THE EFFECT OF PARTICLE SIZE ON THE VISCOSITY AND MECHANICAL PROPERTIES OF SILICA FILLED EPOXY COMPOSITES

by

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In the name of Allah, most gracious, most merciful

"And say: Work (righteousness): Soon will Allah observe your work, and his messenger and the believers"

All praise and glory to Allah the almighty who alone made this small objective to be accomplished. I feel honored and privileged to glorify his name in the sincerest way through this small accomplishment and ask him to accept my efforts. Peace is upon the Prophet, his companions and all who followed him until the Day of Judgment.

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ABSTRAK

Satu model berdasarkan teori telah dikaji keatas kesan pecahan isipadu terhadap kelikatan dalam komposit epoksi terisi silika. Model ini telah dibandingkan dengan data eksperimen. Keputusan eksperimen adalah berdekatan dengan keputusan teori. Tidak ada korelasi diantara saiz partikel silika dengan kelikatan komposit epoksi; ini kemungkinan disebabkan julat lebar dalam saiz partikel kesan dari pemecahan pengumpalan partikel ke partikel yang lebih kecil.

Keputusan kelikatan untuk silika terawat adalah sama dengan silika tidak terawat, ini disebabkan rawatan tersebut tidak memperbaiki kawasan permukaan pengisi akibat julat partikel yang lebar. Kajian terhadap sifat-sifat mekanikal seperti kekuatan dan modulus kelenturan disertakan keputusan penskanan electron mikroskopi telah dilakukan. Epoksi tulen telah mempamerkan kekuatan kelenturan yang tertinggi dibandingkan dengan komposit epoksi terisi dengan 5 dan 10 % isipadu, ini adalah kerana keronggaan telah mempengaruhi kekekalan sampel bagi saiz partikel yang berbeza. Komposit epoksi terisi silika pada 5 % isipadu bagi saiz partikel 75µm mempamerkan modulus kelenturan yang lebih tinggi berbanding komposit epoksi tersisi 10 % isipadu kerana ia mempunyai keronggaan yang lebih.

Keputusan modulus kelenturan bagi komposit epoksi terisi dengan 75µm meningkat dengan pemecahan isipadu, ini adalah kerana taburan saiz partikel untuk 75µm adalah lebih sempit dibandingkan dengan partikel 150 dan 300µm. Kelikatan adalah bergantung kepada pemecahan isipadu. Kelikatan meningkat dengan pemecahan isipadu, kerana korelasi yang tinggi, iaitu 0.774. Kelikatan menurun dengan peningkatan kelajuan, ini telah menunjukkan bahawa semua komposit epoksi adalah besifat sifat *"non-Newtonian"*.

ABSTRACT

A theory-based model on the effect of volume fraction to the viscosity of silica filled epoxy composites was investigated. This model was used to compare to the experimental data. The experimental results were closed to the theoretical results. There were no correlation between different particles sizes for 75, 150, and 300μm of silica with viscosity of epoxy composites; this may be due to the wider range of particle sizes resulted from particle agglomeration breaks up into small particle.

The viscosity results for treated silica are similar with untreated silica, this maybe because the treatment has not improved the surface area of the filler due to the wider range of particles. Study on the mechanical properties such as flexural strength and modulus with scanning electron microscopy results were done. The pure epoxy exhibited the highest flexural strength than epoxy composites filled at 5 and 10 vol. %, this is because the porosity influences on the durability of samples for different particle sizes. Silica filled epoxy composite at 5 vol.% for particle size of 75μm exhibited higher flexural strength than the epoxy composite filled at 10 vol.% because the later had more porosity.

Flexural modulus results for epoxy composites filled with 75μm increased with the volume fraction, this is because the particle size distribution of 75μm is a bit narrower than 150 and 300μm particles. Viscosity is dependent on the volume fraction. The viscosity increased with the volume fraction, because of the relatively high correlation, 0.774. Viscosity decreased with the increasing of the speed, this indicated that all the epoxy composites behaved non-Newtonian behavior.

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LIST OF SYMBOLS, ABBREVIATIONS OR NOMENCLATURE

UTM	Universal testing machine
SEM	Scanning electron microscope
ASTM	American Scoiety for testing and materials
µm	Micron meter
Pa.s	Pascal times second
P	Poise
V	Volume
%	Percent
MPa	Megapascal
Kg	Kilogram
cm	Centimeter
mm	Millimeter
SiO_2	Silicon dioxide
Tg	Glass transition temperature

°c	Degree Celsius
N	Nitrogen
H	Hydrogen
VOC	Volatile organic compound
rpm	Revolution per minute

CHAPTER 1

INTRODUCTION

1.1 Background

The applications of epoxy resin are versatile, these includes: automotive, aerospace and electronics applications (Mimura et al., 2002). These advanced applications demand outstanding material properties of the epoxy resins that are predetermined by the chemical structure of the resin and hardener, as well as by the network achieved after curing (Kumar et al., 2006). Industrial applications require a complex property profile of the cured epoxy resin. For that reason, almost all resins are modified with various fillers and additives to improve the process ability and the mechanical, thermal and electrical properties in the cured state (Mirmohseni et al., 2010). Epoxies are commonly modified by the inclusion of inorganic –particulate fillers silica, alumina, mica, or talc. Because of their high specific weight, the fillers tend to sediment in the resin. In order to prevent this effect, the fillers are usually surface modified (e.g. coated by functional silanes). Due to the functional groups of the modifier, the inorganic particle may be incorporated into the organic network of the cured resin (Nesterov et al., 1999).

Fillers are also added to epoxy resins not only to reduce the price, but to improve some mechanical, electrical properties, resin stiffness, wear resistance, and to reduce the coefficient of thermal expansion (Topcu et al., 2003).

Many additives have been developed in order to modify properties of inorganic fillers filled polymer composites (Ahmad et al., 2008). Among these additives, coupling agents have gained more attention because of their special structures, which have two different functional groups, one that is attracted to the resin and the other that is attracted to the surface of the filler (Mariatti et al., 2007). Coupling agents are usually used for inorganic fillers-contained plastics to improve the adhesion between fillers and polymer, preferably through chemical bonds and significantly improves the performance of reinforcements (Yang et al., 2003).

The addition of silica particles into a polymer matrix to form a composite represent an important role in improving mechanical, electrical, and thermal properties of the composites (Nakamura et al., 1991). Currently particle size is being reduced rapidly, and many studies have focused on how particle size affects mechanical properties. The shape, size, volume fraction, and specific surface area of such added particles have been found to affect mechanical properties of the composites greatly (Moloney et al., 1983).

The structure and shape of silica particle had the effects on the mechanical properties such as fatigue resistance, tensile and fracture properties (Ng et al., 1999). Nakamura et al., (1991) have discussed about the size and shape of silica particle effects on the strength and fracture toughness properties based on particle-matrix adhesion. They have found that the increased of the tensile strength and flexural is affected by the increasing of specific surface area of particles.

Moloney et al., (1983) found that the mechanical properties of epoxy composites were dependent on volume fraction of particles. Furthermore, Ng et al., (1999) discussed different particle sizes of micron effects on the properties of the composites. However, for a composition of two different particle sizes, relatively different particle distribution effects from the single-particle dispersion were found in the correlation between viscosity and fracture toughness. Two-particle composition enabled significant increase in fracture toughness of the composite for a given constant volume fraction while maintaining a lower viscosity compared to single-particle composites. This is because of a uniform particle size distribution due to that the presence of large particles reduced the particle agglomeration (Kwon et al., 2006).

1.2 Problem Statement

The incorporation of inorganic fillers into various polymers or epoxies is a well-known technique to reduce the cost and to modify the specific properties of polymers such as viscosity, toughness, thermal, electrical and modulus (Takao et al., 2001). The effect of fillers on the viscosity of composites may depends on their shape and particle size, volume fraction, aggregate size, surface characteristics and degree of dispersion (Ahmad et al., 2008).

The current problems in engineering applications of epoxy thermosets include low stiffness and strength, and also the exothermic heat generated by curing epoxy resins that causes serious processing difficulties especially when viscosity are too high and cannot meet the requirement especially for the application of electrical and structural such as epoxy molding compounds and under fill materials (Mariatti et al., 2007). To overcome these problems, three different particle sizes of silica are used to understand the influence of particle sizes to the viscosity and mechanical properties of silica filled epoxy composites.

1.3 Objectives of Research

1. To relate theoretical with experimental data on the effect of volume fraction to the viscosity of silica filled epoxy composites.
2. To investigate the effect of particle sizes to the viscosity and mechanical properties of silica filled epoxy composites.
3. To investigate the effect of filler treatment to the viscosity and mechanical properties of silica filled epoxy composites.

1.4 Scope of the Research

The scope of this project is to study the effect of three different particles sizes of synthetic precipitated silica (75, 150, and 300 μm) in epoxy composite. The silica particles are produced using sieving method, and then incorporate into the epoxy resin to fabricate the composites.

A theoretical model is studied to relate with the experimental data to investigate the effect of particles size on the viscosity behavior of epoxy composite. In this project testing of viscosity, flexural test, scanning electron microscope (SEM) are done to study the effect of particles sizes of silica filler (treatment and without treatment) on the epoxy composite. Studies on the particle sizes of silica filled epoxy composites are to investigate their effect into viscosity, regarding filler dispersion, adhesion and interfacial interaction between filler and composite.

In general, to fulfill the requirement, factors such as silica filler particle sizes and distribution need to be considered as these will affect the viscosity and mechanical properties of epoxy composites.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Resin

Polymer resin can be divided into two general classes based on their behavior when exposed to heat, they are thermoplastics and thermosets.

Thermoplastics become soften on heating, can then be formed and shaped by viscous flow. They will retain shape on cooling and this process can be repeated and reversible. This property is due to presence of long chains with limited or no cross-links. Thermoplastics generally consist of very long carbon chains with side groups of H, O, N etc. They are usually supplied in granular or pellet form that can be repeatedly softened by heating and hardened by cooling within a temperature range characteristic of each plastic. In the softened state, it can be shaped into any shaped by molding or extrusion. The change upon heating is substantially physical: scrap or reject parts can be reprocessed. It can be dissolved in suitable solvents and regain their properties when the solvent is evaporated (Biron, 2007).

Thermoset resin can be formed, shaped then "cured" or "set" by a chemical reaction. Once the crosslinking occur, they will permanently cannot be remelted or reshaped by application of heat. Upon heating, thermosetting polymers will become soft, but cannot be shaped or formed to any great extent, and will definitely not flow. Other side groups O, N, H will be present. After been cross-linked there are infusible and insoluble and the scrap or reject parts cannot be reprocessed (Pascaut at al., 2002).

2.1.1 Epoxy Resins

Epoxy represents the most commonly materials used in thermoset plastics because, the applications for epoxy- based materials are widely used including coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements. Epoxy or polyepoxide is a thermosetting epoxide polymer that cures (polymerizes and cross links) when mixed with a catalyzing agent or hardener. Most common epoxy resins are produced from a reaction between bisphenol- A and epichlorohydrin as shown in Figure 2.1.

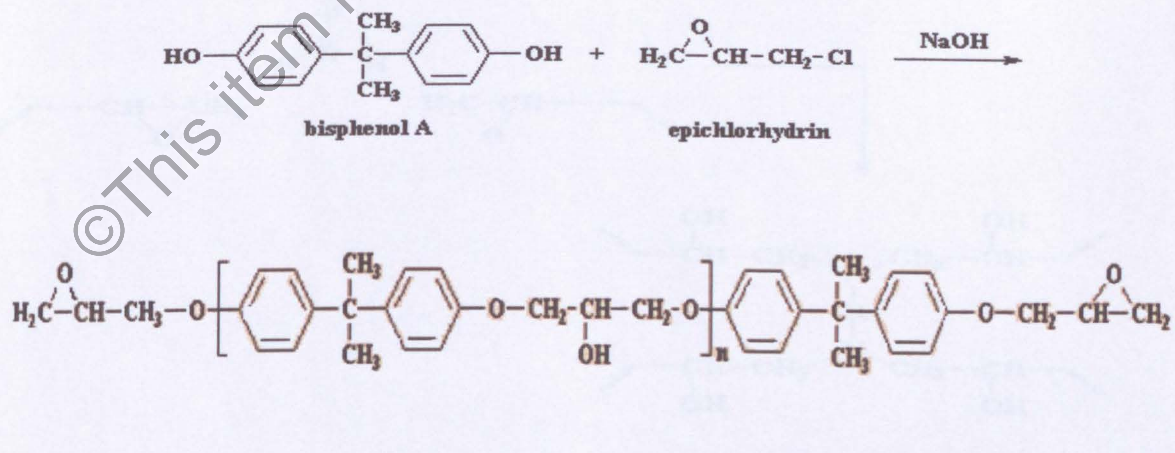

Figure 2.1: The reaction between Bisphenol – A and epichlorohydrin.

The hardener consists of polyamine monomers, for instance triethylenetetramine (TETA). When these compounds are mixed together, the amine groups react with the epoxide groups as shown in Figure 2.2 to form a covalent bond. Each NH group can react with an epoxide group, so that the resulting polymer is heavily cross linked and is thus rigid and strong.

The process of polymerization is called curing and can be controlled through temperature and choice of resin and hardener compounds. The process can take minutes to hours. Some formulations benefit from heating during the cure period whereas others simply require time and ambient temperatures.

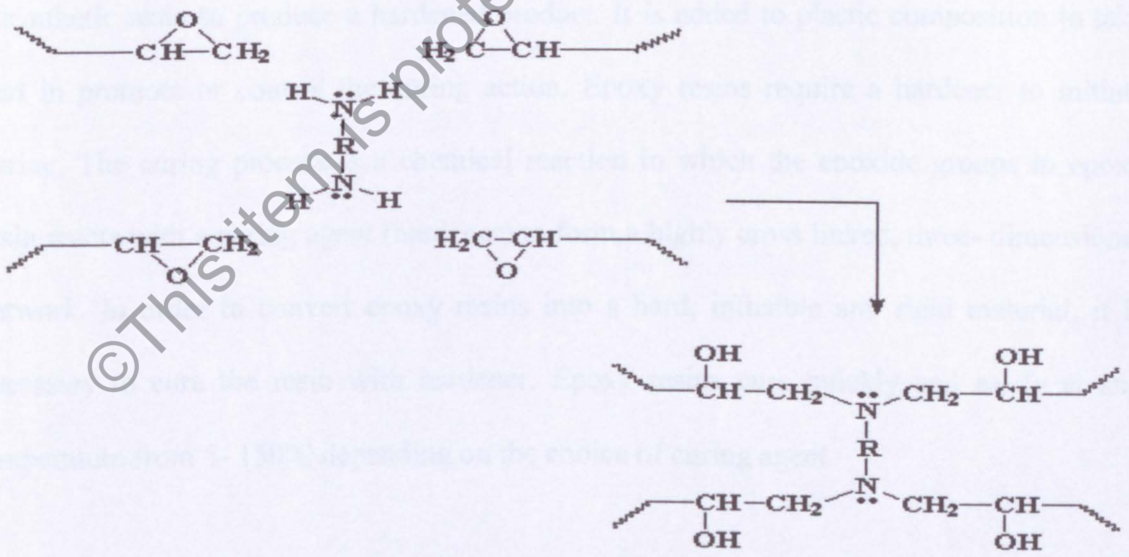

Figure 2.2: The reaction between amide groups and epoxide group.

The chemistry of epoxies and the range of commercially available variations allow cure polymers to be produced with a very broad range of properties. Epoxies generally are known for their excellent adhesion, good- to- excellent mechanical properties, good chemical, heat and environmental resistance, good insulating properties and very good electrical insulating properties. Many properties of epoxies can be modified by addition of filler mechanical properties such as flexure strength and modulus.

2.1.2 Epoxy curing agent

Curing agent often referred as catalysts, hardeners or activators. Often amines are used as curing agents. Hardener or curing agent is a material that chemically combines with a synthetic resin to produce a hardened product. It is added to plastic composition to take part in promote or control the curing action. Epoxy resins require a hardener to initiate curing. The curing process is a chemical reaction in which the epoxide groups in epoxy resin reacts with a curing agent (hardener) to form a highly cross linked, three- dimensional network. In order to convert epoxy resins into a hard, infusible and rigid material, it is necessary to cure the resin with hardener. Epoxy resins cure quickly and easily at any temperature from 5- 150°C depending on the choice of curing agent.

Epoxy hardeners are reacting with the epoxy resins greatly contributing to the ultimate properties of the cured epoxy resin system. Epoxy hardeners provide gel time, mixed viscosity and remold time of the epoxy resin system.

Physical properties of the epoxy resin system such as tensile, compression and flexural properties are also influenced by epoxy hardeners. The performances of epoxy hardeners in the epoxy resins system are dependent on the chemical characteristics of the epoxy resins and the physical characteristics while applying the epoxy resins system. The chemical characteristics of the epoxy resins that influence epoxy hardeners are viscosity, amount and type of diluents and fillers in epoxy resins.

The physical characteristics of the epoxy resins system influenceing the behavior of epoxy hardeners in the epoxy resins system are temperature of the work area, temperature of the resins system (i.e. the heated resins) and moisture (dampness). A wide variety of curing agent for epoxy resins is available, depending on the process and properties required. The commonly used curing agents for epoxies include amines, polyamides, phenolic resins, anhydrides, isocyanates and polymercaptans. The cure kinetics and the T_g of cured system are dependent on the molecular structure of the hardener. The choice of resin and hardeners are dependent on the application, the process selected, and the properties of the cured material. Employing different types and amounts of hardener, which tend to control cross- link density, vary the structure (Tripathi et al., 2007).

2.2 Fillers

Particulate fillers may be used in thermosetting resins to reduce thermal shrinkage in the manufacture of castings or molded products or to lower the coefficient of thermal expansion of finished products. Particulate fillers are also used to increase the hardness and the abrasion resistance in coating applications (Murali, 2009). Functional fillers are used for specific purposes. For instance, alumina trihydrate is used to impart fire retardancy, iron oxides for magnetic properties, and zinc oxide to produce materials exhibiting a non-linear resistivity.

Particulate fillers used in polymers normally have particle size in the region of 5–100 μm in diameter and are used at around 15–30 vol%. The maximum amount used is limited by the resulting deterioration in processing characteristics and fracture toughness (Friedrich et al., 2005). The effect of fillers in polymers have been widely studied over the last 50 years and particular attention has been placed on interfacial adhesion and surface treatments of the filler particles, as a means of improving mechanical properties and to minimize the formation of agglomerates during processing (Zhang et al., 2002).

The importance of particle size has also been examined extensively and it has generally been found that mechanical properties improve with decreasing particle diameter of the filler (Fu, 2008).

Fillers with a high surface area/volume ratio (*S*/*V*) have generally been found to give the best balance of mechanical properties (Tjong, 2006). The level of particle irregularity may be measured as deviation from spherical geometry and the level of surface roughness using the *S*/*V* ratio. Fillers are used in epoxy adhesive formulations to improve properties and to lower cost. Properties that can be selectively improved include both the processing properties of the adhesive as well as its performance properties in a cured joint. However, the use of fillers can also cause certain properties to be worsen. Typically, the formulator has to balance the improvements against property decline (Edward, 2005). The advantages and disadvantages of filler addition in epoxy formulation are listed in Table 2.1

Table 2.1: The advantages and disadvantages of filler addition in epoxy formulation (Edward, 2005).

Advantages	**Disadvantages**	**Advantages and disadvantages (depending on the application)**
Lower cost of product.	Increased weight.	Increase viscosity.
Reduced shrinkage on curing.	Increased water absortion. (depending on the filler)	Increase thermal and electrical conductivity.
Decreased exothermic temperature on curing.	Loss of transparency.	Reduced coefficient thermal expansion.
Improved tensile shear. Strength.	Difficulty in machining. (hard filler)	
Increased surface hardness.		
Improved abrasion resistance.		
Improved heat-aging properties.		
Increased compressive strength.		
Increase electrical strength.		