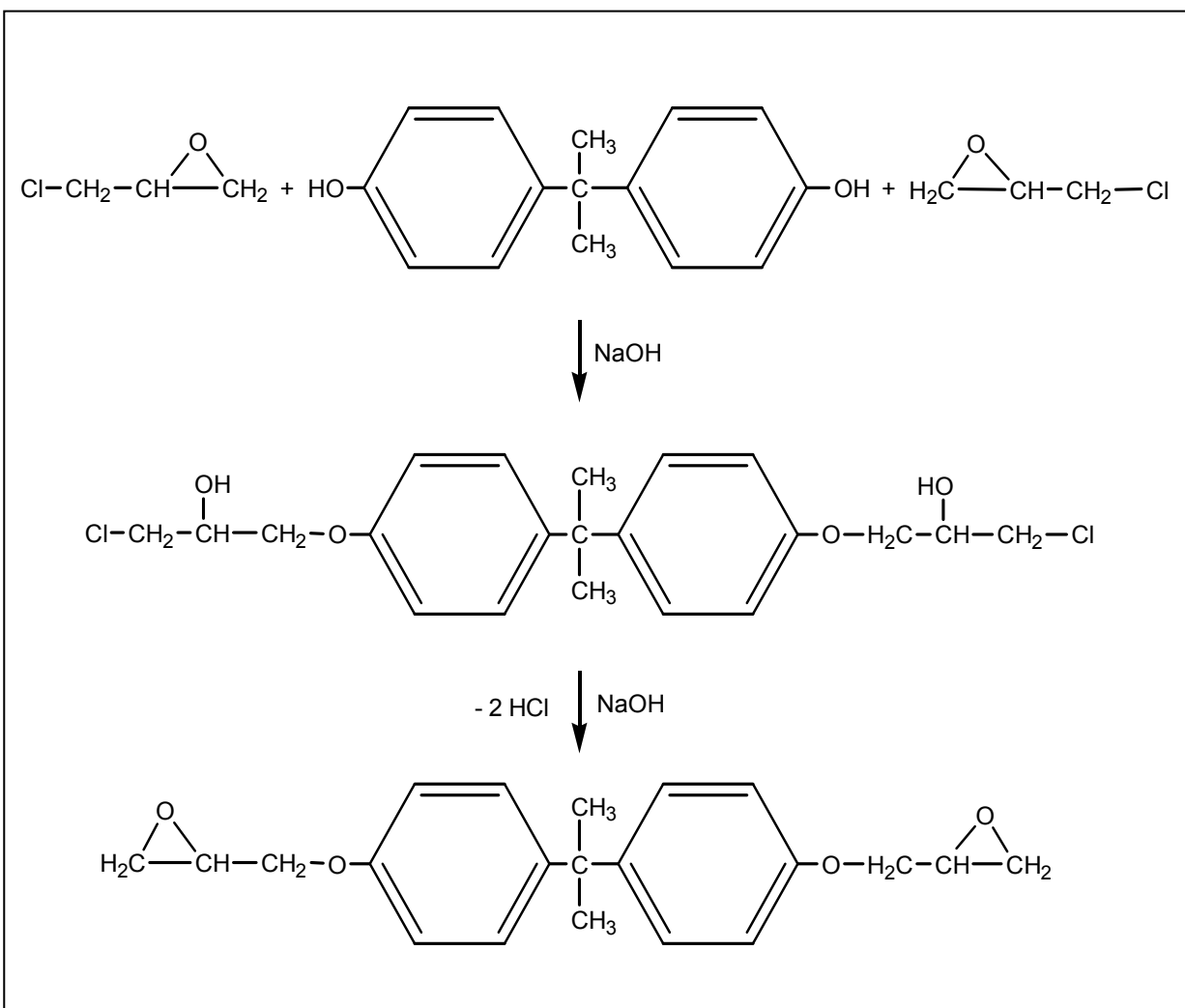


Figure 1.3 2,2-bis(4'-hydroxyphenyl)propane (Bisphenol A)



Scheme 1.1 Reaction between epichlorohydrin and Bisphenol A

In the early years, epoxy resin is mainly used as surface coating materials and S. O. Greenlee had started the modification of epoxy resin that describes in a number of patents. The modification with glycerol is one of the examples that S.O Greenlee has worked on. Others are the esterification of the higher molecular weight materials with drying oils acids and the reaction with phenolic and amino resin (Brydson, 1969).

Industrial sectors are the biggest consumer of the epoxy resins where most of the resins have been modified and enhanced by incorporating with additives. The modification are made due to several factors that restrict the uses of epoxy resins for instance the price of epoxy itself that is too costly, the compatibility with the end uses, environmentally friendly and to reduce the production cost and energy consumption (Milby, 1973).

1.3 Epoxy Resins Classifications

Epoxy resins can be classified into two major groups; namely epoxy resins based on glycidyl ether such as DGEBA and epoxy resins based on non-glycidyl ether (Table 1.1).

Table 1.1 Classification of epoxy resins and their example.

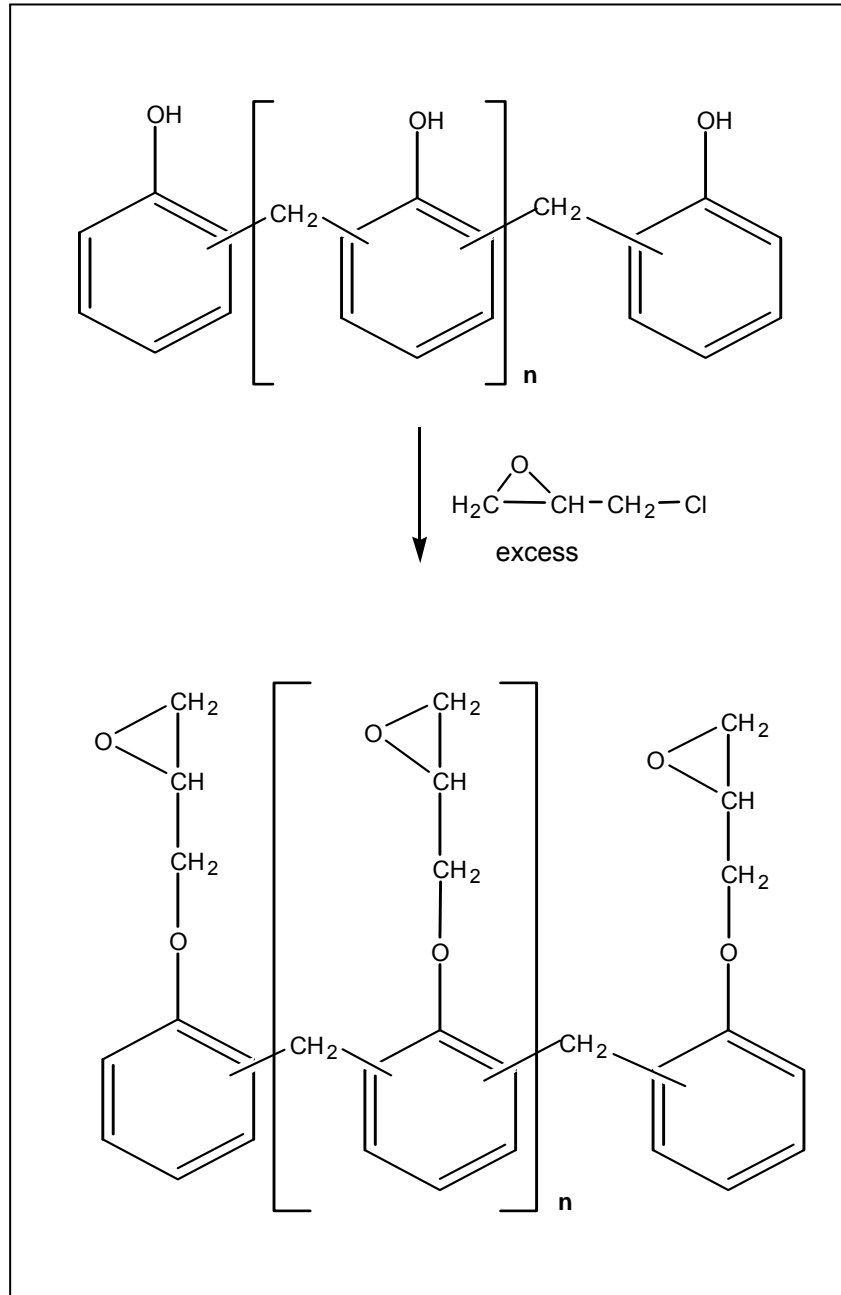
Epoxy resins based on glycidyl ether	Epoxy resins based on non-glycidyl ether
DGEBA	Cyclic aliphatic epoxy
Novolak epoxy	
Polyglycol epoxy	Acyclic aliphatic epoxy
Halogenated epoxy	Glycidyl amine epoxy

1.3.1 Epoxy Resin Based on Glycidyl Ether

This type of epoxy resin is derived from the reaction between epichlorohydrin with polyhydroxyl compounds. According to Brydson (1969), the softening point of this resin after curing is low.

1.3.1.1 Novolak Epoxy Resin

Produced from the reaction of novolak resin and epichlorohydrin, novolak epoxy resin has low molecular weight whereby the nuclei phenolic group are attached at ortho position. The reaction to produce novolak epoxy resin is shown in Scheme 1.2.



Scheme 1.2 Reaction to produce novolak epoxy resin

1.3.1.2 Polyglycol Epoxy Resin

The polyglycol epoxy resin was synthesized by the reaction of epichlorohydrin and polyglycol. The polyglycol could be directly epoxidized through the terminal hydroxyl group that contained in the main chain. For example, poly(propylene glycol). Generally, this type of resin is not used alone but incorporating it with 10-30% of epoxy resin based on Bisphenol A will result in better strength properties.

1.3.1.3 Halogenated Epoxy Resin

This type of epoxy resin is derived from the reaction between halogenated hydroxyl compound and epichlorohydrin. Either tetrabromobisphenol A or tetrachlorobisphenol A are the halogenated hydroxyl compound which is commonly used. The structure of epoxy resin produced is similar with the epoxy resin based on Bisphenol A except that halogen atoms are attached to its aromatic ring. The presence of halogen atom will result in fire retardant resin.

1.3.2 Epoxy Resin Based on Non-glycidyl Ether

This type of resin is derived from the epoxidation of unsaturated compound by using hydrogen peroxide or peracetic acid.

1.3.2.1 Cyclic Aliphatic Epoxy Resin

Introduced in America, the resin classified under this group has a ring structure together with the epoxy group in its molecule. Commercially available resins are as follows;

- I. 3,4-epoxy-6-methylcyclohexymethyl-3-4-epoxy-6-methylcyclohexane carboxilate.
- II. 4-vinylcyclohexane dioxide
- III. dicyclopentadiene dioxide

1.3.2.2 Acyclic Aliphatic Epoxy Resin

Epoxide oil and diene epoxide polymer are the example of acyclic aliphatic epoxy resins that are commercially available.

1.3.2.3 Glycidyl Amine Epoxy

There are a few epoxy resin derived from the amine glycydylolation with epichlorohydrin had been discovered. The resin will lead to highly crosslinking structure.

1.4 Properties and Characteristic of Epoxy resin

According to Brydson (1969), epoxy resin can be characterized through six important parameters as follows;

- I. resin viscosity
- II. epoxide equivalent

- III. hydroxyl equivalent
- IV. average molecular weight
- V. melting point
- VI. heat distortion temperature

Viscosity is the most important criteria that need to be taken into account for easy handling. Molecular weight, chemical composition, molecular weight distribution and the presence of solvent and modifier are the factors that will influence the viscosity.

By titrating with potassium hydroxide (KOH), epoxide equivalent is calculated. Epoxy equivalent carries the meaning of total number of epoxy groups contained in that particular resin. This figure is important in order to determine the average molecular weight for that resin.

The weight of resin that has within itself one equivalent of hydroxyl group is known as epoxy equivalent. Usually it is determined by the reaction between the resin and acetyl chloride.

Epoxy resin has a few properties that need to be considered before it can be used in any application. The properties are as follows;

- I. brittle (Fernandez-Nogaro et al., 1996)

- II. high tensile and tensile modulus (Joaquín et. al., 2002 and Mikroyannidis, 1990)
- III. good dimensional stability (Joaquín et al., 2002 and Mikroyannidis, 1990)
- IV. good rust and chemical resistance (Mikroyannidis, 1990)
- V. good thermal stability (Brydson, 1969)

1.5 Epoxy Usage

Among the industry that uses epoxy resin as their raw materials are;

- I. surface coating (high molecular weight resin)
- II. lamination
- III. adhesives
- IV. composites
- V. moulding
- VI. construction
- VII. engineering

1.6 Epoxy Resin Market

In the international market, Germany is the largest consumer of structural epoxy adhesives except for the epoxy film and paste which consume 25% of the worldwide demands where France is the biggest consumer for the epoxy film and paste. Structural epoxy is used in automotive industries in Germany while France use epoxy film and paste mostly in its aerospace industries. Other countries in Europe, for example the United Kingdom and Ireland used epoxy resin in their marine industries.

1.7 Current Interest in Epoxy Resin

Liquid crystalline epoxy resin (LCER) is the new approach instead of the two common approaches that used functionalized reactive rubbers and thermoplastics to overcome the drawback of epoxy resin which is low fracture toughness (Punchaipetch et al.,2001).

1.8 Liquid Crystal

There are three common states of matters that we are aware of which is solid, liquid and gas. They can be differentiate by the amount of order that the states possesses. The solid state consists of more or less rigid arrangement of molecules where it occupied a certain place and remains there. Moreover, it can also be oriented in a specific way. Due to the large attractive force holding the molecules together, solids are hard and difficult to deform and required a larger external force to disrupt the structure. In liquid state, the molecules are free to be diffused in a random fashion where it is constantly bumping into one another and abruptly changing their motion and direction. The attractive force does exist but it is weaker than the forces in solids. The liquid takes the shape of its container and it is quite easy to deform due to the lack of rigid arrangement (Collings, 2002).

However, some states of matter do not meet the requirements of any of the categories mentioned earlier. It is known as the liquid crystal state. The liquid crystal state is actually an intermediate state between crystalline solids and isotropic liquids states and can be illustrated as in Figure 1.4 (Chandrasekhar, 1977).

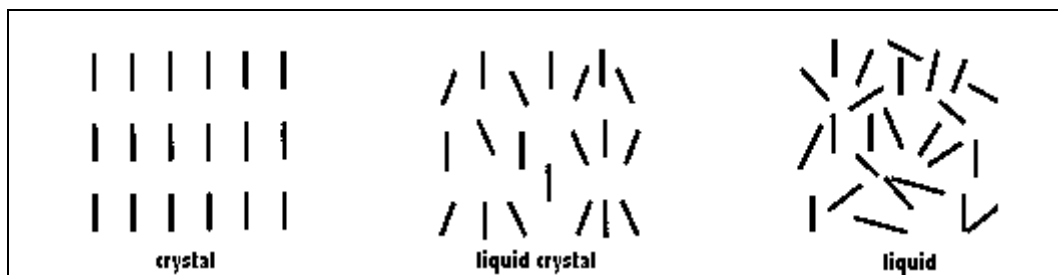


Figure 1.4 Illustration of liquid crystal state

This is why it is neither solid nor liquid. This will result the substances that possess the liquid crystal state to show both solid and liquid properties where they are observed to flow like liquids but they also have some properties of crystalline solid. On further argument, it turns out that the liquid crystal state are much closer to the liquid state than the solid state because it takes a fair amount of energy to convert the substance from a solid to a liquid crystal phase while it just requires a little amount of energy in order to turn the same liquid crystal into the real liquid. The transition of those states can be brought about by purely thermal process (thermotropic) or by the influence of solvent (lyotropic) (Chandrasekhar, 1977).

Friedel had proposed that the nomenclature of thermotropic liquid crystal can be classified broadly into three types namely: nematic, cholesteric and smectic (Chandrasekhar, 1977).

The nematic liquid crystal has a high degree of long range orientational order of the molecules, however inadequate range translational order. Thus, it differs from the isotropic liquid because the molecules are spontaneously oriented with their long

axes approximately parallel (Chandrasekhar, 1977). The name of nematic is derived from the Greek words for thread where it can be observed from the polarized microscope that the shape of the crystal is just like a thread (Collings, 2002).

Another type of liquid crystal is cholestric mesophase. It is actually a nematic type of liquid crystal except that it is composed of optically active molecules. It is deemed that the structure has a screw axis superimposed normal to the preferred molecular direction (Chandrasekhar, 1977). It is also known as chiral nematic liquid crystal where chiral simply means twisted (Collings, 2002).

The final type of the thermotropic liquid crystal is smectic liquid crystal and it possess stratified structures but varieties of molecular arrangements are possible within each stratification (Chandrasekhar, 1977). The smectic word means soap from the Greek word because it had mechanical properties reminiscent of soaps (Collings, 2002).

In order for a compound to have liquid crystal properties, the molecules of the compound needs to posses the criteria below;

- i. The molecule must be elongated in shape; it is significantly longer than its wide.
- ii. The molecule must have some rigidity in its central region
- iii. Ends of the molecules are flexible.

It has been said that an organic chemist indiscriminately synthesizing compounds will find that one in every two hundred compounds synthesized possess the liquid crystal state (Collings, 2002). This includes the polymer that has liquid crystal properties.

1.9 Polymer Liquid Crystal

Like other substances, polymer can also exist in more than one phase. Most of the polymer melts to form a liquid without having any interphase between them. However, some have been identified to hold an interphase called liquid crystal phase. This polymer is known as polymer liquid crystal (Collings, 2002). Polymer liquid crystal has been discovered and partly predicted theoretically by Onsager (Onsager, 1949) and Flory some 50 years ago. Over the last twenty years, the advanced knowledge and the development of new technology in polymer liquid crystal has been so important where it received the top billing. Polymer liquid crystal can be classified into two main groups; namely thermotropic polymer liquid crystal and lyotropic polymer liquid crystal (Collings, 2002).

1.9.1 Thermotropic Polymer Liquid Crystal

Thermotropic polymer liquid crystal is formed when polymeric material is heated to a point where the solid phase melts. Due to this matter, it is sometimes referred to as *polymer melts*. This type of polymer liquid crystal can further be divided into two general classes depending on its monomer. The first class consists of monomers that are fairly rigid, anisotropic and highly polarizable while the second

class consist of amphiphilic monomers. However, there are not many findings and conclusion on the behaviour of polymers can formed from amphiphilic monomers due inadequate research in this area (Collings, 2002). In this research, only thermotropic polymer liquid crystal are investigated and discussed.

1.9.2 Lyotropic Polymer Liquid Crystal

Lyotropic polymer liquid crystal is made up of two or more components. Generally, it consist of an amphiphile (containing a polar head group attached to one or more long hydrocarbon chains) and water (Chandrasekhar, 1977). Macromolecule that posses lyotropic polymer liquid crystal need to be fairly rigid and the macromolecules also need to dissolve in the solvent at high enough concentration to obtain the lyotropic liquid crystal properties (Collings, 2002).

1.9.3 Properties of Polymer Liquid Crystal

The properties of polymer liquid crystal are actually the combination properties of polymer and liquid crystal. These 'hybrids' shows the same mesophases characteristic of an ordinary liquid crystal, yet retain many useful and versatile properties of polymer. In order for polymer to posses liquid crystal properties, mesogens elements must be incorporated into their chains.

The placement of the mesogens played an important role in determining the type of thermotropic polymer liquid crystal formed. The mesogens can be attached to the polymer chain in two ways which is; as the part of the main chain of a polymer

and as the side chains of the polymer. They are called main chain polymer liquid crystal and side chain polymer liquid crystal respectively (Giamberini et. al., 2005). Figure 1.5 illustrates the schematic structure of the main chain polymer liquid crystal (MC-PLC) and side chain polymer liquid crystal (SC-PLC).

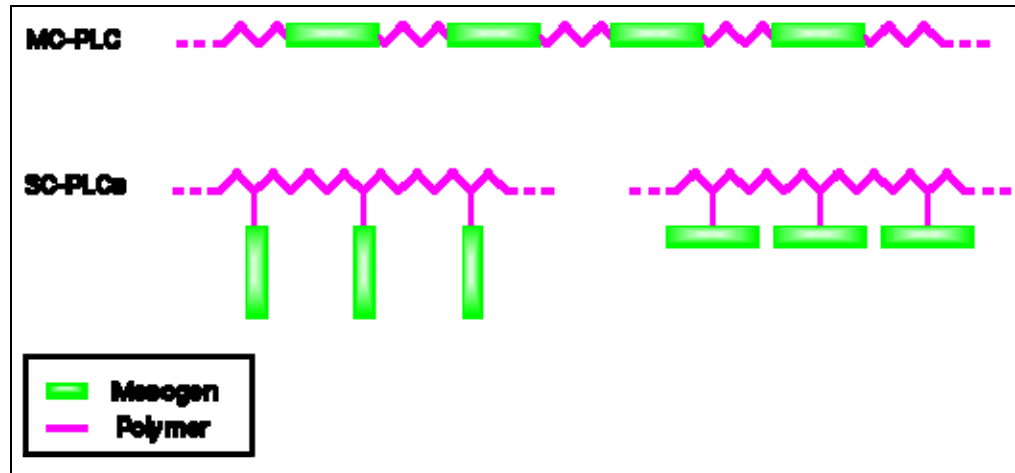


Figure 1.5 Schematic structure of the main chain polymer liquid crystal (MC-PLC) and side chain polymer liquid crystal (SC-PLC)

1.10 Objectives

- I. To synthesize and characterize new azomethine mesogenic diols as curing agent.
- II. To develop and study the thermal and mechanical properties of a new class of liquid crystalline epoxy resin cured by azomethine mesogenic diols.
- III. To study the effects of the ratio of azomethine mesogenic diols to epoxy resin based on Bisphenol A on their thermal and mechanical properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Liquid Crystalline Thermosets

In recent years, liquid crystalline thermosets have become a main focused in academic and industrial research. Many studies has been carried out regarding this exciting area (Lee and Jang, 2006, Lee et al., 1998, Osada et al., 1996). It had been widely investigated for various reasons due to their unique properties (Lee et al., 1998, Mormann and Bröcher, 1998). It is developed to enhance the mechanical and thermal properties of common thermosets as well as to overcome the disadvantages of thermoplastic liquid crystalline polymers (Lee and Jang, 2006). Besides that, electrical and optical properties of liquid crystalline thermosets had also become the factors of development in this field. The excellent properties of liquid crystalline thermosets is due to the preservation of the molecular organization in the mesophase of the liquid crystal precursors and monomers by means of cross linking (Choi et al., 2000).

Liquid crystalline thermosets can be prepared by many routes;

- I. Through self-cross-linking reaction of liquid crystalline monomer or non-liquid crystalline rigid rod monomer (Mormann and Bröcher, 1998).
- II. The reaction between the liquid crystalline monomer with either non-liquid crystalline or liquid crystalline curing agent (Mormann and Bröcher, 1998).

III. Reaction of non-liquid crystalline rigid rod monomer with non-liquid crystalline curing agent (Jahromi et al., 1994).

Research on liquid crystalline thermosets has involved variety of thermosets materials such as polyester (Qin et al., 2004, Frich and Economy, 1997, Hsu et al., 1993), polyacrylate and methacrylate (Litt et al., 2003), polyamide (Tjong and Meng, 1997, Tjong and Meng, 1999), polystyrene (Gohy and Jerome, 2001), polymethylmethacrylate (PMMA) (Cho et al., 2002), vinyl ester (Ambrogi et al., 2002) and polyether (Percec and Tsuda, 1991, Alazaroaie et al., 2003, Hurduc et al., 2001, Callau et al., 2002).

2.2 Liquid Crystalline Epoxy Resin

Epoxy resin is classified under the polyether and it has gained a considerable interest compared to other thermosets materials due to its advantage such as superior adhesion, controllable curing rate, high heat and chemical resistance and high mechanical properties (Lee and Jang, 2006, Choi et al., 2000). By incorporating the liquid crystalline structure into the epoxy network, it could enhanced the properties of the epoxy resin (Choi et al., 2000, Rosu et al., 2004). Molecular weight of liquid crystalline epoxy resin played an important role where it will effect the liquid crystalline phase of the liquid crystalline epoxy network. Low molecular weight liquid crystalline epoxy will show smectic phase during curing while high molecular weight will exhibit a nematic phase (Barclay et al., 1992).

As mentioned earlier, there are few ways to produce liquid crystalline thermosets, in this case is liquid crystalline epoxy resin. Lee et. al.,1998, has synthesized liquid crystalline epoxy resin based on biphenol mesogen namely 4,4'-Di(2,3-epoxypropyloxy)biphenyl and 4,4'-Biphenyl-di[4-(2,3-epoxypropyloxy)benzoate] and hereafter will referred as BP1 and BP2 respectively. Both are cured using diaminodiphenylsulfone (DDS) and diaminodiphenylester (DDE). BP1 and BP2 were characterized using proton nuclear magnetic resonance ($^1\text{H-NMR}$), differential scanning calorimeter (DSC), dynamic mechanical thermal analyzer (DMA) and Leitz optical microscope equipped with hot stage. From the thermal analysis, it is observed that BP1 does not show any liquid crystalline phase during heating but smectic-like phase is detected during cooling. Whereas for BP2, two phases of liquid crystalline detected at 113°C that were caused by smectic transition and 163°C due to nematic transition during heating. The excellent mesophase stability of BP2 is due to the higher aspect ratio of the mesogenic unit compared to BP1.

The curing process were conducted in the ratio of 1:0.45 (biphenol:amine) and from all DSC results, it is observed that DDE is more reactive rather than DDS. The T_g of the cured epoxy are also measured where it is found that BP2 showed higher T_g compared to BP1. Furthermore, from the polarized optical measurements, it is recorded that all the mixtures (BP1 with DDS & DDE and BP2 with DDS & DDE) possess liquid crystalline phases during curing except for the BP1 with DDS. And all the liquid crystalline phases is stable up to decomposition which is below 300°C and

it is proved that the goal of this research that is to prepare a highly heat resistance liquid crystalline network had been achieved.

The method discussed above is for the reaction between the liquid crystalline monomer with non-liquid crystalline curing agent to produce liquid crystalline epoxy resin. In 2001, Panchaipetch et. al. has used another method which is by reacting the liquid crystalline and non-liquid crystalline monomer with non-liquid crystalline curing agent as well as the blend of both monomer with the same curing agent. The monomers are diglycidyl ether of bisphenol F (DGEBP-F) and diglycidyl ether of 4,4'-dihydroxybiphenol (DGE-DHBP). Here, instead of using amine as curing agent, they had decided to use anhydride curing agent which is methyltetrahydrophthalic (MTHPA) due to good thermal stability, electrical insulation and relatively high chemical resistance. It is suitable to be used as matrices in composite as it provide good mechanical properties with low shrinkage. However from the results obtained, only DGE-DHBP cured with MTHPA showed liquid crystalline phase during curing.

There are also some efforts to enhance the properties of liquid crystalline epoxy resin by incorporating a certain functional group into either the backbone of the polymer or through the branched of the polymer. For example, by adding the azomethine group to obtain higher thermal stability and mechanical properties of the cured polymer (Choi et al., 2000).

2.2.1 Liquid Crystalline Epoxy Resin Containing Azomethine Linkage

Although many research have been carried out regarding the liquid crystalline epoxy resin, only few studies about the azomethine liquid crystal epoxy resin have been reported so far.

Choi et. al., 2000, successfully synthesized liquid crystalline epoxy monomers with twin mesogenic azomethines connected by different alkylene spacers ($x = 6, 7, 8$ and 9). The monomers are characterized by using Fourier Transfer Infrared Spectroscopy (FT-IR), $^1\text{H-NMR}$ Spectroscopy, DSC and Polarized Microscope (POM).

From the results of FT-IR and NMR, it is deemed that the correct monomers had been synthesized and all monomers possesses nematic phase as observed by using POM. The melting and isotropization temperatures together with thermodynamic values are found to be decreased with the increase of x value in zig-zag fashion. This revealed the even-odd effect of the methylene spacers where monomers with even numbers of methylene units have a stronger chain interaction and a higher degree of order in their liquid crystalline phase than those with odd numbers.

However, for further studies regarding the curing process, only monomers with the lowest melting and isotropization temperature ($x = 9$) had been chosen. The monomers are cured with four different type of aromatic diamines namely, DDS,

DDE, 4,4'-diaminodiphenylmethane (DDM) and 1,4-phenylenediamine (PDA). Based on the results, DDE gives the lowest curing temperature. It means that it has the highest reactivity with the monomers compared with the others while DDS possess the lowest reactivity. DDM and PDA has an intermediate reactivity due to polar effect.

A stoichiometric mixture of epoxy monomer with $x = 9$ with DDS are then cured under various isothermal condition to investigate the curing behaviour. By using polarized microscope, it is proven that nematic liquid crystalline phase has occurred during the curing process.

In 2001, Ochi and Takashima from Kansai University, Japan has moved one step forward to synthesize another liquid crystalline epoxy resin with mesogenic group and study their bonding properties compared to the bisphenol-A type which is diglycidyl ether of bisphenol-A (DGEBA). The liquid crystalline epoxy resin synthesized were also from the diglycidyl ether type called diglycidyl ether of terephthalylidene-bis-(*p*-aminophenol) [DGETA].

As before, FT-IR and $^1\text{H-NMR}$ has been used to confirm the structure of DGETA. The uncured DGETA has shown two liquid crystalline phases during heating when observed with polarized microscope at temperature of 195°C and 205°C which refers to the smectic and nematic phase respectively. DDM is used as curing agent to cure both epoxy resin; DGEBA and DGETA. No liquid crystal phase

could be observed under the polarized microscope for the DGEBA/DDM system but for the DGETA/DDM system, a well-defined coloured pattern that refers to the smectic phase was observed.

From the bonding properties of the cured resin, it is deemed that the cured liquid crystalline epoxy resin shows higher bonding properties than the commercial bisphenol-A type epoxy resin. This is due to the large deformation of the resin along with the stress direction in cured liquid crystalline epoxy resin. In addition, it is also discovered that the shear strength of this resin could be improved by reducing the internal stress that occurred during curing process.

The study on the influences brought by substituting the alkylene with oxyethylene spacers to the mesomorphic behaviour of liquid crystalline-dimeric epoxy resin with imine group had been conducted by Ribera et. al., 2003. To study the effects, Ribera et. Al, 2003 had synthesized new dimeric liquid crystalline-epoxyimine monomers. They are Bis(2-[4-[(2,3-epoxypropoxy)phenyliminomethyliden]benzoyloxy]ethyl)ether (IBd), 1,2-Bis({4-[(2,3-epoxypropoxy)phenyliminomethyliden]benzoyloxy}ethoxy)ethane (IBt), Bis{2-[4-(2,3-epoxypropoxybenzoyliminomethylidene)phenoxy]ethyl}ether (IIAd) and 1,2-Bis(4-[(2,3-epoxypropoxybenzoyliminomethylidene]phenoxy}ethoxy)ethane (IIAt).

It is observed by using polarized microscope, IBd and IBt, has exhibit a smectic C and smectic A mesophase respectively during heating. In contrast, IIAd

and IIAt shows only nematic mesophase during cooling. The worst mesomorphic behaviour is observed during curing process of the monomers with 2,4-Diaminotoluene (DAT) and 4-aminoacetophenone azine (NA2). Only IBd monomer posses smectic C phase when cured with DAT and nematic phase when cured with NA2. The others shows no liquid crystalline phase during curing although pure monomers posses liquid crystalline properties. As conclusion, the substitution of alkylene spacers by oxyethylene spacers leads to worse mesomorphic characteristics.

Apart from the above reported research, there is still a lot of other research that deals with liquid crystalline epoxy resin. This includes the texture development, mechanical properties and the curing process to suits their final applications (Punchaipetch et al., 2001).

2.3 Curing of Liquid Crystalline Epoxy Resin

Curing is a reaction between the epoxy group with other functional group that has an active hydrogen molecules to give linear, branched or crosslinked products (Sandler and Karo, 1977). In the case of liquid crystalline epoxy resin, it plays an important role to determine as to whether the cured resin will posses liquid crystalline properties or not. The reaction is a very complex process since many reactive processes occur simultaneously (Rosu et al., 2004). The curing behaviour are greatly influenced by the substituents on the mesogenic group, mesogenic structure and bridging group between mesogenic group and epoxide functional