CHAPTER I

INTRODUCTION

1.1 The significance of adhesives

Majority of materials and equipment in our everyday use are assembled from many small parts by using many methods of joining such as welding, bolts and nuts, rivets, crimping, brazing, soldering, adhesive bonding, etc. Recently, adhesive bonding method has played an important role in a lot of assembly industries such as automative, electronic, aircraft, plastic and paper industries.

Adhesive is defined as a non metallic material that is capable of joining bodies together by surface adhesion and internal strength (adhesion and cohesion) without the structure of the bodies undergoing significant change. Adhesive is an essential bonding agent, conveniently and widely used.

1.2 The development of epoxy resin adhesives

Epoxy resins were first synthesized by P. Schlack in 1934 at the Berlin laboratory of I.G. Farben, when he let an alkylenepolyoxide react with amines. [1] The broad interest in epoxy adhesives originates from the extremely wide variety of chemical reactions and materials that can be used for the curing and the many different properties that result.

The development of epoxy adhesives was done by De Trey Freres in Switzerland in 1936.[2] Patents were later licensed to Ciba-Geigy, Switzerland. In the mean time, the De Voe and Raynolds Co. in the United States also developed epoxy resin adhesive for use in packaging.

The commercial significance of bisphenol A / epichlorohydrin-based epoxy resins was first recognized by P. Castan [3] in 1938. Castan, then working for Ciba-Geigy in Switzerland, also developed the important curing reactions for epoxy resins in 1943.

In the late 1940s, Shell Chemical Co. and Union Carbide Corp. began research on epoxy resins. Epoxy resins were used in England in 1944 as structural adhesives to manufacture Dehavilland Hornet twin engine fighter planes. The first structural adhesives were based on phenolic resins, and high curing temperatures were necessary. On the contrary, epoxy resins cure at room temperature, produce no volatile by products, and cause only a minimum of shrinking.

In the 1950s, Dow Chemial Co. and Reichhold Chemicals, Inc. entered the market. The peracetic acid epoxidation of olefins was developed by Union Carbide in the 1960s and multifunctional epoxy resins were introduced by Ciba-Geigy, Celanese, Shell, and Union Carbide in the mid 1960s. In the 1970s Ciba-Geigy introduced hydantoine-based epoxy resins, and Shell introduced hydrogenated bisphenol A-based materials in 1976.

Kuriyama and Okuno [4] of Sunstar Giken Kabushiki has improved crack resistance and toughness of epoxy resin composition for use as adhesive in electronic industry. He added silicone resin particles with epoxy resin. The silicone resin is organo-polysiloxanes having silanol groups which are a crosslinking reaction product.

Asai and Onishi [5] of Ibiden Co.,Ltd. has developed epoxy / amino powder resin adhesive for printed circuit board. The objective of their study is to produce the adhesive by filling amino resin fine powder to epoxy matrix in order to improve heat and chemical resistance property.

Ashida et al. [6] of Nissan Motor have developed new epoxy resin adhesive which has excellent adhesive properties such as impact resistance, tensile shear strength and T-peel strength as well as excellent semi-gelling property.

1.3 The chemical of epoxy adhesives

Epoxy resin adhesives were recognized as the adhesive featuring a versatile chemical functionality and a remarkably low shrinkage on curing. This led to obtain reliable adhesion joints with low internal stress, excellent cohesion, structural integrity, and outstanding adhesion to all kinds of substances. For example, bonds could be made to metals and glass without resorting to the application of pressure during the bonding process and without any problem in bonding irregular surfaces.

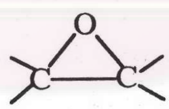
It was of technological significance that the manner in which these adhesives were used was reminiscent of well known metal soldering techniques. Therefore, the discovery of the bonding function of epoxy resins introduced a new concept in adhesives materials and inaugurated the modern approach to the technology of adhesive bonding.

Modern adhesive technology has led to the development of many types of epoxy-based adhesive systems. Adhesives have been formulated to meet various specifications and use criteria. The principal applications are in the field of structural metal bonding, particularly in the aerospace industry and electronic instrument or equipment, as well as in miscellaneous small part assembly of plastics and metals.

The variation of properties with formulation indicates the wide range of structural applications for which epoxy resin adhesives can be designed. For example, phenolic-modified epoxy resins produce the best high-temperature adhesives, whereas nylon-epoxy combinations produce adhesives with the highest joint strengths.

Epoxy resin based adhesives [7] can be produced in various forms : one and two part liquids, film, or solvent based. This wide variety of formulations are indicative of the advanced state of the art of epoxy adhesives.

The epoxy, epoxide, oxirane, or ethoxyline group [8] is a three-membered ring consisting of an oxygen atom attached to two connected carbon atoms :

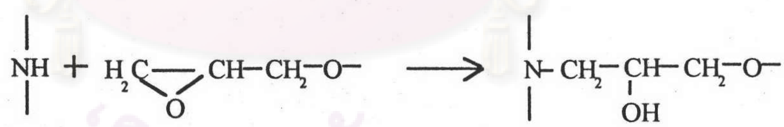


The term "epoxy resin" usually refers to an intermediate molecule which contains at least two reactive epoxy groups. Such resins are categorized as " thermosetting" since they are capable of "curing" to form crosslinked networks. The rings can be opened by either as catalysts for homopolymerization or as reactive hardeners.

Epoxy resins are thermo hardening compounds which contain one or more epoxy resins. There are a large number of compounds that can be classified under this category. They are oligomers that become polymers if they are joined in to a network by cross-linking agents.

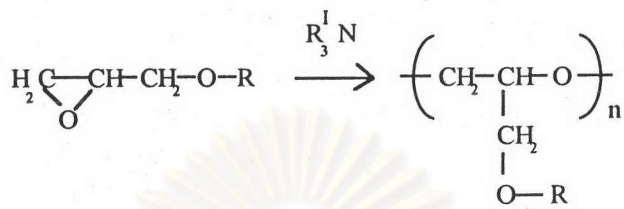
An epoxy is any monomer of oligomer containing at least two oxirane rings. Although ring opening homopolymerization to form a thermoset resin is readily accomplished, it is far more common for the epoxy to react with another monomeric compound or polymer having at least two protonic hydrogens.

The most common epoxies used in adhesives are derived from bisphenol A and epichlorohydrin ("bis-epi" resins) and are usually cured with reactive hardeners containing primary and/or secondary amine groups :



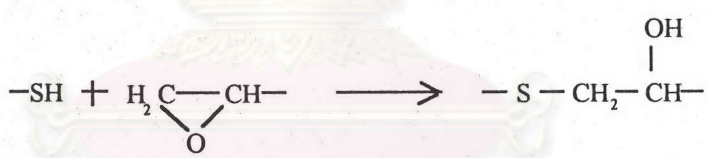
Aliphatic primary and secondary amines react with epoxy groups rapidly at room temperature, but aromatic amines require elevated temperature cures. Each hydrogen atom attached to nitrogen is capable of opening an epoxy ring. In order to crosslink a diepoxide, the primary amine required may be calculated by allowing one amino hydrogen atom per epoxy group.

Epoxy resins can also be homopolymerized by certain catalysts, particularly Lewis acids such as boron trifluoride complexes, acid anhydrides, or Lewis bases such as tertiary amines; forming polyethers :



Acid anhydrides also react with epoxides in the presence of hydroxyl groups to yield ester linkages. Anhydrides provide long pot-lives at room temperature, but require cure at elevated temperatures.

Mercaptans react with epoxy groups to form thioethers :

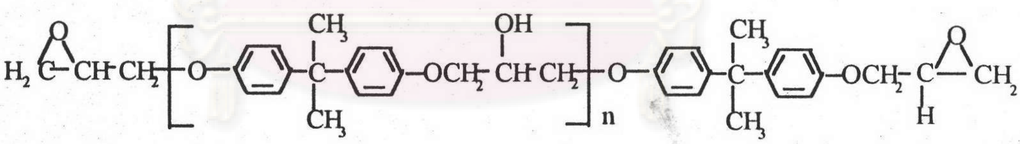


This reaction, accelerated by tertiary amines, makes feasible the incorporation of thiol-terminated polysulfides or polymercaptans as flexibilizing agents. Other compounds which enter into reaction with epoxide groups but are less commonly used include isocyanates, hydrazides, aminimides, axiridines, boron-containing compounds, etc.

The principal epoxies used for commercial adhesives are the reaction products of epichlorohydrin with dihydroxy compounds, particularly bisphenol

A, and include novolacs and aliphatic glycols. The simple diglycidyl ether [4] of bisphenol A (DGEBPA) contains some material with more than one bisphenol A residue and is therefore liquid at room temperature.

In addition to providing an excellent balance of properties, BPA is the most conveniently prepared difunctional phenol. The reaction of acetone with phenol can be controlled to give predominantly the bisphenol A. Commercial epoxy resins based on (BPA) are prepared by reactions of BPA with epichlorohydrin in the presence of a basic catalyst such as sodium hydroxide. In this manner a chlorohydrin intermediate is formed, which undergoes subsequent ring closure in the presence of the base to form the glycidyl ether. They can be described by the following general structural formula [5] :



This idealized formula shows two epoxide end groups. The commercial resins are essentially mixtures of polymers of which the average n varies from zero to apporximately 20. Resins of which the average n is 2 or more are solid at room temperature. However, liquid resins are of the greatest interest to adhesives formulators.

Each of the polymer molecules has n hydroxyl groups, which increase the rate of cure of the resins with amine hardeners. In addition, they result in increased adhesion of the cured epoxy to metals and other polar substrates. Consequently, the more viscous liquid epoxides are usually preferred to the less viscous members of the series for adhesives applications. The hydroxyl groups are also sites for reaction with anhydrides, but these curing agents are less common than amines in adhesives formulations.

1.4 Properties of epoxy adhesives

Epoxy resins have become established as versatile components for structural adhesives. The properties of adhesives depend as much on the curing and modifying agents, as on the epoxy component itself.

Properties of a polymer determine its possible applications. [6] To a large extent, the properties of a cross-linked epoxy polymer network are determined by the epoxy building blocks. Dissection of a epoxy resin reveals the following parts which provide these characteristics :-

- The structure contains C-C and C-O bonds that are thermally and chemically stable. This insures the excellent chemical resistance of compounds based on these structures.

- The polar O-H and C-O-C groups provide excellent adhesion of polymer networks formed with these compounds.
- The phenolic ether groups cause these oligomers to be UV-sensitive.
- The aliphatic sequences resulting from the glycidyl group provide the flexibility of the system.
- The aromatic rings provide stiffness and solvent resistance.
- Epoxies can be cured at ambient temperature allowing their use in on-site construction applications.
- High-temperature cured epoxy resins produce high-molecular-weight thermoset polymers with outstanding temperature and chemical resistance.
- Epoxy resins are normally high in tensile strength and rigid, making them most appropriate for rigid, rather than flexible substrates.
- They also possess outstanding electrical resistance properties, making them popular for electronic applications.
- Due to high viscosity of epoxy adhesives, they exhibit good gap filling capability.
- For this study, to improve the thermal conductive property of epoxy adhesive, the thermal conductive materials such as metal powder, silicon carbide, etc., are used as filler in epoxy adhesive.

1.5 Application of epoxy adhesives

Epoxies are the most widely used in adhesive applications because of their versatility, excellent adhesion, compatibility, ease of application, good electrical properties, and resistance to weathering.

The outstanding characteristic of epoxy resins as adhesives is that they will form strong bonds to almost all surfaces such as steel, aluminium, brass, copper, glass, wood, concrete, paper, cloth, and a number of thermosetting plastics and thermoplastics. It is usually necessary to formulate the resin with specific modifiers in order to obtain completely satisfactory results for the following application :-

Constuction

Furniture

Aircraft / aerospace

Film laminates

Automotive

Engine grout

Electronic assembly

Electrical encapsulation

and Miscellaneous product assembly such as paint brushes, stained glass windows, golf clubs, snow skis, railroad joints, tool handles, appliances, abrasives, battery cases

1.6 Epoxy adhesive in electronic assembly

Because the current economic situation of industries has faced high competition, many adhesive manufacturers have to produce high quality products to serve this demand by developing new product and improving outstanding property for each appropriate bonding application to each industry.

Epoxy adhesives have proven track records and a long history in many industries. Over the last two or three dacades epoxy adhesives have been in steadily increasing use in the electronic industry [9]. Their primary application areas are the interconnection of electrical conductors, the attachment of passive electronic components such as resistors and capacitors, and the attachment of encapsulated active electronic components, or bare silicon chips to substrates or packages.

Three major uses of adhesives in microelectronics are diebonding, bonding circuit elements to the substrate, and sealing the packages. In diebonding, a microdrop of adhesive as small as 0.003" in diameter is dispensed on to substrate in a precise location. The integrated circuit chip is placed accurately into the adhesive which is then heat cured. The diebonding adhesive should have high thermal conductivity to provide effective heat sinking.

The viscosity and surface tension must be high enough to hold the chip in place, and the adhesive must not be too thin and out of its proper location. The processing temperature of the adhesive is much lower than the temperatures required by eutectic bonding, which can degrade the chip properties. Special formulated epoxies are used for adhesive die attachment The adhesives must be capable of withstanding subsequent fabrication stresses, such as the 400^{o}C encountered in thermal compression lead bonding.

The next level of microelectronic adhesive bonding is adhering the IC package chip capacitors, and resistors to hybrid circuits. The same epoxies are used as those for bonding chips.

Probably the most demanding application of thermal conductive epoxy adhesive is the attachment of silicon chips to substrates, with high thermal conductivity being important properties in this regard. Heat dissipation is a major technological problem in the application of these chips because they have a fundamental maximum operating temperature. In addition, their reliability rapidly declines at increased operating temperatures. For these reasons the thermal conductivity of the epoxy adhesives is a parameter of major importance.

Because unmodified epoxy adhesives are excellent eletrical insulators, epoxies are usually poor thermal conductors. Therefore, the dissipation of heat through unmodified system is frequently not sufficient to insure efficient operation of electronic components on printed circuit board in any equipment.

Heat dissipation factor is a major variable of operating temperature which affects the reliability of electronic equipment. In applications where good heat dissipation will be required, thermal conductive fillers can be incorporated into the formulation to improve thermal conductive properties of epoxy adhesives.

The objectives of this study

1 To improve thermal conductivity property of epoxy adhesives used for chips attachment in electronic industry by the addition of thermal conductive materials.

2 To study the preparation of epoxy adhesives filled with thermal conductive materials.

3 To determine the thermal conductive value of prepared epoxy adhesives by using thermal conductivity analyzer measurement.

4 To analyse the thermal conductivity property of each prepared epoxy adhesive

The scope of this study

1 The experiment is the preparation of epoxy adhesives filled with good thermal conductive materials by varying :-

a) Type of fillers : -

- Aluminium metal powder
- Berylium oxide
- Berylium metal powder
- Copper metal powder
- Silicon carbide

b) Percentage of fillers in epoxy adhesives

2 The thermal conductivity of prepared composites are measured by the thermal conductivity analyzer.

3 The Lewis and Nielsen and the Ratcliffe models are used to explain the experimental results.