SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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PREPARATION, CHARACTERIZATION AND PROPERTIES OF EPOXY PARTICLES FILLED EPOXY COMPOSITES

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: **“Preparation, characterization and properties of epoxy particles filled epoxy composites**”. 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.

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LIST OF ABBREVIATIONS

Abbreviations	**Description**
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
BF_3	Boron Triflouride
$CaCO_3$	Calcium Carbonate
CTBN	Carboxyl-Terminated Butadiene-Acrylonitrile
DGEBA	Diglycidyl Ether of Bisphenol A
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric
ENR	Epoxidized Natural Rubber
EP	Epoxy particles
HTPB	Hydroxyl-Terminated Polybutadiene
Na_2CO_3	Sodium Carbonate
o/w	Oil-in-Water
OH	Hydroxyl Groups
PEEK	Polyether Ether Ketone
PES	Polyethersulphones
PSF	Polysulfone
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analyzer
w/o	Water-in-Oil

LIST OF SYMBOLS

Symbols	**Description**
a	Crack length
B	Specimen thickness
J	Impact energy
K_{ic}	Fracture Toughness
P_Q	Maximum Force
T_g	Glass transition temperature
T_5	Temperature when 5 % of weight is lost
T_{15}	Temperature when 15 % of weight is lost
T_O	Onset degradation temperature
T_{max}	Maximum degradation temperature
W	Specimen width

PENYEDIAAN, PENCIRIAN DAN SIFAT-SIFAT KOMPOSIT EPOKSI DIISIS PARTIKEL EPOKSI

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan partikel epoksi (EP) dan untuk menilai potensinya untuk menguatkan dan meningkatkan keliatan komposit epoksi. Tiga set partikel epoksi (EP) disediakan melalui teknik emulsi berasaskan air dan dicirikan dengan menggunakan mikroskoppenskanan elektron(SEM), penganalisis saiz partikel dan analisis keluasan permukaan Brunauer-Emmett-Teller (BET). Sampel kompositEP/epoksi disediakan dengan menggunakan 5 wt% EPyang dimasukkan ke dalam epoksi dan dimatangkan pada suhu bilik. Ujian mekanikal yang dilakukan ialah ujian hentaman Izod, ujian kekerasan dan ujian keliatan patah. Selain itu, permukaan patah komposit juga dianalisis dengan menggunakan SEM. Analisis terma dikaji dengan penggunaan kalorimeter pengimbasan pembezaan (DSC) dan analisis termogravimetri(TGA). PenambahanEP dalam epoksi didapati menyebabkan penurunan sifat mekanikal seperti minimum pengurangan 19% dalam kekuatan hentaman, minimum pengurangan 0.95% dalamkekerasan danminimum pengurangan 61% dalamkeliatan patah. Pengurangan sifat mekanikal adalah disebabkan oleh interaksi yang lemah antara EP dengan epoksi. PenambahanEP dalam epoksi juga menyebabkan penurunan suhu peralihan kaca (T_g) tetapi tiada banyak perbezaan dalam suhu penguraian terma.

PREPARATION, CHARACTERIZATION AND PROPERTIES OF EPOXY PARTICLES REINFORCED EPOXY COMPOSITES

ABSTRACT

The objective of this study was to fabricate epoxy particle (EP) and to assess its potential to reinforced and toughened epoxy composites. Three sets of EP were produced by water-based emulsion method and characterized byusingField Emission Scanning Electron Microcopy (FESEM) Analysis, Particle Size Analysis and Brunauer-Emmett-Teller (BET) Surface Area Analysis. The samples for EP filled epoxy composite were prepared by incorporation of 5 wt% of EP into theepoxy matrix and cured at room temperature. Testing which werecarried out to investigate the mechanical properties of epoxy composites are Izod impact test, hardness and fracture toughness test. In addition, scanning electron microscope is used to analysis the fracture surface of the composite after fracture toughness failure. Thermal analysis of the epoxy composites is studied using differential scanning calorimetry and thermogravimetric analyzer. It was found that the incorporation of EP in epoxy matrix cause the reduction of mechanical properties such as reduction of minimum 19% in impact strength, reduction of minimum 0.95% in hardness and reduction of minimum 61% in fracture toughness. The reduction of mechanical properties is due to the poor interaction between EP and the epoxy matrix. The addition of the EP in theepoxy matrix also result in the decrement of the glass transition temperature (T_g) but not much different in term of thermal decomposition temperature.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymer composites are widely used to replace traditional materials in aerospace, automotive, infrastructure and consumer applications. Polymer composites exhibit desirable mechanical properties, chemical properties, low cost and relatively easy fabrication (Subramanian, 2017). Plastic matrix can be divided into thermoplastics and thermoset. Thermoset matrix has received the attention and interest of scientist in the past decades due to theability to withstand higher load, high temperature and higher chemical resistance than thermoplastics matrix.

Epoxy is one of the thermoset matrices normally used on the composite system. The uniqueness properties of the epoxy resins such as low cure shrinkage, compatibility with a great number of materials, high mechanical properties, good adhesions and good electrical insulation make it as high-performance thermosetting polymers(Motahari et al., 2013). Therefore, it is normally used in the automotive and aerospace applications as well as electrical devices since it fulfills the basic requirements to be the matrices for most composite materials(Park et al., 2005). However, brittleness of epoxy resin is the most critical factor which limits most of its end-use applications(Astruc et al., 2009).

Epoxy resins are low molecular weight, oligomeric or polymeric compounds which consist of more than one epoxy group. They are liquids with high viscosity that undergo a cross-linking process and transform to insoluble and hard plastics(Natarajan and Anu, 2015). Curing agents (or hardeners) is used to cure epoxy either at high or low temperatures. Cured epoxy resin has high chemical and corrosion resistance, good mechanical properties as well as acceptable thermal stability.Due to its high cross-link density, they inherently brittle with low impact strength and low elongation at break(Kostrzewa, 2011).

The modification and improvement of the brittleness issue of epoxy systems can be done by adding the toughening agent.Mathew et al. (2014)and Xu et al. (2016)have found that the toughening agent, especially elastomer is the most commonly used in the epoxy system. The examples of elastomer used in the researcher work are carboxyl-terminatedbutadiene-acrylonitrile (CTBN), hydroxyl-terminated polybutadiene (HTPB) and natural rubber. However, the final modulus of elastomer-toughened epoxy resin are obviously decreased even the toughness of the epoxy system is improved tremendously(Johnsen et al., 2007).

Besides, thermoplastics and particulates fillersare also able to toughen epoxy materials. The main advantage of using thermoplastics as atoughening agent is no obviously decrease in the desirable properties such as modulus and yield strength can be seen. Augustine et al. (2014)showed that incorporation of polyether ether ketone (PEEK) with epoxy able to toughen the epoxy. On the other hand, various particulates such as small particles (< 0.25 microns), platelets, chopped fibers, hollow spheres or new materials such as carbon nano-tubes can be used to toughen the epoxy material. The volume fraction of fillers and particle characteristics influence the strength, modulus and toughness of the matrix (Fu et al., 2008). In a research work by Fellahi et al. (2001), it was found that the toughness of composite is increased about one-fold if 10 phr of kaolin is added into epoxy composite.

Particle size, particle shape and surface area of the particles can affect the mechanical properties of particulate filled composite. The composite strength increases with the decreasing of particle size due to thehigher total surface area for a given particle loading. In addition, the shapes of the particles that provide higher aspect ratio have more contact surface area with the matrix and thus enhance the mechanical properties. The utilization of hollow structure in theparticulatefiller is able to provide bigger surface area even with big particle size and it is believed that factor will be able to reinforce the composite.

Utilization of spherical hollow particles is an alternative way to improve the toughness of the epoxy matrices. Huang et al. (2009) and Zhao et al. (2008) also stated that hollow particles are commonly utilized as low-weight fillers for most materials owing to their specific structures, which are able to accommodate large objects and contribute to the ‘micro-package’ effect. Liang (2010) declared that the unique properties of hollow particles such as low density, low thermal conductivity coefficient, surface permeability, and good mechanical properties have lead the hollow spherical particles to be applied in various potential applications nowadays.

Many techniques are used to synthesize hollow particles. Templating method can be divided into several methods such as organic bead templating method, emulsion templating method and inorganic templating method(Fuji et al., 2013, Hou et al., 2010, Song et al., 2015).These templating methods are able to produce porous structure on the surface of the microspheres but only a few holes on their surfaces(Chen and Lu, 2012). Therefore, the water-based emulsion technique will be able to synthesize epoxy particles (EP) with many holes on their surfaces. Also, the EP fillers produced using this technique possess small particle sizes, low density, and high surface area(Low and Abu Bakar, 2011).

In this study, EP toughened epoxies are going to be prepared. Water-based emulsion technique is employed to synthesize EP. Brittleness issue of epoxy maybesolved by the incorporation of EP in the epoxy matrix. EP contains porous site which is capable of bonding with the epoxy matrix by theinterlocking mechanism. It is expected that bigger particle produced will give higher surface area of contact with thematrix. Therefore, there is potential for improvement of toughness of epoxy composite by adding of EP as particulate filler.

1.2 Problem Statement

Epoxy resin has raised much attention in recent years because it can possess desirable properties to meet the application requirement. However, brittleness properties of epoxy have become an issue during application. Therefore, the improvement of the toughness of epoxy matrices is required. The epoxy particles are utilized to reinforce the epoxy composite to enhance the toughness of epoxy matrices by contributes to the ‘micro-package’ effect.

In this research work, it is suggested to use rigid epoxy particles (EP) to toughen the epoxy composites. Usually, small particle size has big surface area. Yet, epoxy particles are able to provide big surface area even with big particle size through hollow structures. The epoxyparticles will form aninterlocking system with the epoxy matrix that leads to a better toughness and hardness. Since the epoxy particles are made from epoxy, it is expected that the adhesion between the filler with epoxy matrix will be good. Therefore, it can contribute to better properties of the composites.

Theepoxy particles can be produced using water-based emulsion method by mixing epoxy resin, calcium carbonate and polyamide hardener at high stirring speed. However, the preparation ofepoxy particles has its own problem. The problems usually related to the parameter and the material that was used during fabrication. Different parameter of processing and dosage of material used affect the particle size, particle shape and even the formation of holes in the particles. Hence, the method of production of theepoxy particle also needs to be studied.

The purpose of this study is to investigate the effect of different type of rigid epoxy particles on the properties of the epoxy particles filled epoxy composite and to produce abig particle with high surface area.

1.3 Research Objectives

The objectives of the study are summarized as follow:

i. To producethree series of epoxy particles with different amount of epoxy by using water-based emulsion method.
ii. To characterize the epoxy particles produced in term of size, morphology and surface area.
iii. To evaluate the physical, mechanical and thermal properties of epoxy particles filled epoxy composites.

1.4 Research scope

In this research, the epoxy particles were synthesis using water based emulsion method. The properties and the morphology of the epoxy particles were characterized using particle size analyzer, Brunauer-Emmett-Teller (BET) Surface Area Analyzer and Scanning Electron Microscope (SEM). Next, pure epoxy and epoxy particles filled epoxy composites were prepared using casting method. The mechanical properties such as fracture toughness, impact energy and hardness were studied. In addition, the fracture surfaces of the epoxy composites were observed using Scanning Electron Microscope (SEM). The thermal properties of the pure epoxy and epoxy particles filled epoxy composites were investigated using Thermogravimetric Analysis (TGA) and Differential scanning calorimetry (DSC).

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Composites

A composite material consists of continuous phase which is matrix and reinforcing phase which refer fiber or particle. Polymer composites are generally defined by unusually high strength, high stiffness, or modulus of elasticity characteristics compared to other composite materials. The main advantage of polymer compositesis that the polymer composites exhibit desirable physical and chemical properties include high strength to weight ratio, temperature and chemical resistance, dimensional stability and relatively easy processing(Hollaway, 2001).

The matrix, the reinforcement and the interphase determine the properties of the polymer composites.When designing polymer composites, not only the types of matrix and the reinforcement need to consider, but their relative proportions, nature of the interphase and the geometry of the reinforcement also need to take in consideration. The mechanical behavior of the composite is governed by a synergy between the reinforcement phase and the matrix phase(Friedrich and Almajid, 2013). The synergy of the reinforcement and the matrix can strengthen the composite and toughen it. Thus, the compatibility between reinforcement and matrix phase is crucial to producing high mechanical properties of the polymer composites.

The demand of polymer composites in the market is high to replace traditional materials in aerospace, automotive, infrastructure, and consumer applications. This is proven by the fabrication of the latest Boeing-787 airplane with up to 50% composites by weight (Abliz et al., 2013) and increasing of the using of polymer composites in structural load bearing applications by the construction industry via replacement of steel in reinforced concrete(Zaman et al., 2013). The usage of polymer composites enhances the properties of the appliance and prolongsits cycle time, therefore improvement study of polymer compositesis necessary to encourage of low cost material with better properties.

2.2 Matrix Phase

The matrix plays several roles in the overall composite characteristics. It helps bonds the reinforcement together. It protects the reinforcement against theadverse environment. It acts as amedium to transfer the load carried by composite to the reinforcement. The adhesion between thematrix and the reinforcement must be good so that the load able to transfer to the reinforcement via matrix(Hollaway, 2001). Basically, the matrix of the polymer composites can be classified into two main groups which are thermoset and thermoplastics(Holbery and Houston, 2006).

Thermoplastic material is a material that can become pliable or moldable above a specific temperature and solidifies upon cooling(Biron, 2007). They have many physical properties that similar with rubber such as softness, flexibility and resilience. However, thermoplastics achieve their properties by a physical process (solidification) compared to the chemical process (cross-linking) in rubber. They can be processed using common method such as injection molding, extrusion and thermoforming (Kutz, 2016). Generally, thermoplastics well suited to commodity applications due to the combination of high strength, light weight and low processing costs. Yet, some thermoplastics are used in high performance applications such as polyethersulphones (PES) andpolyetheretherketones (PEEK) (Cogswell, 2013). However, thermoset material is dominantly used as amatrixin polymer compositesdue to the extraordinary properties such as strength, chemical resistance and thermal resistance.

Thermosetting plastics are materials that unable to be remolded after the materials cured. Curing is induced by mixing with a catalyst or crosslinking agent often under atmospheric temperature, or by the action of suitable radiation or heat often under high pressure. Before hardening, thermosets behave like thermoplastics which are independent macromolecules. After hardening, they have a three-dimensional structure due to the crosslinking produced. Thermosets have a tight chemical bond make them don’t soften under heat and will char at high temperatures (Lokensgard, 2016). Normally, thermoset plastic products are produced by heating powder or liquid within a mold and allow the material to cure into its hardened form. Thermosets are tough and durable with high temperature performance. Thus, they can be found in a wide range of applications including fiber-reinforced composites, dental fillings, spectacle lenses, electronic chips and aerospace field.

In the uncured state thermosets are mixtures of small reactive molecules, often monomers. Once cure reaction begins, the chains growth and branching occur, the increase in molecular weight of the chains causing the increase in viscosity. Eventually, a network of infinite molecular weight formed by linked several chains together (International and Lampman, 2003). Thermosets generally possess good chemical resistance, dimensional stability, electrical properties and thermal stability. However, thermosets are brittle due to high crosslink density. Enhancement of toughness of thermoset is required to meet the desired properties. Examples of common thermoset plastic are epoxy, polyester and polyurethane.

Epoxy resins are of interest to structural engineers due to their combination of excellent properties (chemical resistance, adhesion, electrical and thermal properties) and their low shrinkage during curing. Reinforced epoxy structures can be used at high temperature as high as 260ºC and provide high strength to weight ratio. Epoxy are used in adhesives, building materials, coatings, electronics and civil engineering applications (International and Lampman, 2003). Considering the excellent properties of epoxy and resulting composites, epoxy was selected as the matrix for this study.

2.2.1 Epoxy Resin

Epoxy resins contain at least two cyclic three-membered-ring structures containing oxygen, called epoxy groups, oxirane or epoxide groups as shown in Figure 2.1, in their molecules (Kanerva et al., 2013). The term epoxy resin is applied to both prepolymer and the cured resin. There isvarious type of epoxy resin such as diglycidyl ether of bisphenol A, epoxy novalacs, cycloaliphatic resins and bisphenol F resins. Theuncured epoxy resins have only poor mechanical, chemical and heat resistance properties, but good properties can be obtained after theepoxy is cured. The uncured resins can be crosslinked by a variety of curing agents or hardeners to form cured plastics with insoluble three dimensional structures. The curing process of the epoxy is anexothermic process and result in thermal degradation if the process is not control.Excellent properties of epoxy such as high strength, high electrical insulation, high adhesion to thesubstrate, low toxicity and low shrinkage make it become a dominant matrix material that used in the development of advanced composite materials. However, its widespread use in many applications is limited because of inherent brittleness and low fracture toughness.

Figure 2.1: Oxirane group.

The most common type of epoxy resin is the diglycidyl ether of bisphenol A (DGEBA). Its physical strength after curing, fluidity and cost advantage make it become most important epoxy resin in industry. DGEBA is produced from the condensation of excess epichlorohydrin and bisphenol A with a stoichiometric amount of sodium hydroxide at about 65ºC as shown in Figure 2.2.

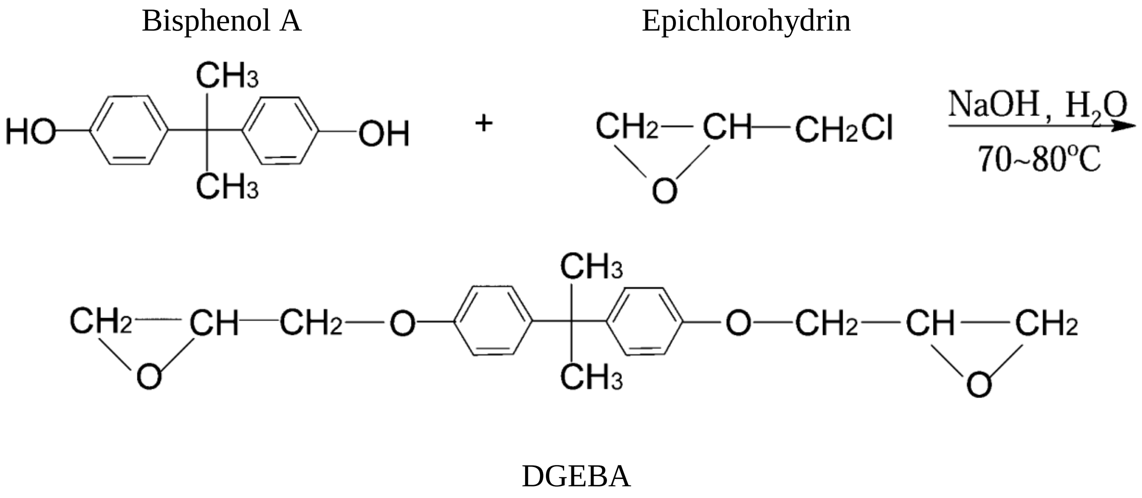

Figure 2.2:Reaction of Epichlorohydrin and Bisphenol A to produce Diglycidyl Ether of Bisphenol A (DGEBA)(Ellis, 2012).

2.2.2 Epoxy Resin Curative

Optimum performance properties of an epoxy are achieved by cross-linking of epoxy resin with a curing agent or hardener to form a three-dimensional infusible network. A variety of substances can be used as hardener;therefore, the choice of the hardener is depending on the application, the handling characteristics such as pot life, viscosity, cost and gel time and the use of properties such as thermal, chemical and mechanical(Thomas and Sinturel, 2014). Aliphatic amine systems have short gelation and cure time and can be cured at room temperature, but they have short pot lives and tend to give high exothermic temperature rises. Aromatic-amine-systems have greater heat resistance, but they are less reactive therefore require a sufficiently high temperature tocure. Acid anhydride hardeners require high temperature and along time tocure since it is the least reactive. However, exotherms are low and curing shrinkage is small. Curing agents are either catalytic or co-reactive(Unnikrishnan and Thachil, 2006).

Catalytic curing agents function as initiators for epoxy resin homopolymerization.Catalytic cures are initiated by Lewis acids and bases such as boron trifluoride (BF_3) and tertiary amines, respectively. The reaction involves two stages which are (i) the difference in polarity cause the opening of theepoxy ring to form ionic structure and (ii) the ion formed reacts with other epoxy ring and result in propagation of epoxy ring opening occurs (Augustsson, 2004). Figure 2.3 shows a general mechanism of epoxide rearrangement catalyzed by BF_3.The advantages of catalytic curing agents are long pots lives and high temperature resistance capacity. The disadvantages are long cure cycles and required high temperature tocure. Normally, the materials are used for electrical encapsulation purposes and adhesives(Thomas et al., 2014).

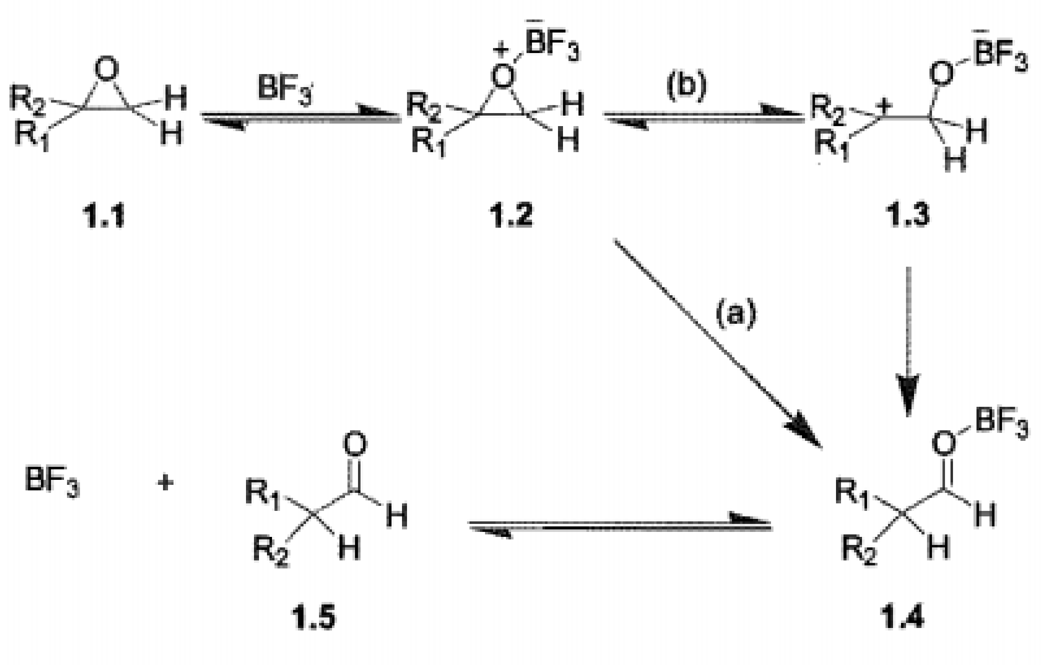

Figure 2.3: Rearrangement of epoxide with BF_3.

Co-reactive cure occurs when co-reactive curing agents incorporated within the macromolecular structure then promote crosslinking catalytically(Pilato and Michno, 2013). The co-reactants can be either basic or acidic curing agents. Polyaminoamides, primary and secondary amines are in thecategory of basic curing agents whereas acidic curing agents involve polymeric thiols, polyphenols and some extent of anhydrides. An example of co-reactive cure is depicted in Figure 2.4via the reaction of epoxy with aprimary amine. The polyamine is the most widely used curing agent in epoxy resin chemistry(Thomas and Sinturel, 2014) and therefore it will be used in this research as a comonomer in the epoxy polymerization process.

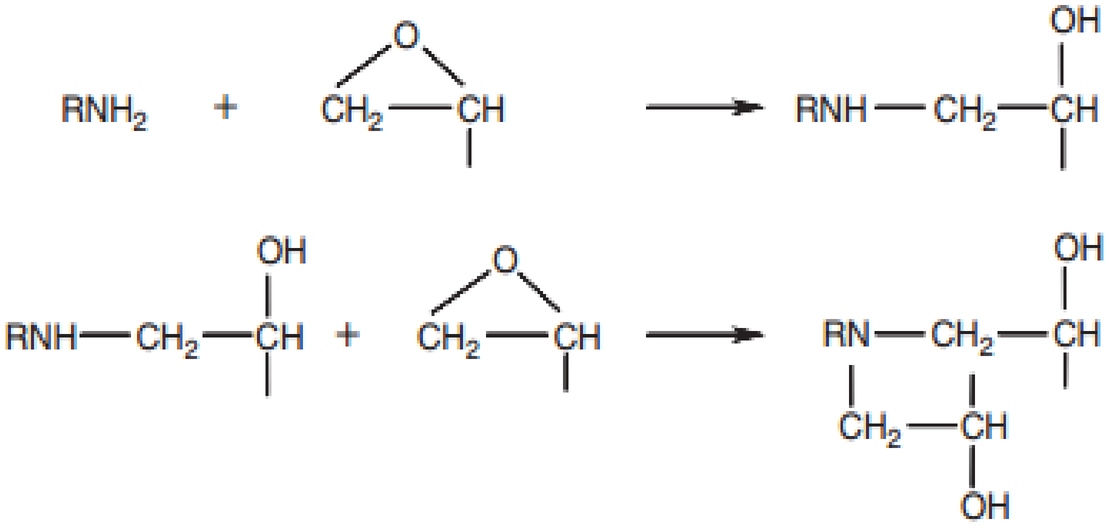

Figure 2.4:Reaction between epoxy and primary amine(Thomas and Sinturel, 2014).

2.2.2.1 Polyamine

Polyamine curing agent is most widely used curing agent in theepoxy industry. Approximately 50% of all the epoxy curing agents used in the United State in the year 2001 belong to primary amines, secondary amines and their adducts(Mark, 2004). Amines can further divide into aliphatic amine with straight carbon chain, aromatic amine with the amino group bond to benzene ring and cycloaliphatic amine with ring-shape carbon chain.

The functionality of an amine determinesby the number of amine hydrogen atoms present on the molecules (Cazes, 2005). A primary amine group with two hydrogens bond to it can react with two epoxy groups, whereas a secondary amine with one hydrogen will only react with one epoxy group. Tertiary amine group with no active hydrogen will not react readily with the epoxy group, but has thecatalytic effectof accelerating epoxy reactions.

Augustsson (2004) reported that primary amines react much faster than secondary amines. The reaction of an epoxy group with a primary amine initially reduce the amine to a secondary amine and yield a secondary hydroxyl (-OH) groups. The secondary amine reacts with another epoxy group to give a tertiary amine and two secondary hydroxyl groups. The reaction is complete as the tertiary amine is unreactive.

Curing agents used in epoxy resin contribute to the properties of the crosslinked products. Therefore, the decision of thetype of curing agent needs to be considered carefully since the curing agents influence the curing rate, morphology, crosslink density and eventually affect the fracture toughness of modified epoxy resins.

2.2.2.2 Polyamide

Besides polyamine, polyamide curing agent is another widely used curing agent for epoxy. Polyamide is formed by the condensation reaction between dimer acid and polyamine, and contains reactive primary and secondary amines in its molecules. Polyamide amine reacts with epoxy resin to cure at or below normal temperature with moderate heat generation.

Polyamides are versatile curing agents. The polyamides react with epoxide group through the amine functionality in the polyamide backbone. The unreacted amine NH groups in the backbone provide good intercoating adhesion and the fatty acid provides good moisture resistance and mechanical properties(Augustsson, 2004). Polyamide has higher molecular weight compared to polyamine. They are inexpensive, less toxic to handle and mainly used in coating and adhesion formulations.

The disadvantages of polyamide are it cures slowly that is has a long pot life and darker colour than polyamine-cured epoxy. Polyamide-cured epoxy loss structural strength rapidly with the increasing temperature, this limit their use to applications not subjected to temperatures above 65ºC(Mark, 2004).

2.3 Modification of Epoxy Composite

Epoxies exhibit outstanding properties such as high strength, good elevated temperature resistance and low creep due to high crosslink density. The drawbacks of epoxies are poor crack resistance and low toughness and brittle nature at room temperature (Hsieh et al., 2010). This limits their application as structural materials since they have a poor resistance to the initiation and growth of thecrack. Therefore, epoxy materials are to be toughened for many end-use applications. Toughness refers to measure of the resistance of the material to failure without compromise in their enviable thermomechanical properties. There are a few toughening ways for epoxy such as rubber toughened epoxy, thermoplastic toughened epoxy and particulates filled epoxy.

2.3.1 Rubber Toughened Epoxy

Many researcher works have been established that the incorporation of a second phase of a dispersed rubber can improve the toughness of epoxy materials. Carboxyl-terminated butadiene-acrylonitrile (CTBN), hydroxyl-terminated polybutadiene (HTPB) and natural rubber appear to be successful approaches for enhancement toughness of epoxy materials among numerous research of incorporation of liquid rubbers.

Carboxyl-terminated butadiene acrylonitrile liquid rubber (CTNB) has been widely used to enhance the toughness of the epoxy materials. Thomas et al. (2004) studied the toughened of epoxy with CTNB using an anhydride hardener. The incorporation about 15 wt% of the elastomer showed anincrement of fracture energy increased from 0.3 to 3.1 $MPam^{1/2}$ by compared to virgin epoxy. The main sources of energy dissipation and toughness enhancement of the composite are theshearyieldings of the matrix and bridging of particles. Akbari et al. (2013) investigated mixing of epoxy with CTBN by using dicyandiamide as the curing agent. The results found that the maximum toughness was achieved at 15 phr CTNB and a two-phase morphology of the blends where the rubber particles were dispersed in the epoxy matrix was observed by SEM.Xu et al. (2016) introduced benzoyl peroxide to initiate the cross-linking reaction of CTBN so that the compatibilization and interfacial adhesion between epoxy and CTNB improved. The impact strength of pre-crosslinked CTNB epoxy blend enhanced significantly than those of non-crosslinked CTNB/epoxy blends because of improvement of interfacial strength caused by the localized interpenetrating network.

Besides CTNB, hydroxyl-terminated polybutadiene (HTPB) liquid rubber also employed to modify epoxy materials. Ozturk et al. (2001)studied the modification of epoxy by HTPB with the addition of silane coupling agent to enhance the interaction between HTPB and the epoxy matrix. From the result of Charpy impact tests, the specimens with 2% silane coupling agent and 1% HTPB resulted in 44% increment of impact strength. This is due to the rubber particles and improved interaction able to absorb more loaded energy leading to higher toughness of epoxy system. Zhou and Cai (2012) employed(HTPB) liquid rubber to modify epoxy resin using 2,4,6-tri (dimethylaminomethyl) phenol as a catalyst, and methyl hexahydrophthalic anhydride as a curing agent. The impact strength of HTPB-modified epoxy was obviously superior to pure epoxy, where the 10 phr of HTPB into epoxy showed the best improvement.

Natural rubber also has raised the concern from researchers to toughened the epoxy materials.Mathew et al. (2014) investigated epoxidized natural rubber (ENR) toughened epoxy by using nadic methyl anhydride as a hardener and N,N-dimethylbenzyl amine as an accelerator. 10 wt % ENR modified epoxy blends had the maximum impact strength and fracture toughness. Rubber particles toughened the epoxy via enhancement of stress transfer through the deformation of rubber particles. Tan et al. (2013) also studied themodification of epoxy with liquid ENR. His research also proved that ENR could improve thetoughness of epoxy resin by adding the rubbery phase. The composite with 3 wt% of LENR possessed the highest mechanical properties for both flexural and impact properties.

Incorporation of rubber in theepoxy matrix has proven that it is able to toughen epoxy composite.However, the presence of the rubbery phase typically increases the viscosity of the epoxy monomer mixture and reduces the modulus of the cured epoxy polymer.

2.3.2 Thermoplastic Toughened Epoxy

Many types of research on the thermoplastics toughening of epoxy resin have been carried out in the decade using a variety of different thermoplastic types.The main benefit of using thermoplastics as atoughening agent for epoxy resin is no significant decrease in the desirable properties such as modulus and yield strength, where this happened when rubbers used as toughening agents (Hodgkin et al., 1998).

Park and Kim (2001)had studied the blending of thermoplastic polysulfone (PSF) with epoxy initiated by 1wt%N-benzylpyraziniumhexafluoroantimonateasacationiclatentcatalyst. The fracture toughness of the PSF/epoxy blend system increased with the increasing of PSF in the blends. The increment of fracture toughness due to the decrease of crosslink density during the reaction between PSF and epoxy. Rajasekaran et al. (2008) also studied the intercrosslinked network of PSF-bismaleimide modified epoxy matrix system with diaminodiphenylmethane as curing agent. From his research, high energy absorption and chain entanglement between epoxy and PSF increased the impact strength in the blending of PSF and epoxy.

Besides PSF, polyether ether ketone (PEEK) also used to toughen epoxy materials. In research of Francis et al. (2005), the blending of DGEBA epoxy resin with hydroxyl terminated poly(ether ether ketone) oligomers based on methyl hydroquinone was studied using melt mixing. The blending of PEEK success improved the fracture toughness of epoxy due to the local plastic deformation of the matrix, crack pinning and crack path deflection. The thermal stability of amine cured epoxy resin was not affected by the blending of hydroxyl terminated poly (ether ether ketone) oligomers based on methyl hydroquinone into the epoxy resin. In Augustine et al. (2014) research, they proved that blending of hydroxyl terminated poly ether ether ketone epoxy with epoxy amino–novolac–phthalonitrile resinable to reduce the brittleness of epoxy and improved their lap shear strength. Toughening of epoxy-amino novolac phthalonitrile networks occurred through phase separation of PEEK segments in cured matrix.

2.3.3 Particulate-Filled Epoxy

Many research on the effects of particulate fillers on the mechanical properties of epoxy resin have been carried out. The volume fraction of fillers, particle characteristics and their influence on strength, modulus and toughness of the matrix has been extensively studied. The toughness, strength and modulus of the filled material had improved through the variation of some of these parameters (Fu et al., 2008). The particulates can be very small particles (<0.25 microns), platelets, chopped fibers, hollow spheres or new materials such as carbon nano-tubes. The particulates provide desirable material properties whereas the matrix acts as abinding medium for structural applications.

Kaolin is one of the examples of particles used to toughen the epoxy composites. Fellahi et al. (2001) used kaolin as atoughening agent to modify epoxy materials. The curing parameters affected by the addition of kaolin in neat epoxy such as decrease in cure times and the cure temperature. The kaolin and the epoxy react chemically result in lowering of glass transition temperature(T_g) and the decrease of crosslink density. The toughness of the kaolin filled epoxy reached a maximum at 10 phr kaolin content. From the SEM analysis, it is shown that the prevailing toughening mechanism for the epoxy resin under consideration is through localized plastic shear yielding induced by the presence of kaolin particles associated with crack pinning.

Wetzel et al. (2003) introduced calcium silicate into anepoxy polymer matrix for reinforcement purpose. The influenced of calcium silicate particles on the impact energy and the flexural energy were studied. The optimum amount of 2 vol % of calcium silicate into the composite matrix are able to push flexural modulus to even higher levels and further increase the wear resistance. The impact energy of calcium silicate reinforced epoxy higher than theneat matrix. The calcium silicate activates energy dissipating mechanisms such as particle pull-out, matrix shear yielding and crack front pinning.

Pham et al. (2017) investigated the approach of toughening epoxy with nano-silica. Nano-silica was fabricated using a thermal treatment method from rice husk with a particle size distribution in therange of 40-80 nm. From the mechanical test result, the addition of 0.07 phr of rice husk based nano-silica enhanced the fracture toughness of the neat epoxy by 16.3% from 0.61 to 0.71 MPa $m^{1/2}$. In addition, the T_g of 0.07 phr nano-silica dispersion with epoxy shifted to ahigher temperature from 140 to 147ºC compared to neat epoxy resin. The dispersion of nano-silica particles throughout the epoxy prevented and altered the path of crack growth along with a change in the fracture surface morphology of cured epoxy proved by SEM.

Recently, hollow particles have attracted the attention from the scientists to be potential particulate filler in polymers due to their inner void. However, limited research regard hollow particles toughened epoxy materials. Therefore, hollow particles are chosen to toughen the epoxy matrix in this study due to its possibility to toughen the epoxy matrix by theinterlocking mechanism.

2.4 Effect of Particle Size and Particle Shape of Particles

The mechanical properties of particulate filled composite are determined mainly by their particle characteristics such as particle size, particle shape and surface area.

Particle size is an important property on the effect on particulates filled composite. The composite strength usually increases with the decreasing particle size. This is because smaller particle size provides ahigher total surface area for a given particle loading. The increment of the strength with the increment of thesurface area of the filler particles indicates that smaller particles have more efficient stress transfer mechanism (Fu et al., 2008). Thomas and Zaikov (2008) stated that the impact strength usually decreases with decreasing particle size. However, the particle size solely is not enough to characterize of any filler. The particle size distribution is also important to the properties of the composite. Large particles size particulates easily debond from the matrix during loading whereas the tendency of the particulates increases with the decreasing of particle size. Insufficient homogeneity, rigidity and low impact strength may cause by extensive aggregation. Under dynamic loading conditions, aggregated filler particles act as crack initiation sites (Pukánsky, 2000).

Particle shape of the particulates used in polymer affect the composite properties such as stiffness, tensile and impact strength and the surface smoothness of a component (Rothon, 2002). The typical shape of the particulates is likely to be found as shown in Figure 2.5. The genesis of the particles, particles chemistry, crystal structure and the process particles have undergone determine particles shape (Rothon, 2003). Parakhonskiy et al. (2015) reported that non-spherical particles have a lower uptake than spherical particles attributed to a larger curvature radius and lower aspect ratio. Shapes of particles that provide high aspect ratio are preferable since it has more surface area to contact with the matrix.

The specific surface area of particulates affects the composite properties. The surface area of adsorption of the particulates on the polymer matrix increase when the size of particulates decrease and the aspect ratio of particulates increase. Matrix and particulates interaction influences mechanical properties of such as tensile strength and impact resistance (Thomas and Zaikov, 2008). The large specific surface area of particulates lead to thestrong interaction of the polymer with this surface and result in stiff and brittle composite. However, stiffness and fracture resistance usually stay within theacceptable limit, therefore sufficient large specific surface area of particulates is required to obtain strong interaction with polymer yet maintain stiffness.

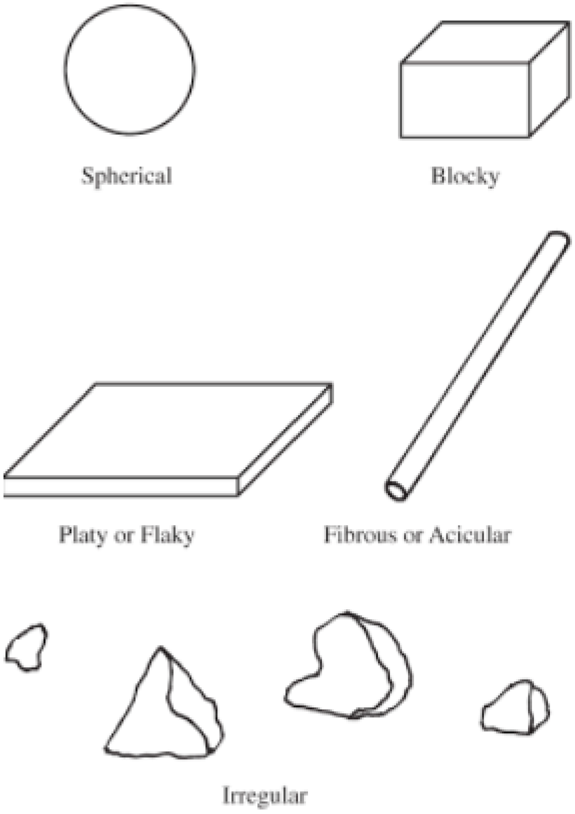

Figure 2.5: Thetypical shape of the fillers(Rothon, 2002).

Based on theory, smaller size particle will showbigger surface area. The introduction of epoxy particles into theepoxy matrix in this study is to provide the option of bigger surface area with bigger particle through the hollow structures. Parakhonskiy et al. (2015) study shows that porous $CaCO_3$ with high surface area to volume ratio able to improve their uptake by thecell. This inspired that biggerepoxy particles may reinforce the epoxy matrix effectively as compared to small particle size.

2.5Introduction of Hollow Particles

Hollow particle is a kind of powder contained interior hollow structure. Many research studies have been devoted to the development of preparing micro/nano-sized hollow particles. The uniqueness properties of hollow particles such as low density, high specific area, surface permeability, low thermal conductivity coefficient and good mechanical properties have attracted tremendous interest in research work (Liang and Li, 2007).Huang et al. (2009) and Zhao et al. (2008)also stated that hollow particles are commonly utilized as low-weight fillers and catalysts for most materials owing to their specific structures, which can accommodate large objects and contribute to the 'micro-package' effect.

Hollow particles can be used in various field by filling it hole with different materials based on the end use. Hollow particles have the potential applications in drug delivery, confined reaction vessels, coating, absorptive filters and as filler to reinforce materials (Low and Abu Bakar, 2011). For instance, calcium carbonate nano-sized hollow spheres were used to develop enteric drug delivery system in the form of tablets. Colonic drug is encapsulated by calcium carbonate and pass through stomach and small intestine and then released at the colon site (Render et al., 2016). Hollow silica is used as optically transparent and thermally insulating polymer additive where the polyethersulfone (PES)/hollow silica composite film shown a lower thermal conductivity (0.03 ± 0.005 W m·K−1) than pure polymer films (Ernawati et al., 2016).

A general way of preparation of hollow particle is to deposit desired material on the surface of templates. The templates used can be organic spheres, inorganic particles or metal crystals. The templates act as sacrifice material which allows the desired material to coat the surface on it, once the desired material has formed the shape, the templates are removed to form hollow particles(Hamada et al., 2017).The mechanism of the templateis as shown in Figure 2.6. Templating method can be divided into several methods such as organic bead templating method, emulsion templating method and so on.