



**EFFECT OF HYBRID LAYERED  
SILICATES/GEOPOLYMER FILLERS ON  
PROPERTIES OF EPOXY COMPOSITES**

by

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## LIST OF ABBREVIATIONS

Al	Alumina
Al <sub>2</sub> O <sub>3</sub>	Aluminium Oxide
ASTM	American Society for Testing And Materials
C	Carbon
CEC	Cation Exchange Capacity
DGEBA	Diglycidyl Ether Of Bis-Phenol A
DMA	Dynamic Mechanical Analysis
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
H	Hydrogen
IPDA	Isophoronediamine
KOH	Potassium Hydroxide
MMT	Montmorillonite
M <sub>w</sub>	Molecular Weight
N	Nitrogen
Na <sub>2</sub> SiO <sub>3</sub>	Sodium Silicate
NaOH	Sodium Hydroxide
NH <sub>3</sub>	Ammonia
OMMT	Organo-MMT

SEM	Scanning Electron Microscope
Si	Silica
TEM	Transmission Electron Microscopy
TGA	Thermogravimetry Analysis
XRD	X-ray Diffraction
XRF	X-Ray Fluorescence

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## **Kesan Pengisi Silikat Berlapis/Geopolimer Hibrid pada Sifat Komposit Epoksi**

### **ABSTRAK**

Silikat berlapis biasanya digunakan sebagai bahan pengisi dalam polimer termasuk termoset untuk meningkatkan sifat matrik dari segi mekanikal, fizikal dan sifat halangan. Montmorillonit tergolong dalam kelas silikat berlapis yang mempunyai potensi besar sebagai pengisi kerana luas permukaan dan aspek nisbah dengan ketebalan lapisan masing-masing adalah kira-kira 1 nm. Walau bagaimanapun, penggunaan montmorillonit sebagai pengisi tunggal mempunyai batasan dari segi membantu matriks untuk mencapai prestasi mekanikal yang tinggi apabila dikenakan pelbagai beban mekanikal (mampatan dan lenturan). Oleh itu, dalam tesis ini, penggunaan pengisi hibrid telah dikaji menggunakan organo-montmorillonit dan pengisi geopolimer untuk mendapatkan bahan komposit berasaskan epoksi dengan sifat gabungan yang lebih besar. Bahan mentah pengisi geopolimer yang digunakan dalam kajian ini adalah dari Arab Saudi. Berdasarkan pencirian sumber-sumber mineral ini, ia menunjukkan kesesuaian untuk dijadikan sebagai pengisi geopolimer. Penyediaan komposit dan komposit hibrid dijalankan oleh kaedah pencampuran ricih mekanikal pada suhu bilik. Kesan tambahan pengisi organo-montmorillonit dan hibrid organo-montmorillonit/geopolimer pada epoksi telah dikaji dengan teliti oleh ujian mampatan dan lenturan, analisis haba, analisis belauan sinar-X dan ujian penyerapan air. Komposisi epoksi/organo-montmorillonit disediakan dengan pembebanan organo-montmorillonit dari 1 phr hingga 7 phr. Keputusan menunjukkan bahawa pemuatan optimum organo-montmorillonit dalam epoksi dicapai pada pembebanan 3 phr. Penemuan ini membawa kepada pembangunan komposit hibrid menggunakan kandungan organo-montmorillonit yang optimum dan lima jenis pengisi geopolimer (abu terbang, kaolin, tanah liat putih, pozolonit dan pasir silika) dengan pembebanan dari 1 phr hingga 7 phr. Walau bagaimanapun, di antara lima jenis pengisi geopolimer, kaolin telah menunjukkan sifat mampatan dan lenturan terbaik pada kira-kira 36.65 MPa dan 20.18 MPa. Data ini disokong oleh analisis lain seperti termogravimetri, belauan sinar-X dan analisis mekanikal dinamik. Berdasarkan hasil penyelidikan ini, dapat diketengahkan bahawa penggunaan pengisi hibrid organo-montmorillonit/geopolimer dapat meningkatkan kekuatan, kestabilan termal dan daya tahan epoksi dibandingkan dengan pengisi organo-montmorillonit tunggal. Peningkatan ini membawa kepada medan penerokaan yang menarik dan mencipta novelti untuk penghasilan silikat berlapis/pengisi geopolimer hibrid dalam komposit epoksi.

## **Effect of Hybrid Layered Silicates/Geopolymer Fillers on Properties of Epoxy Composites**

### **ABSTRACT**

Layered silicates are commonly used as filler materials in polymers including thermoset to improve the matrix's mechanical, physical and barrier properties. Montmorillonite belongs to the class of layered silicates which has great potential as filler due to its high surface area and aspect ratio with thickness of each individual layer is about 1 nm. However, the use of montmorillonite as single filler has limitation in terms of assisting the matrix to achieve high mechanical performance when subjected to various mechanical loads (compression and flexural). Therefore, in this thesis, the use of hybrid fillers was investigated using organo-montmorillonite and geopolymer fillers to obtain epoxy based composite material with greater combination properties. Raw materials geopolymer filler used in this study is from Saudi Arabia. Based on characterization of these minerals resources, it indicates the suitability of being a geopolymer filler. The preparation of the composites and hybrid composites was conducted by mechanical shear mixing method at room temperature. The effect of the organo-montmorillonite and hybrid organo-montmorillonite/geopolymer fillers addition on the epoxy was thoroughly studied by compressive and flexural tests, thermal analysis, X-ray diffraction analysis and water absorption test. Epoxy/organo-montmorillonite composite was prepared with varies organo-montmorillonite loading from 1 phr to 7 phr. Results demonstrated that optimum loading of organo-montmorillonite in epoxy was achieved at 3 phr loading. This finding has leads to development of hybrid composites using optimum organo-montmorillonite content and five types of geopolymer fillers (fly ash, kaolin, white clay, pozolonite and silica sand) with loading from 1 phr to 7 phr. However, among five types of geopolymer fillers, kaolin has presented the best compressive and flexural properties at about 36.65 MPa and 20.18 MPa. The data was supported by other analysis such thermogravimetry, X-ray diffraction, and dynamic mechanical analyses. Based on these research outcomes, it can be highlighted that the use of hybrid organo-montmorillonite/geopolymer fillers can more efficiently improve the strength, thermal stability and durability of the epoxy as compared to the single organo-montmorillonite filler. These improvement has led to the exploration of exciting fields and creating novel for the production of hybrid layered silicates/geopolymer filler in epoxy composites.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

Polymer composites having layered silicates (clay) as filler have been extensively studied in recent years involving the use of various types of polymer matrices such as polyamide, polystyrene, polyurethane, polypropylene, phenolic resin, unsaturated polyester, and epoxy resin (Fu & Qutubuddin, 2001; Leszczyńska et al., 2007; Pavlidou & Papaspyrides, 2008; Fengge Gao, 2012; Shiravand et al., 2016; Taghaddosi et al., 2017). The incorporation of layered silicates in polymer matrices provides several benefits to the composites properties such as enhancement in mechanical, physical and barrier properties. For instance, several works proved that the layered silicates can significantly improve the creep resistance, toughness, thermal stability, hardness, abrasion resistance, permeability and biostability of the host polymer (Alexandre & Dubois, 2000; Sinha Ray & Okamoto, 2003; Pavlidou & Papaspyrides, 2008; Azeez et al., 2013). Additionally, the advantages of layered silicates offered high aspect ratio nanolayer structure, unique intercalation and exfoliation behavior, which lead to efficient stiffening and strengthening effects. Natural and synthetic layered silicates are abundantly available and low in cost. There are many types of layered silicates exist in clay mineral sphere that classified by the characteristic of layered silicates commonly by their sheet structure, chemical structure and mineral group such as kaolinite, montmorillonite or smectite, illite and chlorite (Alexandre & Dubois, 2000; Okamoto, 2003; Uddin, 2008). However, among the different types of clay minerals, montmorillonite (MMT) is the most commonly used for the preparation of

composites. MMT drew special attention among smectite group by the ability to show extensive inter layer expansion or swelling because of structure of montmorillonite consist of an octahedral sheet of alumina or magnesia that is surrounded by two tetrahedral sheet of silica. Besides, MMT has great potential in terms of specific area and high aspect ratio with thickness of each individual layer is about 1 nm and width around 500 nm (Zhu et al., 2011). Literatures suggest that MMT has been used as reinforcing filler in various types of thermoplastic, thermoset, thermoplastic elastomer and copolymer matrices (Sinha Ray & Okamoto, 2003; Mittal, 2009; Osman et al., 2014; Taghaddosi et al., 2017).

Thermosetting polymers received greater interest for structural and high performance applications as compared to other types of polymers due to their strength and thermal stability, which are originate from their three-dimensional network of bonds (crosslinking). Among thermoset materials, epoxy resin are enormously highlighted by many researcher since the materials shows versatility with excellent chemical, heat resistance, high adhesive strength, good impact resistance, hardness and good adhesion to many substrates (Sinha Ray & Okamoto, 2003; Ramesh & Velmurugan, 2006; Phonthammachai et al., 2011). Moreover, the properties of the epoxy composites can be tailored and improved by incorporating various types of nanoparticle such as montmorillonite, carbon nanotubes and nano-titania, thus demanded by many industrial applications such as adhesive, construction material, piping, composites, laminates and coating (Isik et al., 2003; Jumahat et al., 2012a; Jumahat et al., 2012b).

In the growth of nanotechnology research area, the incorporation of nanoparticles such as nanoclay was observed as an effective way to toughen epoxy resin. The researches on epoxy/layered silicate nanocomposites are widely explored and commonly reported.

However, the use of single filler has limitation in terms of assisting the matrix to achieve high mechanical performance when subjected to various mechanical loads (compression and flexural) (Miyagawa et al., 2006; Jumahat et al., 2012a). The enhancement in mechanical properties was sometimes accompanied by reduction in thermal properties (Li et al., 2012). Therefore, researchers have started to employ hybrid fillers in order to obtain composite materials with greater combination properties.

Hybrid composite is another method allowing a third phase materials integrate into composites system whereby the incorporation of two reinforcement material into epoxy resin significantly demonstrated beneficial improvement in mechanical properties compared to single filler (Wang et al., 2011). Currently, there are three types of reinforcement materials for epoxy hybrid have been studied; soft rubber particles, rigid inorganic fillers and semi-rigid organic fillers where substantial differences in mechanical properties have been reported (Liang & Pearson, 2010). There are many other publications reported on epoxy composites incorporating two or more particulate reinforcement (hybrid fillers) (Chenggang & Morgan, 2009; Liang & Pearson, 2010; Wang et al., 2011). However, only small number of published researches focused on the use of two physically/chemically different silicate/clay materials as hybrid fillers in epoxy matrix (Wang et al., 2011; Osman et al., 2016a). Specifically, there is no published work on the use of layered clay and clay geopolymer as hybrid fillers in epoxy matrix. Therefore, this thesis reports on the morphology, compressive and flexural properties of novel epoxy composites with layered clay (organo-MMT) and geopolymer fillers to highlights the potential of these materials for use in structural applications.

Geopolymer is a new family type of thermosetting inorganic polymer resin (Song et al., 2013). It is a cementitious material that formed by aluminosilicates produced by

predominantly silica (Si) and aluminum (Al) materials. Generally, the process of geopolymerization involves chemical reaction under highly alkaline condition. The discovery of geopolymer based materials contribute to excellent mechanical properties, high early strength, abrasion resistance and thermal stability that lead to many application fields such as ceramics, binder, matrices for hazardous waste stabilization, fire resistance and for high tech materials (Colangelo et al., 2013). Currently, geopolymer based composites become trendy among researcher in order to improve several properties of geopolymer materials such as brittleness and their low flexural strength in order to extent the limit of application in structural materials by incorporation of organic polymer such as polyvinyl acetate, polypropylene, polyvinyl alcohol or water soluble organic polymers (Colangelo et al., 2013). However, the organic polymer commonly acts as additives in geopolymer system. Meanwhile this research emphasized geopolymer as filler in the composites system.

This study was embarked with the analyze and characterize five types of raw materials for geopolymer filler (geo-fillers) purpose and study the effect of different geo-filler and organo-MMT addition in epoxy hybrid composites. This thesis focuses on finding the optimal loading of montmorillonite in epoxy system and the effect of dissimilar types of geo-filler addition to the physical and mechanical properties of neat epoxy and epoxy/organo-MMT composites.

## 1.2 Problem Statement

Epoxy is a commonly used polymer to replace heavier non-polymeric materials for structural applications such as ceramic and metal. However, the mechanical and physical properties of epoxy can be severely reduced when exposed to harsh and corrosive environment such as in the oil and gas pipeline. The structure of epoxy can chemically degrade and leads to deterioration in its mechanical and physical properties. These may hampered the long-term use of epoxy in the structural applications, where mechanical and physical integrity are required to allow stability in various environmental conditions. In that case epoxy has been restored by adding nanofiller such organo-montmorillonite (organo-MMT).

Organo-MMT is promising reinforcing nanofiller for epoxy matrix due to its high aspect ratio, hydrophobicity and capability to enhance the mechanical properties of the matrix when added in small quantities. However, due to the morphology and structure properties found in the nanoclay type filler it affects the stability of the mechanical properties of the composite. Therefore, due to this limitation of single nanofiller, researcher have initiated the idea of using hybrid filler in epoxy matrix to obtain composite with greater combination properties. However, only small number of published researches focused on the use of two physically/chemically different silicate/clay materials as hybrid fillers in epoxy matrix (Wang et al., 2011; Osman et al., 2016b). So far, there is no further study was conducted using layered silicates and geopolymer as hybrid filler in epoxy composites.

Geopolymer is a new revolution of existing concrete that formed by alkaline activation from aluminosilicates source. These inorganic materials have been studies over

past decade by many researcher and have superior characteristic such high compressive strength, low shrinkage, acid resistance and thermal resistance. Therefore, the use of organo-MMT and geopolymer filler (geo-filler) in producing the epoxy hybrid composite engenders better strength and durability as compared to neat epoxy, thereby, a novel and exciting field of exploration. It was anticipated that the incorporation of these hybrid fillers would improve the physical and mechanical properties of the epoxy without compromising its lightweight characteristic.

### **1.3 Research Objectives**

This thesis focuses on development of epoxy composites with hybrid filler using layered silicates (organo-MMT) and geopolymer filler (geo-filler) with different types of geopolymer source materials to improve the mechanical and physical properties of the composites. The details objectives of the study are as follows:-

1. To characterize the layered silicates (organo-montmorillonite) and geopolymer fillers (geo-filler) used to produce the hybrid composites.
2. To investigate the optimum loading of organo-montmorillonite addition on compressive, flexural, thermal and water absorption properties of epoxy.
3. To analyse the compressive, flexural, thermal and water absorption properties of the optimize organo-montmorillonite/geopolymer epoxy composites.