EFFECT OF FILLERS ON RHEOLOGICAL, MECHANICAL AND DEGRADATION PROPERTIES OF EPOXY SYSTEM

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อิทธิพลของสารตัวเติมที่มีผลต่อกระแสวิทยา สมบัติเชิงกล และสมบัติการเสื่อมสภาพของระบบอีพ็อกซี่

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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งานวิจัยนี้ได้ศึกษาคุณลักษณะกระแสวิทยาของอีพ็อกซี่ที่เติมแป้งมันสำปะหลัง และ เถ้าลอยเป็นสารตัวเติมโดยเปรียบเทียบกับการใช้สารตัวเติมที่ใช้ในอุตสาหกรรม 4 ชนิด คุณสมบัติเชิงกลของระบบอีพ็อกซี่เสริมแรงด้วยผ้าใยแก้ว(จีเอฟอาร์พี) ที่เตรียมจากระบบอีพ็อกซี่ที่เติมสารตัวเติม โดยใช้สารเคมีทำแข็ง 3 ระบบ คือ ทีอีทีเอ ดีดีเอส และ ตัวทำแข็งผสมระหว่างทีอีทีเอ กับ ดีดีเอส นอกจากนี้ได้ทำการศึกษาการเสื่อมสภาพของ จีเอฟอาร์พี ที่เตรียมขึ้นในสภาวะธรรมชาติ ประกอบด้วยสภาวะเสื่อมสภาพกลางแจ้งในสภาพอากาศธรรมชาติ สภาวะเร่งในเครื่องเร่งสภาพอากาศ การฝังกลบ และ การแช่ในน้ำ โดยจะใช้การวิเคราะห์ทางสถิติช่วยในการประมวลผลการทดลอง

จากผลการวัดค่า ดัชนีไทโอโทรปิก พบว่าแป้งมันสำปะหลัง และ เถ้าลอย ไม่สามารถไปใช้เป็นสารตัวเติมแบบไทโอโทรปิกในระบบอีพ็อกซี่ ส่วนการศึกษาตัวแปรการแข็งตัวของระบบอีพ็อกซี่เนื่องจากสารตัวเติมพบว่ามีแนวโน้มไม่ชัดเจน ซึ่งผลการวิเคราะห์ทางสถิติพบว่าระยะเวลาถึงอุณหภูมิ $50^{o}C$ ($t_{50^{o}C}$) และ ระยะเวลาการแข็งตัว (t_{cure}) ขึ้นอยู่กับชนิดของสารตัวเติมเพียงอย่างเดียวโดยไม่ขึ้นอยู่กับปริมาณของสารตัวเติม ผลการทดลองสมบัติเชิงกลพบว่าแป้งมันสำปะหลัง และ เถ้าลอยช่วยเพิ่มค่าแรงต้านทานแรงดึงของจีเอฟอาร์พีที่ใช้ตัวทำแข็งทีอีทีเอ และ ตัวทำแข็งผสมระหว่างทีอีทีเอ กับ ดีดีเอส และ พบว่าการเติมสารตัวเติมทำให้คุณสมบัติการต้านทานการแตกหัก และ สมบัติเชิงความร้อนด้อยลง

ผลการทดลองพบว่าจีเอฟอาร์พีที่ใช้ตัวทำแข็งผสมระหว่างทีอีทีเอ กับ ดีดีเอสเกิดการเสื่อมสภาพภายใต้สภาวะสัมผัสกับอากาศธรรมชาติ แต่ผลการทดลองไม่แสดงการเสื่อมสภาพของจีเอฟอาร์พี ที่ใช้ตัวทำแข็งทีอีทีเอ และ ดีดีเอส ภายในระยะเวลาการทดลอง ผลการทดสอบภายใต้สภาวะใต้สภาพเร่งอากาศ ประมวลผลทางสถิติพบว่า จีเอฟอาร์พีที่ใช้ตัวทำแข็งทั้งสามชนิดคือ ทีอีทีเอ ดีดีเอส และ ตัวทำแข็งผสมระหว่างทีอีทีเอ กับ ดีดีเอส เกิดการเสื่อมสภาพ และ สารตัวเติมมีผลต่อระยะเวลาการเสื่อมสภาพของจีเอฟอาร์พีที่ ใช้ตัวทำแข็ง ดีดีเอส

การทดลองการเสื่อมสภาพ จากการฝังกลบ พบว่าเกิดการเสื่อมสภาพของ จีเอฟอาร์พีที่ใช้ตัวทำแข็งทีอีทีเอภายในระยะเวลา 180 วัน และ ชนิดของสารตัวเติมไม่มีผลต่อการเสื่อมสภาพ สำหรับจีเอฟอาร์พีที่ใช้ตัวทำแข็งดีดีเอส และ ตัวทำแข็งผสม ไม่พบการเสื่อมสภาพเกิดขึ้นในระยะของการทดลอง 180 วัน ผลการศึกษาสภาวะจำลองโดยแช่จีเอฟอาร์พีในน้ำเสีย และ น้ำทะเล เป็นระยะเวลา 180 วัน ผลการคำนวณเชิงสถิติพบว่า จีเอฟอาร์พีในน้ำเสีย ที่ใช้ตัวทำแข็ง ทีอีทีเอ เกิดการเสื่อมสภาพขึ้น แต่ไม่สามารถบ่งชี้ชัดเจน สำหรับจีเอฟอาร์พีที่ใช้ตัวทำแข็งดีดีเอส และ ตัวทำแข็งผสม ในการศึกษาการเสื่อมสภาพในน้ำทะเลพบว่า จีเอฟอาร์พี อาจจะเกิดการเสื่อมสภาพเกิดขึ้น เมื่อใช้ตัวทำแข็งทั้งสามชนิด คือ ทีอีทีเอ ดีดีเอส และตัวทำแข็งผสมของ 2 ชนิด นอกจากนี้ยังพบว่าสารตัวเติมมีผลต่อการเสื่อมสภาพของ จีเอฟอาร์พี ที่ใช้ตัวทำแข็งผสมระหว่างทีอีทีเอ กับ ดีดีเอส

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EPOXY SYSTEM/ FILLERS/ RHEOLOGICAL/ FLY ASH/ CASSAVA STARCH/ DEGRADABLE/ THIXOTROPIC/GLASS FIBRE REINFORCED

The rheological characteristic of the epoxy filled with cassava starch and fly ash was measured and compared with the four common commercial fillers. Mechanical properties of the GFRP derived from those epoxy systems and using TETA, DDS and TETA/DDS as curing agents were also investigated. Environmental degradation under photo degradation, both natural and accelerated conditions, landfill and water incubation were studied. The statistical analysis was employed to verify the experimental results.

From the thixotropic index measurement, fly ash and cassava starch could not be used as the thixotropic fillers in the epoxy. The cure data of the filled epoxy resin were ambiguous. However, the statistical tests revealed that the $t_{50^{\circ}\mathrm{C}}$ and the t_{cure} of the epoxy systems were affected by only the type of filler but did not change with the fillers content. The mechanical properties indicated that cassava starch and fly ash enhanced the tensile properties of the GFRP derived from TETA and TETA/DDS as curing agents. The fracture and thermal properties were incompetence by adding fillers.

The GFRP cured with TETA/DDS did degrade under natural exposure condition. Vice versa, the TETA and DDS cured could not be observed within the given experimental time. In the accelerated condition and based on statistical tests, the GFRP specimens cure with TETA, DDS and TETA/DDS were degraded under accelerated condition. The GFRP obtained from epoxy cured with DDS hardener also did degrade and moreover the filler used showed an effect on the degradation time.

Under the landfill and the statistical resolution, it was found that the degradation of GFRP cured with TETA hardener was occurred within 180 days and the fillers added did not have an effect on degradation. Vice versa, the degradation of the system cured with the DDS and TETA/DDS were not be observed within the given experimental time. When the reinforcements were soaked into the seawater and waste water for 180 days, the statistical calculation showed that the degradation of TETA cured GFRP could be accomplished in waste water but it was difficult to declare for the DDS and TETA/DDS systems. Under the seawater, the degradation might be occurred when TETA, TETA/DDS and DDS used as curing agents. Moreover, the degradation rate would be affected by the fillers used for the TETA/DDS system.

School of Polymer Engineering Student's Signature P. Thananowan

Academic Year 2005 Advisor's Signature

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Epoxy resins are the most important thermosetting polymers and widely used as matrix in reinforced composites, adhesives in the aerospace industry, surface coatings, etc. Most of commercially available epoxy resin is oligomers of diglycidyl ether of bisphenol A(DGEBA).

An epoxy resin becomes an insoluble thermosetting polymer when it reacts with a cross-linking agent or hardener. The cured resins have good thermal, electrical and mechanical properties, but they are brittle and have poor resistant the crack propagation. To alternate this deficiency, the epoxy resins are mixed with curing agents, modifying agents, such as low molecular weight polymers, reactive oligomeric compounds, plasticizers, fillers and reactive diluents which improve the viscosity of the resin so that the process ability of system is not impaired.

In the composite industries, the fillers are added into epoxy matrix to assist the manufacturing process such as enhance the thixotropic properties, cost reduction and sometime improve the mechanical properties of the finishing product.

As mentioned above, the epoxy resin widely and commonly used in composite industries is typically required filler added. Consequently, the research study on common fillers such as fumed silica, calcium carbonate and titanium dioxide have been conducted for years. The main topics are focused on mechanical properties

(Hassain, et.al., 1996; Srivastava, 1999; Brito and Sanchez, 2000 and Lee and Yee, 2000), curing parameters (Miranda and co-workers, 1997; Nunez, et.al., 2000 and Akasuka, 2001), degradation properties (Montserrat, et.al., 1998 and Hepburn and co-researchers, 2000). However, non of the previous research studies published on the rheological, mechanical and degradation properties of epoxy resin filled with cassava starch and fly ash. Especially in the area of outdoor application goods made from reinforced composites in which prolong degradation would enhance the life time use and also retain the mechanical stability of the products. Contradictorily, using natural fillers, especially starch based, would assist the deterioration rate of the off-used product when they are finally disposed as solid waste.

1.2 Objectives

The main research objectives of this study are as follow;

(i) To study the thixotropic properties, viscosity and the cure parameters of the epoxy filled with six difference types of fillers.

(ii) To compare and contrast the mechanical by mean of impact strength, tensile strength, flexural strength and heat distortion temperature of the epoxy systems using six types of fillers.

(iii) To investigate the effect of fillers employed on the degradation behavior of the epoxy systems.

and (iv) To observe the effect of the curing systems on the degradation rate of epoxies.

1.3 Scope of Work

The main area of this research work includes study the dependency of fillers on processing parameters such as thixotropic properties, viscosity and cure time of the epoxy filled with these filler. The fillers used were fumed silica, talc, titanium dioxide, sodium borosilicate glass, fly ash and cassava starch. The later two have not yet been commercially used. Starch has potentially competence as biodegradable filler. Diglycidyl Ether of Bisphenol A(DGEBA) epoxy cured with three different curing catalogues, aliphatic amine, TETA, aromatic amine, DDS, and their mixture, were investigated. The impact strength, flexural strength, tensile strength, and heat distortion temperature(HDT) were examined. The degradation conditions of the glass reinforced composites prepared by the epoxy systems filled with those six fillers had been manipulated; the landfill condition, water incubated, open-air and accelerated exposure. The weight loss of the specimen measured by the refluxing specimen in acetone in order to remove the degraded product and surface hardness using Shore D hardness tester were used to monitor the degradation reaction rate.

CHAPTER II

LITERATURE REVIEW

2.1 Fillers in Polymeric Materials

In the past recent year, the biocompatible, biodegradable and biomaterial have become most up-to-date and innovative trend for the material industry. It is due to the fact that rapid rise of polymer consumption especially in the form of packaging materials and industrial construction especially in automotive, become a real menace for the environment. They give rise to an intensive search for new polymeric systems which allow the removal and the management final polymer waste as economically and environmentally. One of the possible ways of overcome this problem is to introduce the biodegradable additive into the non-biodegradable polymers, e.g. polyethylene, polypropylene, poly(vinyl chloride), polystyrene and all thermosets. Starch is the natural additive that inexpensive and easy to be biodegraded. Starch was already used as a filler in polyolefins, polystyrene and ethylene-methyl acrylate copolymer. Many researchers studied the behavior and properties of starch containing polyolefin systems (Zuchowska, Steller and Meissner, 1998). In this work, mechanical, rheological, and degradation properties of this filler in epoxy will be reported. There are a hand-full of publications that presented on the mechanical, rheological properties and degradation of the filler added epoxy systems. The influencing of the fillers on the properties of epoxy systems is briefly summarized in the following sections.

2.2 Influence of Filler on Mechanical Properties of Epoxy

Many researchers have studied the influence of fillers on mechanical properties of the epoxy composites. Normally, the thermal and mechanical behaviors of the polymeric materials are strongly alternated by the filler added such as type, size, load and shape. Moreover, the properties have also very complex and depend on the chemical structure and the crosslink density when thermosets resins combined with the metallic fillers. Knowing that the mechanical behavior in composite also depends on the quality of adhesion between matrix to fiber and matrix to filler, Brito and Sanchez (2000) stated that this factor was mainly responsible for the different observations in the breaking strength of the given composites. According to Nielsen (1980, quoted in Brito and Sanchez, 2000) and Kunori (1980, quoted in Brito and Sanchez, 2000), strong interphases adhesion between disperse and continuous phases produce a high breaking strength in the composite. Brito and Sanchez (2000) were also studied influence of Zn, Cu, Al on the mechanical behavior in epoxy matrix composites. At stoichiometric ratio, the results showed that the composite with aluminum was the one which presented the weakest filler–matrix adhesion. Besides, all composites under investigation were decrease in the mechanical property with the addition of the filler. The fillers added composites showed the lowest breaking strength comparing with the non-filled matrix.

Srivastava (1999) investigated the effects of water immersion on mechanical properties, flexural strength, interlaminar shear strength and impact energy, of the aluminum tri-hydrate and polyethylene filled and unfilled quasi-isotropic glass fiber reinforced polymers(GFRP). Interlaminar shear strength and flexural strength were obtained with variation of immersion time and weight percent of filler content. The tested properties were increased with increasing filler content in the GFRP. Immersion in water resulted a significant increase in flexural strength, interlaminar shear strength and impact energy. Aluminum tri-hydrate contained GFRP composites show higher values in flexural strength, interlaminar shear strength and impact energy than those of polyethylene filled and unfilled GFRP, thus the toughness was improved.

Compressive properties of epoxy composites reinforced with fly ash and fibers which have differing in aspect ratio were studied by Kulkarni (2003). Retention of strength and modulus were observed for a greater range of fiber volume fractions and followed by fly ash added into the system. A slight decrease in density was also observed at higher fly ash content. The system was advantages for weight specific applications. Kishores, et al. (2002) were also studied the impact response of the fly ash loaded epoxy system. It was observed that with the increasing in filler volume fraction, there was a net reduction in the impact strength. The Ductility Index of the system, on the other hand, was shown an increase with the filler content. From visual observations on the failed samples, analyses of the crack length, shift of crack and point of which the slope of the crack reaches 45°, the results showed that a curvilinear path for the crack was gave place to straighter ones as the ash content in the matrix increased. Consequently, the crack shift also was reduced when filler particles were introduced at larger quantities into the resinous system.

Hussain, et al. (1996) investigated the effects of different coupling agents on the mechanical properties of the titanium dioxide particulate filled epoxy composite. The titanium dioxide coated with silane coupling agent were compared with titanate coupling agent coated titanium dioxide dispersed composites. Young’s modulus and flexural strength of titanate coupling agent treated composites were significantly improved compared to silane coupling agent treated one. It was suggested that a strong interfacial bonding between the filler and the matrix existed when the titanate coupling agent was used and explained by the adhesion model.

Mechanical properties of carbon fiber reinforced composites and aluminium trioxide particles dispersed carbon fiber hybrid reinforced composites were studied by Hussain, and co-workers (1996). Mechanical properties were improved by incorporating 10% by volume of the nano- or micro-sized aluminium trioxide particles into the epoxy matrix. It was revealed that Young' s modulus and flexural strength of nano-sized filler dispersed carbon fiber reinforced plastics(CFRP) composites showed a higher modulus compare to micron-sized filler dispersed samples.

Epoxy can be toughened by rigid inorganic fillers. Lee and Yee (2000) were investigated the effect of inherent matrix toughness on the fracture of filled thermosets by using glass beads and epoxies. The toughness of system was improved by incorporation of glass beads in epoxy resin. It was also found that the toughness was gained when longer chain epoxies were employed.

Kawaguchi and Person (2003) examined the fracture toughness behavior of three different types of glass filled epoxies, large glass sphere, small glass sphere, and glass fibers. The surface of each type of filler was treated. The fracture toughness was found to increase with increasing filler content and was not affected by changes in particle-matrix adhesion.

Mechanical properties of silica filled epoxy resin were tested by Wang, et al. (2002). The results were shown that Young' s modulus and yield stress increased with increasing the filler content at low temperature. However, adding of particles to the epoxy resin was produced a large disturbance of stress distribution.

2.3 Effect of Filler on Curing Parameters of Epoxy Resin

In composite processing, the kinetics of curing reaction of epoxy resin is very important. Cure time and time to reach 50°C are very crucial especially in hand lay-up lamination. Fillers may either increase or decrease the kinetics of curing reaction. Antoon and Koenig (1981, quoted in Miranda, et al., 1997: p1017) reported that silica filler had slightly accelerated the reaction while a high surface area of E-glass were retarded the reaction rate.

Miranda and co-workers (1997) were studied the reaction kinetics of the diglycidylether of bisphenol-A(DGEBA) and 4,4'-diaminodiphenylmethane(DDM) as curing agent in the presence of quartz flour as filler. At higher temperatures and at the conversion higher than 50%, it was found that the reaction rate was decreased for the systems with filler concentrations higher than 10 wt%. Vice versa, at filler concentration lower than 10 % there was no effect to the reaction rate.

Influences of inorganic fillers on curing reactions of epoxy resin were also reported by Akatsuka, et al. (2001). The gel time of epoxy resins containing alumina(Al_2O_3) fillers were longer than the unfilled systems. It was indicated that Al_2O_3 fillers delayed the curing reactions.

Nunez, et al. (2000) studied the kinetic of curing reaction of an epoxy system consisting of DGEBA with 1,2 diamine cyclohexane(DCH) having calcium carbonate($CaCO_3$) as filler. The values of activation energy of filled system were higher than unfilled system. It indicated that the presence of filler hinder the crosslinking process. Nunez et al. (2001) also studied the same system in order to calculate the time-temperature-transformation(TTT) isothermal cure diagram. The results showed that the TTT diagram of the three component epoxy system, DGEBA /1,2 DCH/$CaCO_3$, was differed from the non-filled system.

Epoxy resin filled with various carbons was studied by Wu and Chung (2004). The epoxy resin system consisted of the diglycidyl ether of bisphenol F(DGEBF) and triethylene tetramine as curing agent was investigated. Three types of carbons, carbon fiber, carbon nanofiber and carbon black were employed. The carbon black accelerated the curing reaction by decreasing the maximum exothermic heat flow temperature. The rate of carbon black filled was faster than the carbon nanofiber and carbon fiber.

2.4 Degradation of Cured Epoxy Resin

2.4.1 Thermal Degradation of Epoxy Resin

Many researchers have been investigating the thermal degradation of cured epoxy resin because it is a major problem for the use of this matrix. Many applications of epoxy resin are required the long term thermal aging stability such as adhesives, coatings and composites. Barral, et al. (1995) studied the thermal degradation for the system contained DEGBA and 1,3-bisaminomethylcyclohexane(1,3-BAC). The dynamic mechanical analysis(DMA) showed that the peak value of the dynamic loss factor(tanδ), the glass transition temperature(T_g) and the dynamic storage modulus(E’) above T_g were changed considerably with increasing thermal degradation. Below the T_g, E’ was changed moderately with increased the thermal degradation. From this resulted they argued that thermal degradation during the stage prior to the onset of the severe degradation involves structural changes in the epoxy system, such as further crosslinking and loss of dangling chains in the crosslinked network.

The thermal and thermo oxidative degradation of the epoxy adhesive based on tetraglycidyl-4,4’-diaminodiphenylmethane(TGDDM) cured with a combination of two curing agents, dicyandiamide(DDA) and 4,4’-diaminodiphenylsulphone(DDS) were studied by Buch and Shanahan (2000). The results showed that degradation and weight loss were divided in two stages. In the first stage, weight loss occurs independently of the environmental used. They concluded that this stage corresponded to the thermolysis. The second stage of degradation was occurred only in the presence of oxygen. Disappearance of the organic material was occurred from thermo oxidation**.**

Damian and co-workers (2001) conducted experiment on thermal oxidation of epoxy networks. Their work could be applied for the low activity radio active wastes encapsulation. The results revealed that the first degradation step was related to a surface degradation phenomenon rather than the presence of structural irregularities. This result was similarly to the work studied by Zhang, et al. (1994).

The effect of silica filler on thermal degradation kinetics of epoxy resin with anhydride were also investigated by Montserrat, et al. (1998). The results were indicated that the addition of silica filler increased the thermal degradation of the resin.

Hepburn and co-researchers (2000) observed the degradation of the filled epoxy resin, DGEBA and phthalate anhydride. The resin was combined with one of three common filler materials, silica, alumina and wollastonite. They concluded that the fillers showed the variation of the reaction rate when chemical, radiative, electrical and thermal stresses were applied.

2.4.2 Hygrothermal Aging of Epoxy Resin

Water absorption and desorption in an epoxy resin with the degradation were studied by Xiao and Shanahan (1997). The model material, DGEBA/DDA, in the study of water absorption and absorption/desorption behavior during hygrothermal aging at 90°C was employed. The result showed that the model experiment was agreed with experimental results. Using the model, it was lead to an estimate of the average molecular weight of the segmented chains correspondingly to the structure most probably obtained after degradation of the resin. Their theory could be used to estimate the average molecular weight of the inter crosslink chains after aging. Xiao and Shanahan (1998) also studied the irreversible hygrothermal aging effect on DGEBA/DDA epoxy resin. The DMTA data showed that the glass transition temperature of DGEBA/DDA was irreversibly decreased after hygrothermal aging.

Zhou and Lucas (1999) reviewed the nature of the absorbed water and the related with hygrothermal effects in epoxy resins. The data showed that water molecules were bound with epoxy resins through hydrogen bonding. Two types of bonded water were found in epoxy resins. Type I bonding related the water molecules forming a single hydrogen bond or dispersion bonding with the epoxy resin network. Type II bonding resulted from water molecules forming multiple hydrogen bonds with the resin network. The variations of T_g on the two types of bonding with epoxy were also reported. They found that Type I bond broke the initial interchain Van der Waals force and hydrogen bonds, resulted in the increase chain segment mobility. It behaved as plasticizer causing large depression in the T_g. However, type II bonding water molecules do not act as a plasticizer but rather from bridges between structural segments resulting in secondary crosslinking.

As seen from the literature reviews, there is no investigation to determine the effect of starch and fly ash fillers influence on the rheological, mechanical and degradation properties of epoxy resin. Therefore, the study of these fillers in epoxy resin would be interesting issue in the field of composite materials. In this research work was aimed to study the effect of the fillers influence on the properties of epoxy resin system. The outcome from this study could be beneficial for the composites industry.

CHAPTER III

EXPERIMENTAL METHODOLOGY

3.1 General Background

There were four main research topics; processing parameters, mechanical, thermal and degradability properties of six types of fillers mixed with three epoxy resin systems, investigated in this study. The Diglycidyl ether of bisphenol A(DGEBA) cured with three different hardener systems namely triethylene tetramine(TETA), 4,4'-diamino-diphenylsulphone(DDS) and mixture of TETA and DDS were employed as the polymer matrix. Viscosity and cure time of the filled epoxy resin were investigated to manifest the processing parameters. Tensile , impact, and flexural strength and also heat distortion temperature of the glass fiber reinforced polymer or GFRP were examined. Photo degradation rate of GFRP were investigated under both natural exposure and artificially accelerated conditions. The landfill and water incubated conditions on the constructed sites were also tested. The details of experimental procedures are described as follows.

3.2 Specimen Preparation

3.2.1 Materials and Chemical Reagents

The main materials used in this study can be classified into three categories; (*i*) epoxy prepolymer and the curing agents, (*ii*) fillers and (*iii*) miscellaneous chemical reagents.

The DGEBA based epoxy resin, EPOTEC YD-127, was supplied from Thai Epoxy and Allied Products Co., Ltd. The TETA was used as low temperature curing agent and it is available from Vista Co., Ltd.. The aromatic hardener, DDS, was obtained from Vantico Co., Ltd. and normally used as high temperature curing agent. Both epoxy and curing agents were used without further purification. The fundamental properties, as obtained from the specification data sheet of these materials are summarized in table 3.1.

Table 3.1 The properties of epoxy and curing agents.

Property	**Value**
EPOTEC YD-127:	
Epoxide Equivalent Weight(EEW, g/eq)	183
Brookfield Viscosity @25°C(cP)	9300
TETA:	
Amine Hydrogen Equivalent Weight(AHEW, g/eq)	146
Viscosity @20°C(cP)	26
Boiling point(°C)	277
DDS:	
Amine Hydrogen Equivalent Weight(AHEW, g/eq)	62
Melting Point(°C)	175

Fumed silica, commercially available as Reolosil QS-20LS with particle size ranking 5-50 nm, was supplied by Shinamon, Co., Ltd.. Fly ash was obtained from Mae Moh Power Plants operated by Electricity Generating Authority of Thailand(EGAT). Sodium borosilicate glass hollowed microsphere, Q-CEL 519, was purchased from Potters (Thailand) Ltd.. Titanium dioxide(TiO_2), Tronox CR-834, was supplied by Louis T Leonowens (Thailand) Ltd.. Cassava starch was available from Sanhuangvong Co., Ltd. Talcum was supplied from Chemmin Co., Ltd.. All of solid fillers were used as received. There were no further surface modification. The fundamental properties as also reported in the material data sheet(MDS) of these materials are summarized in table 3.2.

A commercial grade of acetone was used as the common solvent in the extracting process by refluxing. It was locally supplied by Wittayasrom Co., Ltd. It was used as received. Potassium sulfate and sodium nitrate was used as anaerobic bacterial supplement nutrition in the topsoil. They were supplied by Carlo Earba^{TM} and directly used without any further purification.

3.2.2 GFRP Preparation

The laminated samples were prepared by hand lamination process. DGEBA and the curing agent were mixed at the calculated stoichiometric ratio known as phr. The phr, corresponding to the epoxy used, of DGEBA/TETA, DGEBA/DDS were 13, and 34, respectively. However, the mixing ratio of epoxy and the mixture of TETA/DDS at 50:50 by weight were 19. This phr was calculated from the following equations;

$$AHEW_{mixture} = \frac{Total\ Weight}{\frac{w_1}{AHEW_1} + \frac{w_2}{AHEW_2}} \qquad (3.1)$$

and then $$phr = \frac{AHEW_{mixture}}{EEW} \times 100 \qquad (3.2)$$

Where, w_1 and w_2 are weight fraction of curing agents.

Table 3.2 Typical properties of fillers.

Material Properties	Value
Reolosil QS 20LS:	
Specific Surface Area(m^2/g)	219
Bulk Density(g/l)	40
pH	4.2
Particle Size(nm)	5-50
Q-CEL 519:	
Bulk Density(g/l)	1.0×10^{-4}
Particle Size(μm)	50
Bulk Density(g/l)	800
Tronox CR-834:	
pH	6.7
Particle Size(μm)	0.17
Talcum Powder Haicheng No. 37:	
Content of SiO_2(%)	57
Content of MgO(%)	30
Particle Size(μm)	1.4-19

Fumed silica and the other fillers were mixed at 2 phr and 5 phr, respectively with DGEBA in the first hand. The woven glass mat having the area density of 300 g/m^2 was used as reinforcement. The resin to fiber weight ratio was approximately controlled at 80:60. Three layers of the woven were stacked. Curing schedules including the post cure and annealing of those GFRP specimens are summarized in table 3.3. For the room temperature curing system, the vacuum bag process was applied. On the other hand, the compression molding was used for curing the DDS system. Approximately 15 cm × 15 cm with the thickness of 1.5 mm, of the laminated sheet were prepared.

Table 3.3 Cure condition of GFRP preparation.

Curing Agent	Cure condition	Post cure	Sample annealing
TETA	Room Temperature	60°C for 12 hr	60°C for 8 hr
DDS	120°C for 90 min	120°C for 12 hr	120°C for 8 hr
TETA/ DDS	Room Temperature	120°C for 12 hr	120°C for 8 hr

3.3 Performance Testing

3.3.1 Viscosity Measurement

The viscosity of the epoxy resin mixed with filler was measured by using the Brookfeild^{TM} dial reading viscometer mode RVT. Amount of 470 g of DGEBA were added into the 600 ml beaker at 25°C. Pre-determine amount of filler was added and vigorously stirred using the electrical driven hand mixer. After a few minutes of stirring, the homogenized mixture was obtained. At the desirable spindle size and rotational speed at 5.0 rpm of viscometer were selected for the measurement. According to the calculation, the shear rate of 16.08 s^{-1} was created at this rotor speed. Three dial reading was recorded to calculate the average of viscosity. Then, the viscosity was computed according to equation 3.3 and factor values for the equation are given in appendix A.

$$Vis\cos ity\ (m.Pa \bullet s) = Dial\ reading \times Factor \qquad (3.3)$$

3.3.2 Cure Parameters

According to ASTM D2471, the processing parameters, time to reach 50°C(t_{50^oC}) and cure time(t_{cure}) were obtained. Time and temperature were monitored using digital thermocouple, BryMen^{TM} BM 810, interfaced with PC computer through the BR 81X PC interface tool kit. The digitized data, then, were processed through the commercial software, Excel^{TM}, and the time-temperature were plotted. The quantity of epoxy resin and hardener mixed were 45g. Predetermined fillers content was priority added into epoxy. To achieve well homogenize mixing, the filler and 45g of epoxy were mixed with hardener in the polystyrene cup using the electrical driven mixer for 30 second. The cup was immediately immersed into the water circulation bath at 35°C. The digital thermocouple probe, type J, was placed into the mixture. Temperature and time was recorded. The t_{50^oC} and t_{cure} was determined from the constructed time-temperature curve as shown in figure 3.1.

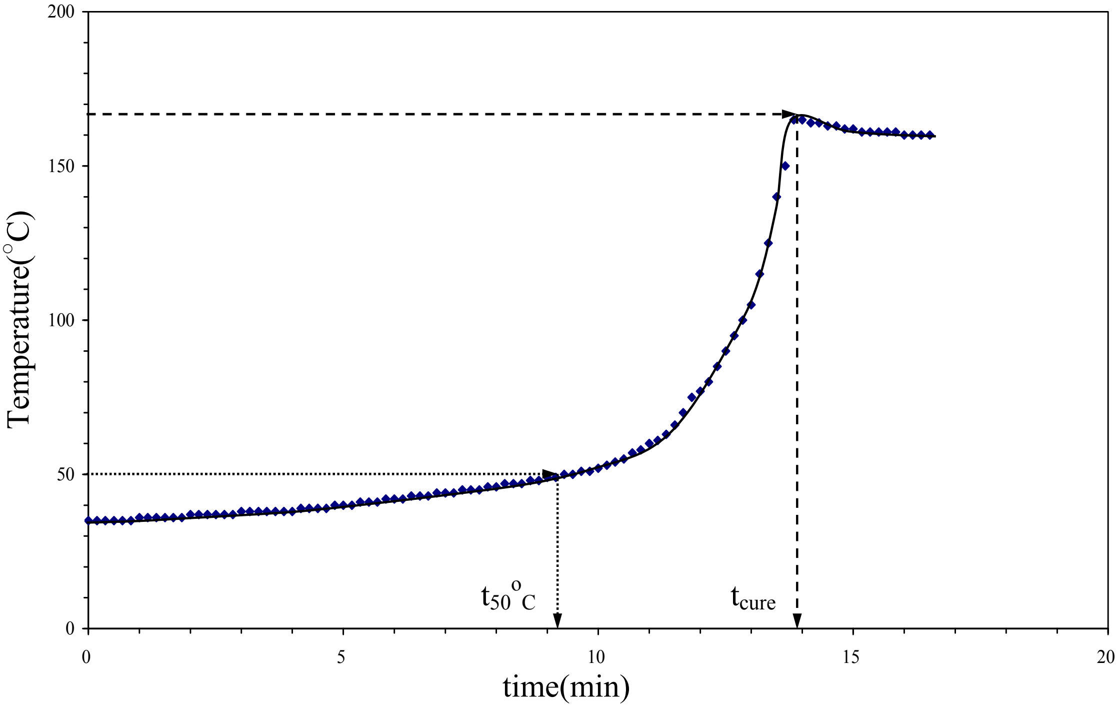


Figure 3.1 Time-temperature plotted of epoxy curing system.

3.3.3 Mechanical and Thermal Properties

3.3.3.1 Tensile and Flexural Testing

Tensile properties of the three layers laminated GFRP sample were obtained according to the ASTM D3039/D3039M using Instron Universal Testing Machine Model 5569 with the load cell of 50 kN. Tensile properties, by mean of tensile strength(σ_u), strain at break(ε_f) and Young's modulus(E) were reported. The constant strain rate of the cross head speed was electronically controlled at 2 mm/min. The rectangular shape specimen with 25 mm in width, approx. 1.5 mm in thickness and 250 mm in overall length were obtained by saw cutting from the GFRP sheet specimen. The saw mark on the specimen was removed by polishing using water sand paper. The specimen were then post cured and annealed at the given conditions. The gauge length of 140 mm was assigned. Ten specimens for each sample were tested and the average value was calculated.

The ASTM D5943 was assigned to investigate the three points bending flexural properties of GFRP using the Instron Universal Testing Machine Model 5565 with the load cell of 5 kN. The maximum load, maximum stress and flexural modulus were resolved. The test specimen was strained at the constant rate of 10 mm/min. The calculated span length of the test corresponded to the specimen geometry was 80 mm. The rectangular specimens, with three layers of stacking and 11 mm in width, 2 mm in thickness and 100 mm in overall length were saw cut and then polished from the laminated sheet. The curing condition of the specimen was achieved as the same manner as described earlier.

3.3.3.2 Heat Distortion Temperature Determination

Heat distortion temperature(HDT) of the GFRP was obtained according to ASTM D648. The manual DTUL/VICAT from Atlas with the standard load of 1820 kPa or 264 psi was applied. Silicone oil was used as heating transfermedia at the ramp rate of 120°C/hour. The specimen of rectangular specimens with 130 mm in length, 15 mm in width and 2 mm in thickness were tested. Three specimens were performed under the calculated loading weight at the assigned standard load. The HDT was recorded directly from the thermometer when the specimen had been deflected to 0.25 mm or 0.010 in.

3.3.3.3 Izod Impact Testing

According to the ASTM D 256, method A, the notched izod impact was investigated using Atlas Basic Pendulum Impact Tester Model BPI. The total striking impact energy of 5.4 J was assigned. The laminated specimens with 2 mm in thickness, 64 mm in length and 12 mm in width were saw cut and polished from the laminated sheet. The specimens were notched by notching machine with 2 mm of notch depth and then post cured. Ten specimens were tested on each sample. The impact strength(J/m^2) was calculated and reported.

3.3.3.4 Hardness Testing

In order to follow up the progress of degradation rate of the epoxy sample, the Duro Tech Model M202 SHORE D Scale was used for hardness measurement. The ASTM D2240 testing procedure was adopted. The 5 kg load was assigned. The degraded specimens with 1×1 cm^2 obtained from the degradation sites were examined. Five randomized positions for identification were specified on the outer surface of the sample. Consequently, the average value was obtained.

3.4 Degradation Observations

3.4.1 Photo Degradation under Natural Exposure Condition

The photo degradation performance that duplicates the open-air dumping of GFRP was experimented under tropical climate at the open site of Suranaree University of Technology. The specimen with 1×1 cm^2 of double layers GFRP was prepared.

According to ASTM D1435-85, Standard Practice for Outdoor Weathering Plastic, the samples were exposed to natural weather by attachment on the standard exposure rack as shown in figure 3.2. The rack as built in angle of 45° to the vertical and its plane was set to direct to the south. From this position, the sample had been exposed to the sunlight for all day long. Only one side of samples was directly exposed to the sunlight and the natural climate condition. The specimens were allowed to expose to the natural weather condition for a period of 180 days, started from August 2003 to February 2004. The test specimen was routinely sampled in every 15 days. The weight loss and hardness of sample were measured to monitor the proceed of degradation.

Figure 3.2 The standard arrangement for natural exposure experiment.

3.4.2 Photo Degradation under Accelerated Condition

The degradation time of the plastic sample under open-air dumping normally consume several months. The appropriate time for decomposition can be shortened into a weak when the accelerated chamber is used. This was successfully performed for the polystyrene foam degradation. The test results greatly correlated to the results of the experiment carried out under natural environment (Meekum and Kenharaj, 2002). In order to accelerate the degradation time of the GFRP, the Standard Weatherometer S 3000 manufactured by Atlas Electric Device Co., Ltd., was employed. The equipment mainly consisted of a boro-borosilicate inner filter, the Xeon arc lamp, compressed air system and deionized water using as spraying water. The boro-borosilicate inner filter and Xeon arc lamp were used to generate the continuous UV light at 340 nm. In this study, the power of the lamp irradiation was constantly controlled at 0.70 W/m^2 which was equivalent to the UV energy dose on the sample surface of 2.52 kJ/(m^2-hr). The compressed air and deionized water were mainly used to simulate the humidity by mean of rain shower and maintain the test chamber temperature. During the experiment, the boro-borosilicate inner filter was replaced with a new one in every 400 testing hours. The black panel temperature was calibrated by using the standard resistivity thermocouple device(RTD) supplied from manufacturer.

According to the weathering data of Nakorn Ratchasima Province obtained by the Climatology Division, Meteorological Department of Thailand as shown in table 3.4. It is shown that the average temperature, relative humidity and rainfall, and total solar radiation in this area were 27.7°C, 70.2%, 90.3 mm. and 8985 MJ/m^2, respectively. Consequently to the data obtained, the artificial test conditions of the standard weatherometer were set as summarized in table 3.5. The parameters were chosen as similarly as the real climate conditions except for the chamber temperature. The lowest temperature for the equipment is capability at 65°C. Therefore, testing temperature at 27.7°C that is equivalent to average value obtained for the Nakorn Ratchasima region was unable to establish. The irradiation intensity of the Xeon lamp set at 0.70 W/m^2 when exposed to the surface of the samples for 1964 hours was equivalent to the total solar radiation of 6898.5 MJ/m^2 per year obtained by sunlight in this region. The mathematical calculation for the equivalent means is shown in appendix A. The twelve pieces of rectangular GFRP specimen prepared from two layers lamination with 1.0×6.5 cm^2 were attached to the standard specimen holder and finally transferred onto the circular sample rack holder. The holder had been rotated at speed of 1 rpm. The specimens were also collected in every 116.9 hours of testing cycle. The weight loss and hardness test were used to investigate the degradation rate of GFRP.

Table 3.4 Meteorological data of Muang district Nakorn Ratchasima Province.

Meteorogical data	**Average value (per year)**
Temperature (°C)[a]	27.7
Relative Humidity (%)[a]	70.2
Rainfall (mm)[a]	90.3
Total solar radiation (MJ/m^2)[b]	6898.5

[a] Data collected from January 2000 to 2001 by Nakorn Ratchasima Climate station

[b] Data collected from January 2000 to 2001 by Khonkan Climate station

[Source: Nakorn Ratchasima and Khonkan Climate station, Climatological Division, Meteorological Department]

Table 3.5 The test parameters used for Standard Weatherometer equipment.

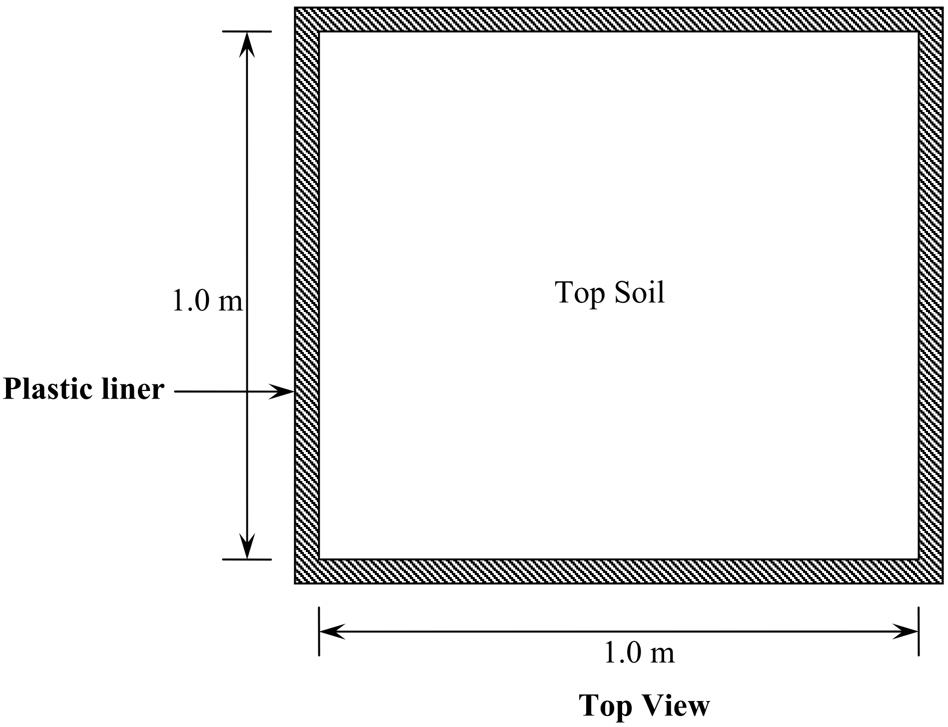
Condition	**Set-up Value**
Temperature(°C)	65±4
Spraying cycle(per hour)	2 mins
Irradiation(W/m^2)	0.70
Relative humidity(%)	70

3.4.3 Landfill Degradation

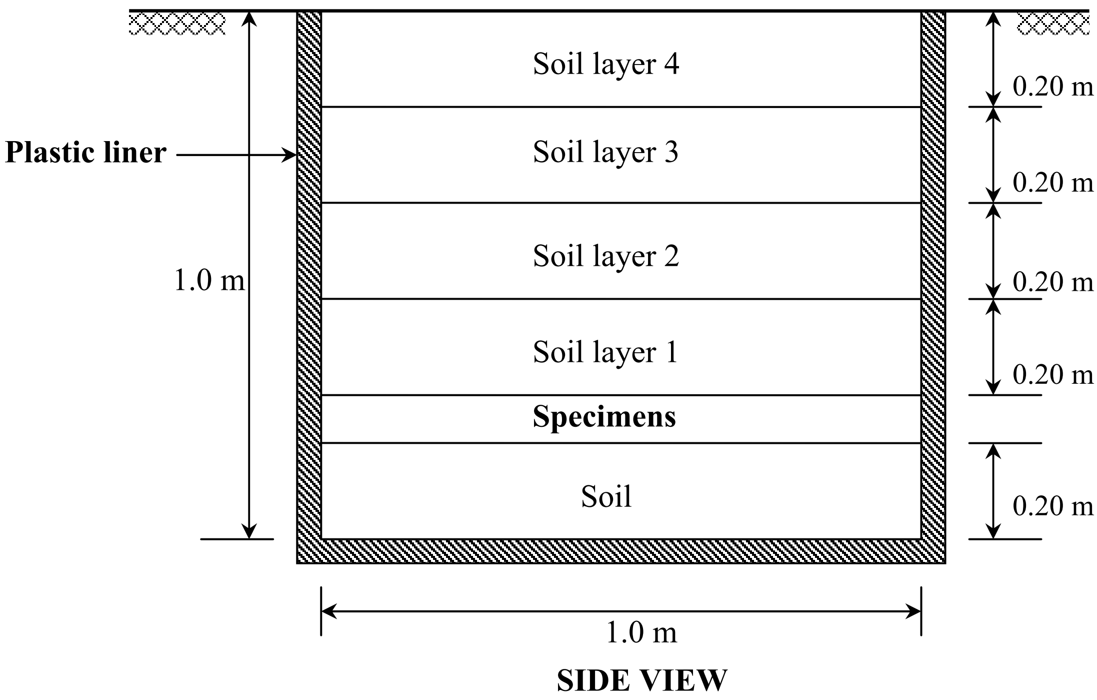
The landfill site was constructed at Suranaree University of Technology in order to study the decomposition of the GFRP sample under simulated landfill conditions. The individual landfill cell with dimension 1.0×1.0×1.0 m^3 were constructed and lined with plastic film as shown in figure 3.3. The bottom of the cell was overlaid with the excavated soil at the thickness of approximately 20 cm. The GFRP samples were then regularly laid over. The sample was covered with the multi-layers of topsoil which was sprayed with anaerobic bacterial nutrition, inorganic Sulfate and Nitrate aqueous solution. Approximately four layers of 20 cm of topsoil were used to fill-up the cell. In each of experiment, the concentration of inorganic Sulfate and Nitrate solution for spraying on the topsoil was 500 ppm. The sample was buried for a period of 180 days, started from August 2003 till February 2004. The test specimens were collected in every 15 days by using the hollowed metal pipe puncher. The GFRP samples were cleaned by washing with water several time and dried at 110°C under vacuum for 4 hours. The weight loss and hardness of GFRP sample were then investigated to study the degradation rate of GFRP. For the weight loss determination, the GFRP specimens were refluxed in acetone at 65°C for 4 hour in order to remove the degraded polymer chain.

3.4.4 Degradation Under Water Incubation

The degradation of the GFRP in two different water sources was studied. Wastewater and seawater were employed to duplicate the different deterioration environmental conditions. The swine wastewater from Suranaree University of Technology farm and seawater from Gulf of Thailand were used. To study the affect of fillers on the decomposition time of the GFRP in the waters, the square sample 1×1 cm^2 were used. The sample had been immersed in the 200 ml of glass jar contained with the desired soaking waters. The lid was opened to freely expose to the atmosphere. The incubation period used for investigation in this experiment was lasted from August 2003 to February 2004 for the total of 180 days. The water level was kept constant by toping with more water. The sample was randomly collected in every 15 days in order to evaluate the weight loss and hardness of the sample.



(a)



(b)

Figure 3.3 The cell lay-up in landfill condition experiment (a) top view (b) side view.

3.4.5 Degradation Evaluation

Hardness testing and weight loss analysis were used to investigate the sample degradation. The samples taken from the natural, accelerated, landfill and water incubated condition were cleaned by washing in water several times or until the specimen were visibly cleaned. It was then dried at 100°C under vacuum for 4 hours. The hardness of the degraded sample was tested as the same manner as described from the previous section.

In order to measure the weight loss of the sample, the GFRP specimens were dried in oven at 110°C for 4 hour under vacuum. The weight of the specimens(w_1) was then recorded. Accordingly, the GFRP specimens were refluxed in acetone at 65°C for 4 hour in order to remove the degraded polymer chain. The refluxed specimens were removed and again dried in vacuum oven at 110°C for 200 hours. It was observed that drying time less than 200 hours, performed on the referee sample, was not adequately removed the solvent residual. According to the previous work published by Gu and Liang(2003), it was reported that the epoxy cured with aliphatic amine was thermally degraded at temperature above 330°C. It was also observed that the residual volatile was removed at temperature around 200°C. Therefore, at this drying temperature the thermal degradation would not be occurred. Consequently, the weight of the refluxed sample was weighted and recorded(w_2). The weight loss is calculated according to the equation 3.4. Three specimens for each sample were tested and the average value was calculated.

$$Weight \quad loss(\%) = \frac{w_1 - w_2}{w_1} \times 100 \tag{3.4}$$

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Rheological and Curing Properties

4.1.1 Viscosity of Epoxy Resin

Viscosity of epoxy resin is one of the most important properties in the composite manufacturing process. Molecular weight strongly influence on viscosity of the epoxy resin. Otherwise, viscosity of epoxy resin is normally adjusted by adding the fillers. The thixotropes materials are added to prevent resin drainage prior to cure. A small amount of thixotrope materials results in high resin viscosity at low shear rates while the viscosity remains low at high shear rates (Mallick, 1997). A thixotropic material becomes more fluid with increasing time of applied force. The applied force could be string, pumping or shaking. This effect is sometimes called ‘work softening’. It is often reversible, so that if it left undistributed for some time a thixotropic slurry regains its viscosity.

The dependency of the viscosity of DGEBA, employed in this study with type and concentration of the fillers used are shown in figure 4.1. The result illustrates that viscosity of DGEBA is rapidly increased when 2% by weight of fumed silica was added. Vice versa their viscosities are almost unchanged with the fillers concentration for the rest. Except for the sodium borosilicate glass where its viscosity is obviously increased when more than 8% of the filler added. However, the thixotropic capability of the borosilicate is less than the fumed silica.

Table 4.1 is also shown the thixotropic index measurement as summarized in appendix A of the fillers. They are calculated from the viscosity measured at 1.0 rpm divided by viscosity at 10.0 rpm. The results confirmed that fumed silica has the highest index when compared with the other fillers used in this study. At this point forward, it can be pronounced that fly ash and starch can not used as thixotropic fillers in the epoxy based composites. It may only be used as filler for volume reduction.

This outcome indicated that fumed silica is still most suitable thixotropic material. Fly ash and starch can not be used for this purpose.

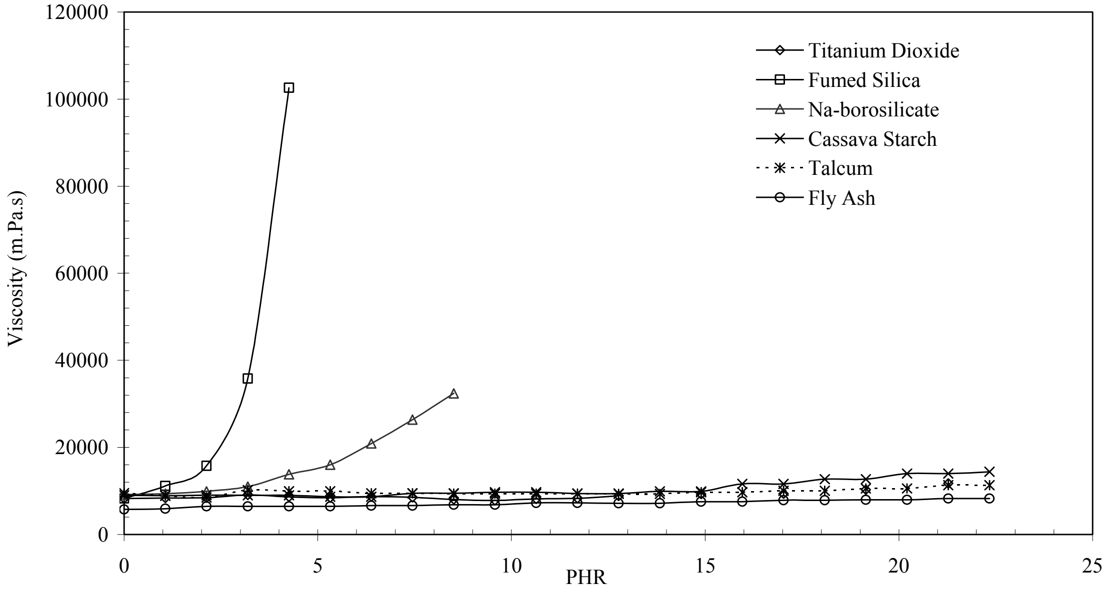


Figure 4.1 Dependency of the viscosity of epoxy resin on the filler contents.

Table 4.1 Thixotropic Index of the fillers.

Fillers	Thixotropic Index
Fumed silica[a]	2.71
Fly ash[b]	1.11
Talcum[b]	1.05
Titanium dioxide[b]	1.05
Cassava starch[b]	1.08
Sodium borosilicate glass[b]	1.06

[a] phr=5, [b] phr=10

4.1.2 Cure Properties

The effect of fillers added onto epoxy resin on the cure properties is prime interested in this research work. Fillers, fumed silica, fly ash, talcum, titanium dioxide, cassava starch and sodium borosilicate glass respectively was investigated. The dependency of the fillers content incorporated in the resin on the cure parameters were also observed. The fundamental curing parameters used for epoxy selection are t_{cure} and $t_{50^\circ C}$. The time-temperature plots for each of filler used are summarized in appendix C. The t_{cure} and $t_{50^\circ C}$ values resolved from the plots were concluded in table 4.2.

Table 4.2 The cure times of the fillers filled DGEBA epoxy cured with TETA at 35°C.

phr	**Neat resin**[a]		**Fumed silica**[b]		**Fly ash**		**Talcum**		**Titanium dioxide**		**Cassava starch**		**Na-borosilicate**	
	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}
1	18	24	20	24	18	23	17	24	18	23	15	20	18	23
3	18	23	17	21	19	23	15	23	19	23	14	19	16	21
5	17	23	18	22	18	23	16	24	19	24	14	19	16	21
7	16	22	18	21	19	22	17	24	19	24	14	18	15	21
9	15	21	17	21	19	23	17	26	18	22	13	17	13	18
11	13	20	14	18	18	22	17	26	17	23	15	18	17	21

Remark: [a]Neat resin is not related with phr, [b]phr of fumed silica is 0.5, 1, 1.5, 2, 2.5 and 3 respectively

General observation from the table, it is shown that there is slightly changed in the t_{cure} and $t_{50^\circ C}$ of the epoxy with the filler concentration. Especially when comparing between the filler content at 1 phr and 11 phr, the difference is quit obvious. However, the tendency of the change is ambiguous.

In order to make clear conclusion for the dependency of the concentration and the type of fillers on the cure parameters of epoxy resin, the two factors analysis of variance or two-way ANOVA method was employed. The basis principle of the analysis is to divide the variance of total data(SS_T) into three component parts namely, the summation of variance from factor A(SS_A), the summation of variance from factor B(SS_B) and variance within groups or variance of error(SS_E), as shown in equation 4.1.

$$SS_T = SS_A + SS_B + SS_E \tag{4.1}$$

The SS_A, SS_B and SS_E are calculated by using the following equations;

$$CM = (\sum\sum X_{ij})^2 = T^2 / n \tag{4.2}$$

$$SS_T = \sum\sum(X_{ij} - \overline{\overline{X}})^2 = \sum\sum X_{ij}^2 - CM \tag{4.3}$$

$$SS_A = b\sum(\overline{A}_{i.} - \overline{\overline{X}})^2 = \sum A_i^2 / b - CM \tag{4.4}$$

$$SS_B = a\sum(\overline{B_{.j}} - \overline{\overline{X}})^2 = \sum B_{.j}^2 / a - CM \tag{4.5}$$

$$A_i = \sum_{j=1}^{b} x_{ij} \ , \ \overline{A_{i\cdot}} = A_i / b \tag{4.6}$$

$$B_j = \sum_{ij}^{a} x_{ij} \ , \ \overline{B_{\cdot j}} = B_j / a \tag{4.7}$$

$$T = \sum \sum X_{ij} = \sum A_i = \sum B_j \tag{4.8}$$

$$n = ab \tag{4.9}$$

$$\overline{\overline{X}} = T / n = T / ab \tag{4.10}$$

Where

x_{ij} = the data from level ith of factor A and level jth of factor B; i= 1, 2 ..a; j= 1, 2..., b

A_i = the summation of the data from level ith of factor A and all level of factor B

B_j= the summation of data from level jth of factor B and all level of factor A

T = the grand total of all data

n = the number of total data

a = the number of factor A

b = the number of factor B

$\mu_{i.}$ = mean value of the data from level ith of factor A; i=1, 2,…,a

$\mu_{.j}$ = mean value of the data from level ith of factor B; j=1, 2,…, b

$\overline{\overline{X}}$ =the average of total data

From the results presented in table 4.2, The factor A of the experimental data, as given by the type of the fillers, is 7 as neat resin, fumed silica, fly ash, talcum, titanium dioxide, cassava starch and sodium borosilicate glass respectively. The factor B can be specified by the concentration of fillers that have six groups, phr equal to 1, 3, 5, 7, 9 and 11 respectively. Therefore, b is equal to 6. The test hypothesizes, null(H_o) and alternative(H_1), utilized in this study are given as;

H_o: $\mu_{1.}=\mu_{2.}=\mu_{3.}=\mu_{4.}=\mu_{5.}=\mu_{6.}=\mu_{7.}$

It means that the cure time of epoxy resin does not depend on
the type of the fillers.

And **H_1:**$\mu_{.i}\neq\mu_{.j}$ at least 1 pair of data; i ≠j; i, j = 1,2,…,k

It means that the cure time of epoxy resin does depend on
the type of the fillers.

The statistical *f*-test could then be used to verify the level of confidence regarding to the hypothesizes acceptation/rejection. The value of the f_{cal} can be calculated by using equation 4.11, and compare with the critical value ($f_{1-\alpha,\ a-1,\ (a-1)(b-1)}$ or f_{crit}) that is shown in the statistical table of the *f* distribution in Appendix D. If the $f_{\text{cal}} < f_{\text{crit}}$, then the H_o is accepted. Vice versa, the H_o would be rejected.

$$f = \frac{MS_A}{MS_E} \tag{4.11}$$

$$\text{Mean square}\,(MS_A) = \frac{SS_A}{v_1} \tag{4.12}$$

$$\text{Mean square}\,(MS_E) = \frac{SS_E}{v_3} \tag{4.13}$$

where v_1= degree of freedom of SS_A=a-1

and v_3= degree of freedom of SS_E= (a-1)(b-1)

In this study, the level of significance(α) for accepting H_o is 0.05. The calculated f values of the experimental data obtained by using the equations 4.1 to 4.13 are shown in table 4.2.

Table 4.3 ANOVA table of two factors, type and concentration of fillers, test.

Source of Variation	**Degree of Freedom**		**Sum of square**		**Mean Square**		**Calculated** f_{cal}		**Critical** f_{crit}	
	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}	$t_{50^\circ C}$	t_{cure}
Factor A	6	6	82.81	128.81	13.80	21.47	8.62	15.11	2.42	2.42
Factor B	5	5	16.12	17.05	3.22	3.41	2.01	2.40	2.53	2.53
Error	30	30	48.05	42.62	1.60	1.42				
Total	41	41	146.98	188.48						

According to the statistic test results, it reviews that the calculated, f_{cal}, of factor A and factor B for the t_{cure} are 15.11 and 2.40 respectively. And the critical value(f_{crit}), obtained from the statistical table of factor A and factor B are 2.42 and 2.53. As result, the f_{cal} of only factor A is greater than the critical value, then the H_o is rejected. From the statistical testing, it is reinforced that the t_{cure} of epoxy resin does depend on only the type of filler. Also, the calculated f of factor A and factor B for

$t_{50^{\circ}C}$ are 8.62 and 2.01 respectively. And the critical value, obtained from the statistical table of factor A and factor B in appendix D, are 2.42 and 2.53. Also, the calculated f of only factor A is greater than the critical value, then the H_o is rejected. However, the value obtained from factor B is less than the critical value. This is indicated that the $t_{50^{\circ}C}$ of the epoxy system does not depend on the filler content. From the statistical testing results, it can be concluded that the $t_{50^{\circ}C}$ of the epoxy resin employed in this work does depend on only the type of filler but does not depend on the fillers content. The dependency of the filler types could be due to their acidity as especially for the inorganic fillers.

4.2 Mechanical and Thermal Properties of GFRP

The ultimate tensile strength(σ_u), Young's modulus(E) and Tensile strain at break(ε_f) of GFRP cured with three hardening systems, TETA, DDS and TETA/DDS, and filled with six fillers are summarized in table 4.4. In the samples cured with TETA and using fly ash and cassava starch as filler, they are found that the ultimate tensile strength and Young's modulus are slightly higher than sample using fumed silica but obviously higher than neat resin, fumed silica, talcum, titanium dioxide and sodium borosilicate glass. There is no significantly difference with in the strain at break. On the other hand, the tendency is difference in the DDS system. They are observed that the tensile properties of cassava starch and fly ash added are lower than neat resin but similarly to those fillers used. However, in the TETA/DDS system, the ultimate tensile strength of fly ash added are the highest among all fillers but in these curing system the ultimate tensile strength of the starch added is less than fumed silica and fly ash. These imply that cassava starch and fly ash could be used as the fillers to improve the mechanical properties of the TETA/Epoxy system but they do not enhance the tensile properties of the high temperature cure system, DDS.

Impact strength(G_c), flexural strength(σ_{max}) and HDT of GFRP cured with three hardening systems are summarized in table 4.5. It is obviously seen that the impact strength and flexural strength of the TETA, DDS and TETA/DDS cured and using fly ash and cassava starch as filler, respectively, are lower than the unfilled resin. As well as the starch filled samples where the HDT are depressed except for the DDS cured system. Generally HDT of epoxy is slightly increased by adding the filler as visibly seen for the other fillers used in this study. For the toughness properties reported, they are incompetence by all fillers except for fumed silica. This is due to the fact that introduction foreign particle into epoxy would create more void content in the matrix. Consequently, the fracture toughness would decrease.

In order to verify and compare the dependency of one filler to the others and also its curing systems on the properties of GFRP. The Kruskal-Wallis ANOVA test, as the mathematically calculation are described in appendix E, was adopted. Typically, two statistical hypothesizes, null(H_o) and alternative(H_1) will be identified as shown below;

$\boldsymbol{H_o}$ **:** The seven types of the filler can not be differentially evaluated

and $\boldsymbol{H_1}$ **:** One type or another of the filler can be differentially evaluated

If H_o is accepted, it means that the properties of GFRP do not depend on the fillers. Vice versa, accepting H_1 means that using different fillers would cause in the variation of the properties of the GFRP.

In this study, the level of significance(α) for accepting H_o was given at 0.05 or 95% confidential. For example, using the 35 data samples, 5 specimen for 7 samples, of the tensile property by means of ultimate tensile strength(σ_u) of TETA curing system, the tested data are summarized in table 4.6.

From table 4.6, the σ_u are ranked from the smallest, 48.11 MPa, assigned as R_1 to the the largest, 112.79, R_{35}. If the calculated T or T_{cal} is greater than critical value T or T_{crit}. at the region of approximate size of α=0.05, the H_o will be rejected. The random sample(k) assigned as the type of filler is equal to 7 and hence the degree of freedom(k-1) equal to 6 and there are no ties. The quantile of a chi-squared random variable, which is equivalent to T_{crit}, taken from table D2 in Appendix D, is 12.6. The calculated T for testing σ_u of the samples the using equation E5, as shown in appendix E, is equal to 27.5. It is seen that the T_{cal} is a higher than the T_{crit}. Therefore, H_o is rejected or accepting H_1. It means that the ultimate tensile strength of TETA/Epoxy system does depend on the fillers used.

From the results tested and summarized in table 4.5 and using the statistical approach similar to the procedure described above, the statistical test results are reported in table 4.7. All the T_{cal} values obtained from mechanical properties except strain at break are higher than the T_{crit}. As expected the test results for the HDT is less than the T_{crit}. From this statistical data it indicated that the mechanical properties of the GFRP cured with TETA system depend on the fillers employed. Contradictorily, the thermal property by mean of HDT does not significantly depend on the fillers.

The statistical approach was also used to analyses the DDS/Epoxy and TETA/DDS/Epoxy systems and the results are reported in table 4.8 – 4.9. The similar conclusions are observed. It is also found that the HDT of the systems are not depended on the fillers incorporated. From the results obtained above, it can be conclude that, cassava starch and fly ash can be used to enhance the tensile properties of the GFRP derived from TETA and TETA/DDS as curing systems. However, the fracture and, perhaps, thermal properties of the reinforcement samples were incompetence by adding fillers especially fly ash and starch. Those mechanical properties are fluctuated by type of filler used.

Table 4.4 Tensile properties of GFRP cured with TETA, DDS and TETA/DDS mixture system.

Filler	TETA			DDS			TETA/DDS mixture		
	σ_u (Mpa)	E (MPa)	ε_f (%)	σ_u (MPa)	E (MPa)	ε_f (%)	σ_u (MPa)	E (MPa)	ε_f (%)
Neat resin	63.01±8.60	4.68±0.27	1.70±0.15	104.51±4.55	5.63±0.52	2.22±0.14	86.61±7.33	5.11±0.34	2.10±0.18
Fumed silica^a	92.41±12.4	6.08±0.30	1.70±0.15	60.57±6.02	4.30±0.29	1.75±0.14	104.43±6.48	5.37±0.95	2.31±0.34
Fly ash^b	102.66±6.8	6.31±0.62	1.99±0.13	66.37±6.72	5.16±0.07	1.59±0.13	107.71±16.54	5.96±0.50	2.20±0.37
Talcum^b	83.08±5.34	5.66±0.28	1.88±0.12	61.68±5.10	4.94±0.23	1.57±0.11	97.92±15.65	5.58±0.42	2.09±0.27
Titanium dioxide^b	81.29±6.02	5.78±0.23	1.78±0.11	81.83±3.99	5.84±0.24	1.72±0.06	75.86±6.73	6.16±0.83	1.61±0.17
Cassava starch^b	95.47±8.56	6.18±0.46	1.94±0.14	82.97±3.46	5.46±0.31	1.83±0.08	98.48±2.34	5.37±0.90	2.27±0.26
Sodium borosilicate glass^b	72.25±6.95	4.94±0.39	1.86±0.23	61.33±7.05	4.53±0.09	1.71±0.17	80.37±4.45	5.09±0.61	1.96±0.22
Remark: ^{a}phr=2, ^{b}phr=5									

Table 4.5 Mechanical and thermal properties of GFRP cured with TETA, DDS and TETA/DDS mixture system.

Filler	**TETA**			**DDS**			**TETA/DDS mixture**		
	G_c (kJ/m^2)	σ_{max} (MPa)	HDT (°C)	G_c (kJ/m^2)	σ_{max} (MPa)	HDT (°C)	G_c (kJ/m^2)	σ_{max} (MPa)	HDT (°C)
Neat resin	67.25±13.17	221.10±10.70	87±2	54.47±11.96	240.18±13.67	128±2	56.61±13.48	183.01±11.64	126±2
Fumed silica^a	68.37±8.58	225.51±13.95	89±2	81.98±9.46	227.82±13.43	147±1	57.09±10.19	160.83±11.47	130±1
Fly ash^b	55.46±8.64	163.51±13.74	87±1	41.48±4.60	210.43±11.19	150±1	44.151±8.07	138.15±13.82	132±2
Talcum^b	51.95±8.42	165.08±9.69	89±1	50.68±6.49	227.84±9.04	136±1	48.93±5.30	127.97±8.74	126±2
Titanium dioxide^b	37.25±12.37	152.76±9.58	86±2	43.27±12.32	175.63±16.63	144±2	41.74±2.74	166.96±2.65	125±1
Cassava starch^b	51.55±7.73	189.57±16.06	86±1	50.66±8.03	196.62±15.30	144±2	51.55±7.73	121.77±22.65	120±2
Sodium borosilicate glass^b	48.74±5.03	185.14±12.97	87±1	46.39±11.53	185.09±9.73	144±1	40.23±7.10	164.19±19.42	131±1
Remark : ^{a}phr=2, ^{b}phr=5									

Table 4.6 The ANOVA test of the tensile properties of TETA system.

Neat resin		**Fumed silica**^{a}		**Fly ash**^{b}		**Talcum**^{b}		**Titanium dioxide**^{b}		**Cassava starch**^{b}		**Sodium boro silicate glass**^{b}	
σ_u (Mpa)	Rank (Rij)	σ_u (Mpa)	Rank (Rij)	σ_u (Mpa)	Rank (Rij)	σ_u (Mpa)	Rank (Rij)	σ_u (Mpa)	Rank (Rij)	σ_u (Mpa)	Rank (Rij)	σ_u (Mpa)	Rank (Rij)
70.01	6	112.79	35	97.59	29	84.74	18	88.11	22	93.70	26	74.27	9
64.37	3	89.51	23	96.64	28	84.70	17	77.31	13	89.63	24	72.71	7
67.24	5	80.89	16	99.31	30	76.42	10	80.83	15	101.83	31	76.96	11
48.11	1	84.91	19	107.57	33	90.19	25	86.39	21	106.47	32	60.27	2
65.33	4	93.93	27	112.17	34	79.37	14	73.79	8	85.74	20	77.06	12
R_i	19		120		154		84		79		133		41
n_i	5		5		5		5		5		5		5
R_i^2/n_i	72.2		2880		4743.2		1411.2		1248.2		3537.8		336.2
Remark : ^{a}phr=2, ^{b}phr=5													

Table 4.7 Summary of the Kruskal-Wallis test of TETA curing system.

Test properties	**R_i^2/n_i**							**df (k)**	T_{cal}	T_{crit}	**Conclusion**
	Neat resin	**Fumed[a] silica**	**Fly ash[b]**	**Talcum[b]**	**Titanium[b]**	**Cassava starch[b]**	**Na-borosilicate[b]**				
σ_u	3.8	24.0	30.8	16.8	15.8	26.6	8.2	6	27.5	12.6	H_1 accepted
ε_f	15.0	18.5	18.5	18.5	18.5	18.5	18.5	6	6.0	12.6	H_0 accepted
E	4.6	26.0	27.0	16.4	19.2	19.2	6.8	6	24.7	12.6	H_1 accepted
G_c	53.2	56.6	38.1	31.4	5.4	5.4	26.0	6	42.3	12.6	H_1 accepted
HDT	10.3	16.8	11.3	17.5	6.5	6.5	8.2	6	10.4	12.6	H_0 accepted
σ_{max}	30.2	30.0	9.4	9.2	7.4	7.4	19.2	6	26.9	12.6	H_1 accepted

Remark : [a]phr=2, [b]phr=5

Table 4.8 Summary of the Kruskal-Wallis test of DDS curing system.

Test properties	R_i^2/n_i							df (k)	T_{cal}	T_{crit}	Conclusion
	Neat resin	Fumed[a] silica	Fly ash[b]	Talcum[b]	Titanium[b]	Cassava starch[b]	Na-borosilicate[b]				
σ_u	33.0	9.0	13.6	9.8	25.2	25.6	9.8	6	27.1	12.6	H_1 accepted
ε_f	19.5	19.5	16.0	12.5	19.5	19.5	19.5	6	9.2	12.6	H_0 accepted
E	26.4	4.2	18.9	14.3	31.0	24.1	7.1	6	28.6	12.6	H_1 accepted
G_c	42.2	64.5	18.1	40.5	18.2	39.1	25.9	6	39.1	12.6	H_1 accepted
HDT	2.0	17.0	20.0	5.0	11.7	10.8	10.5	6	18.5	12.6	H_1 accepted
σ_{max}	31.6	35.2	16.8	25.2	4.6	11.2	11.4	6	26.6	12.6	H_1 accepted
Remark : [a]phr=2, [b]phr=5											

Table 4.9 Summary of the Kruskal-Wallis test of TETA/DDS mixed system.

Test properties	R_i^2/n_i							**df (k)**	T_{cal}	T_{crit}	**Conclusion**
	Neat resin	**Fumed silica**[a]	**Fly ash**[b]	**Talcum**[b]	**Titanium**[b]	**Cassava starch**[b]	**Na-borosilicate**[b]				
σ_u	13.4	26.6	27.4	21.2	5.8	22.2	9.4	6	20.7	12.6	H_1 accepted
ε_f	17.5	20.8	24.1	17.5	11.1	17.5	17.5	6	12.1	12.6	H_0 accepted
E	10.1	18.4	25.6	20.2	26.2	13.4	12.1	6	11.8	12.6	H_0 accepted
G_c	50.1	54.0	24.2	39.5	19.4	44.3	17.0	6	33.3	12.6	H_1 accepted
HDT	8.7	15.7	18.5	8.5	6.8	2.0	16.8	6	17.4	12.6	H_1 accepted
σ_{max}	31.6	21.0	12.4	6.4	24.0	6.6	24.0	6	26.8	12.6	H_1 accepted

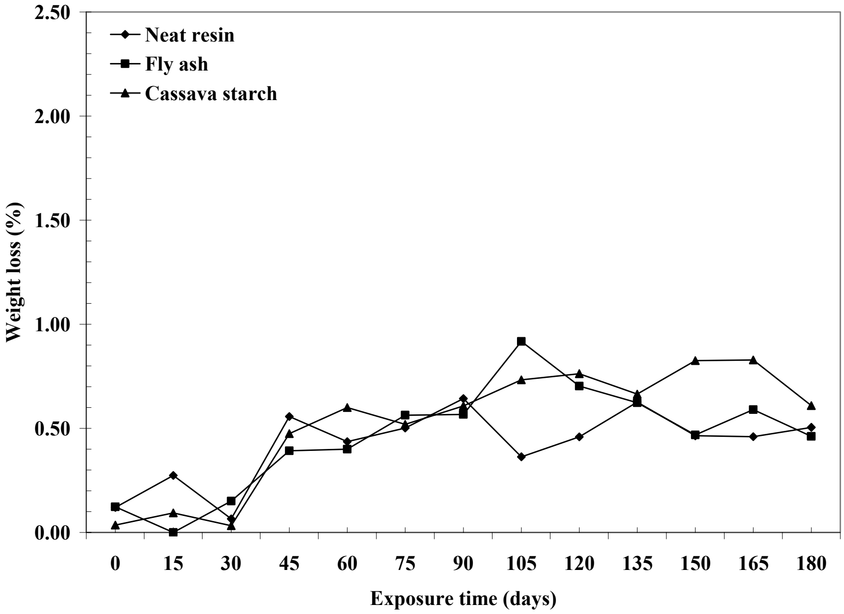
Remark : [a]phr=2, [b]phr=5

4.3 Photo Degradation

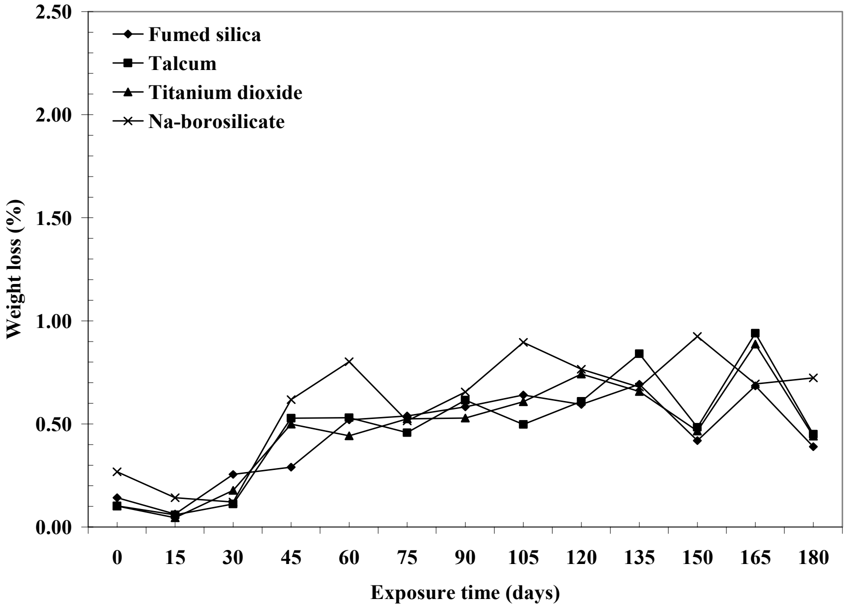
4.3.1 Under Natural Exposure

In order to determine the deterioration of the GFRP, the polymer degradation experiment under natural exposure was designed for a period of 6 months. Hardness testing and weight loss analysis were used for following the progress of the GFRP degradation. The results are shown in figure 4.2(a) and (b) where the % weight loss of the GFRP cured with TETA plotted with exposure times. Consequently, the hardness of TETA system under natural exposure condition are shown in figure 4.3(a) and (b). Form the % weight loss plotted with the exposure times, the data are highly scattered. Similarly to those plotted between hardness and the explosion times for all filler used. Within the possible errors and close observation, the plots seem to indicate that the weight reduction is started within the period of 30-60 days of exposure period. It would begin at the surface of the sample. From the visual observation, at this stage of degradation the sample had turned to dark brown.

The % weight loss and the hardness of TETA/DDS system under natural exposure condition shown in figure 4.4(a) - (b) and figure 4.5(a) - (b), respectively. The degradation was visibly noticed from the 30th and the loss continuously increased. The degradation of sodium borosilicate glass is more visible than other fillers. The data of hardness of the sample are highly scattered. The certain discussion could not be drawn. However, within the given error the plots seem to indicate that the hardness reduction is begun within the period of 30 - 60 days of exposure.

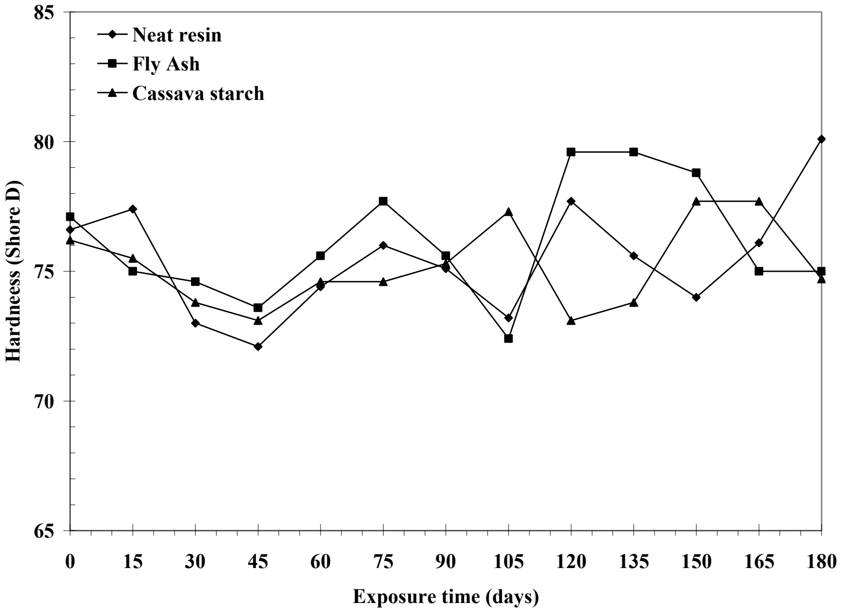


(a)

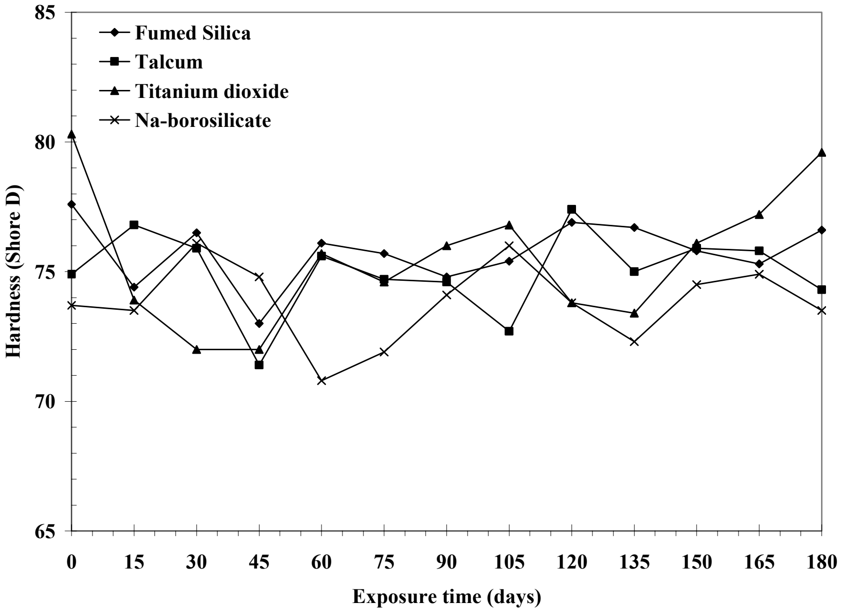


(b)

Figure 4.2 Weight loss of TETA system under natural exposure condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

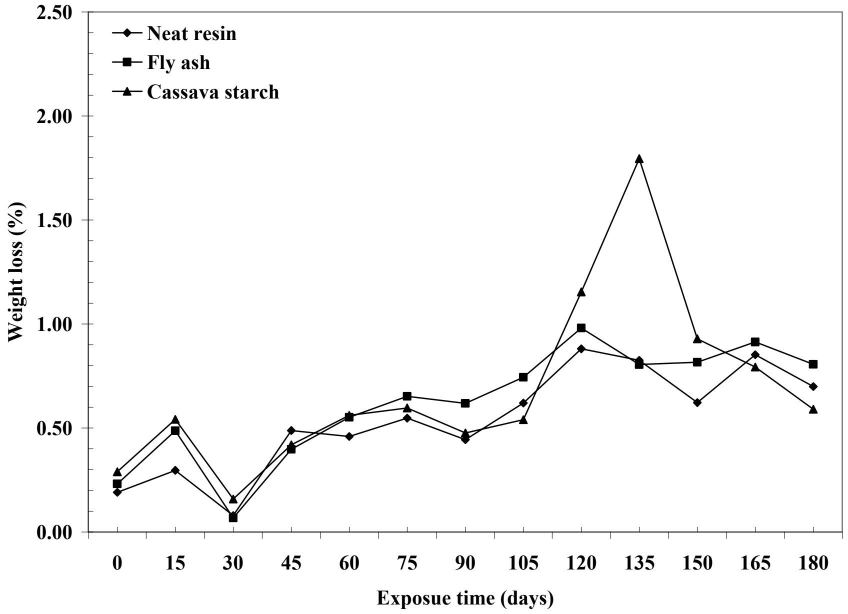


(a)

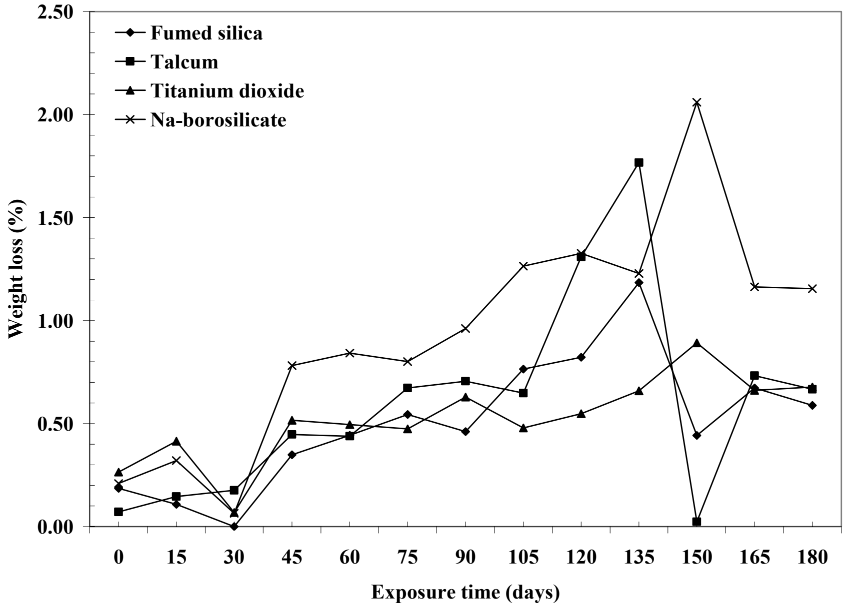


(b)

Figure 4.3 Hardness of TETA system under natural exposure condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

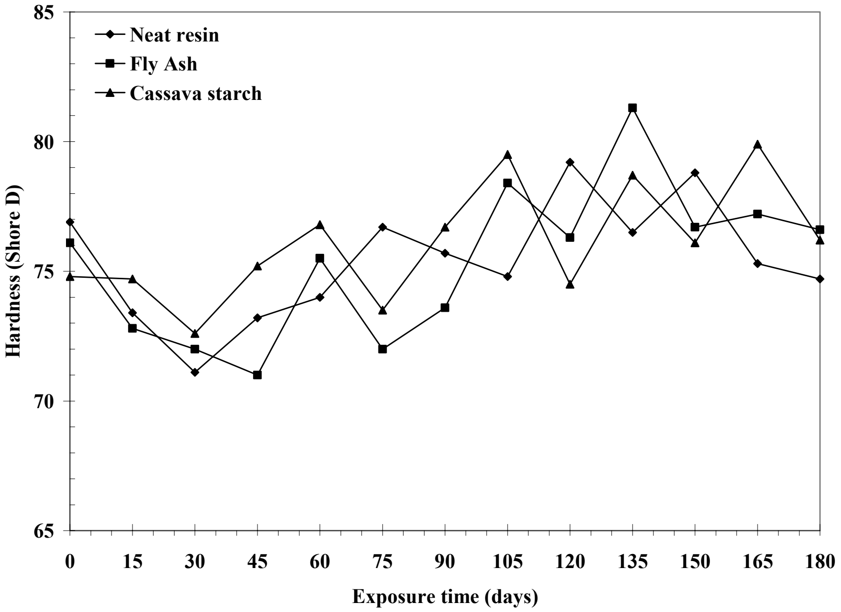


(a)

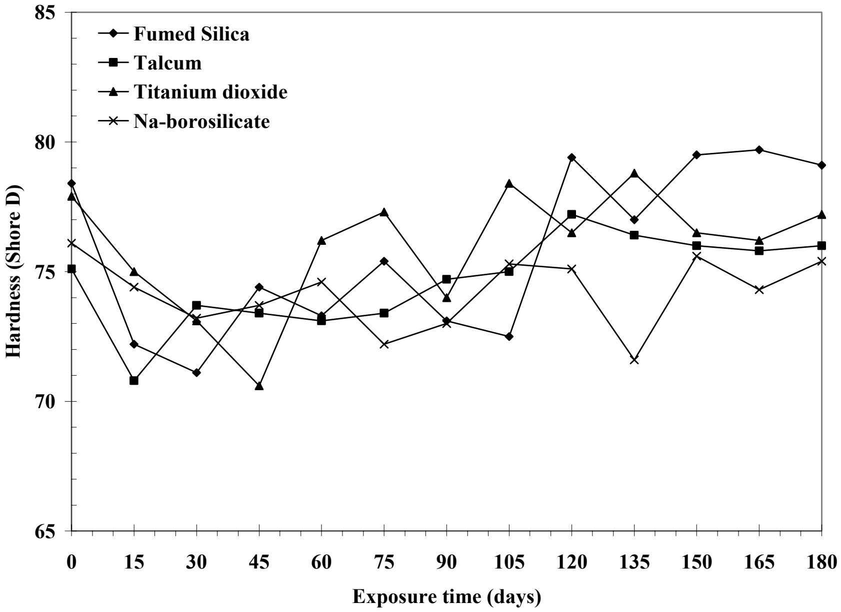


(b)

Figure 4.4 Weight loss of TETA/DDS system under natural exposure condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

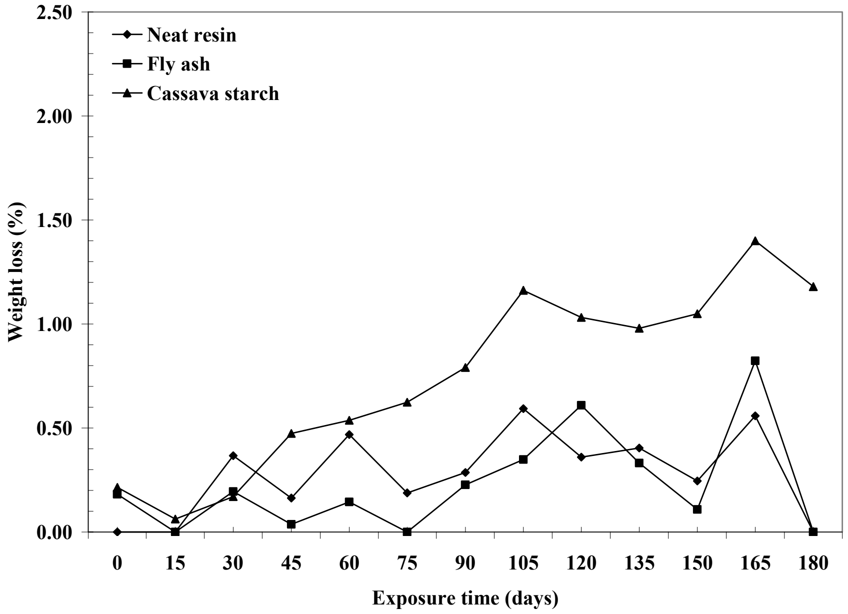


(a)

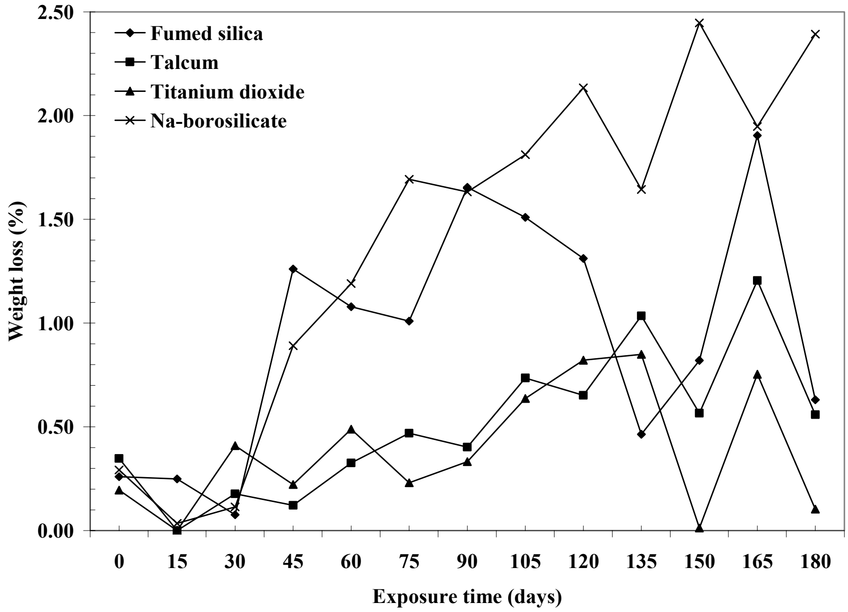


(b)

Figure 4.5 Hardness of TETA/DDS system under natural exposure condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

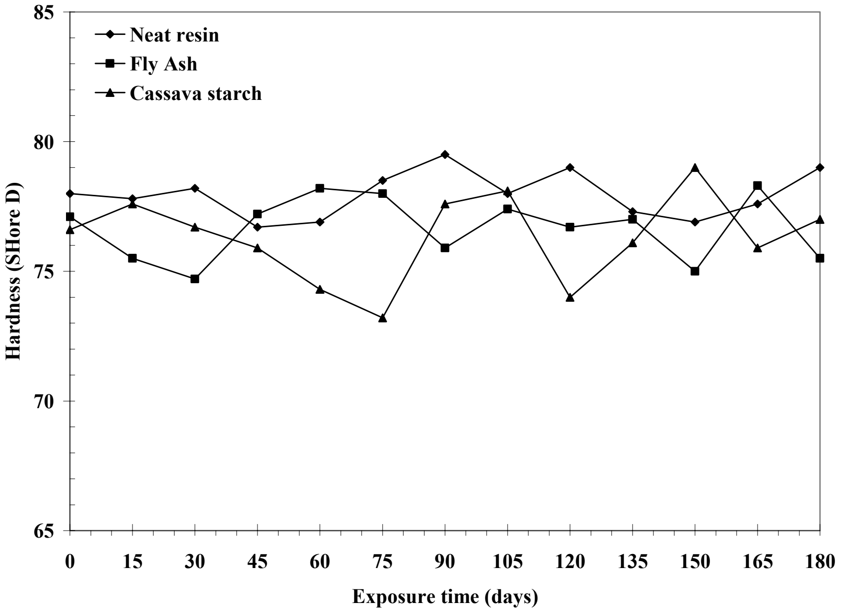


(a)

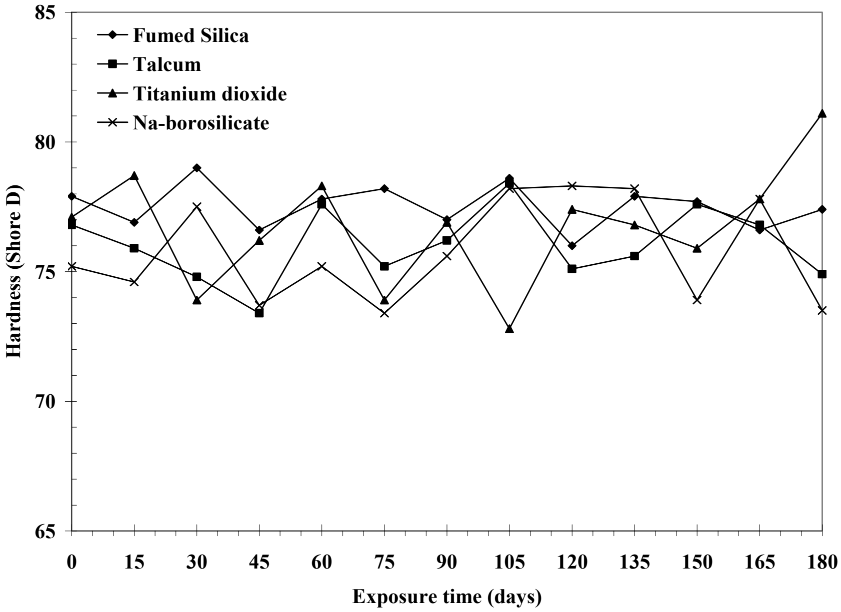


(b)

Figure 4.6 Weight loss of DDS system under natural exposure condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



(a)



(b)

Figure 4.7 Hardness of DDS system under natural exposure condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

The % weight loss and the hardness of DDS system under natural exposure condition also shown in figure 4.6(a) - (b) and figure 4.7(a) - (b). Similar trend that found for the previous systems is repeated. They are indicated that the degradation is occurred within the period of 30-60 days. However, the weight reductions of cassava starch, talcum and sodium borosilicate glass are more obviously noticed than the other fillers.

Taking the results obtained, they would pronounce that GFRP prepared using TETA, TETA/DDS and DDS as hardener and filled with those given fillers when subjected to the natural exposure they are begun to degrade with in 1-2 months. The surface degradation as found by Hepburn, Kemp and Cooper (2000) would responsible for the degradation.

In order to have the solid conclusion on the dependency of the type of fillers and degradation time of the GFRP, the two factors analysis of variance or two-way ANOVA method is performed using the same principle as mentioned earlier.

From the results presented in figure 4.2s, The factor A of the experimental data that assigned by the type of the fillers is classified into seven groups; neat, fumed silica, fly ash, talc, titanium, starch and sodium borosilicate glass respectively, and equal to 7. The factor B that given by the degradation time and clustered into six groups; 30, 60, 90, 120, 150 and 180 days and therefore, it equals to 6. So that, the test hypothesizes adopted in this study are;

H_o(A): $\mu_{1.}=\mu_{2.}=\mu_{3.}=\mu_{4.}=\mu_{5.}=\mu_{6.}=\mu_{7.,}$ it means that the weight loss of GFRP does not depend on the type of the fillers

and **H_1(A):**$\mu_{.i}\neq\mu_{.j}$ at least a pair of data; i ≠j; i, j = 1,2,…,7, it means that the weight loss of GFRP does depend on the type of fillers and;

H_o(B): $\mu_{1.}=\mu_{2.}=\mu_{3.}=\mu_{4.}=\mu_{5.}=\mu_{6}$, it means that the weight loss of GFRP does not depend on the time

and **H_1(B):** $\mu_{.i}\neq\mu_{.j}$ at least a pair of data; $i\neq j$; i, j = 1,2,…,6, it means that the weight loss of GFRP does depend on the time

The Statistical Package for Social Science(SPSS) Windows^{TM} based commercial software was applied to resolve the statistical analysis. According to the SPSS calculation, if the level of significance(α) is less than the given value, then, the hypothesis H_o will be accepted. Vice versa the H_o will be rejected.

Table 4.10 shows the two way ANOVA test for the weight loss experiment using SPSS with the level of significance of 0.05. For the natural exposure condition, it is found that the calculated significance of all curing systems for both factors is less than the level of significance. From this statistical determination, the preliminary conclusion could be drawn that all curing systems under open air degradation are depend on the type of filler and all time.

Table 4.11 shows the two way ANOVA test results for the hardness analyzed using SPSS at 0.05 level of significance. The results review that the calculated numbers of the filler factor, A, and the time factor, B, of the TETA and DDS curing systems are greater than the critical level of significance. However, reverse trend is observed for the TETA/DDS. These figures had led to the conclusion the degradation of GFRP, prepared from these hardeners, do not depend on the type of fillers added and also the exposure time. Vice versa the TETA/DDS system is depended on only factor A, the exposure time.

From the ANOVA tests based on the weight loss and sample hardness observation, it could announce that the degradation of the TETA/DDS cured reinforcements sample had been underwent degradation under natural exposure condition. Vice versa, the degradation of the system cured with the TETA and DDS could not be occurred within the given experimental time in this study.

Table 4.10 Summary results of the two ways ANOVA test of % weight loss under natural exposure condition.

Curing system	**Factor**	**TypeIII sum of Square**	**Df**	**Mean square**	**Sig.**	**Conclusion**
TETA	Filler(A)	0.260	6	4.339E-02	0.001	H_1(A)Accepted
	Time(B)	2.113	6	0.352	0.000	H_1(B)Accepted
DDS	Filler(A)	8.202	6	1.367	0.000	H_1(A)Accepted
	Time(B)	3.533	6	0.589	0.007	H_1(B)Accepted
TETA/DDS	Filler(A)	1.279	6	0.213	0.008	H_1(A)Accepted
	Time(B)	4.548	6	0.758	0.000	H_1(B)Accepted

Table 4.11 Summary results of the two ways ANOVA test of hardness under natural exposure condition.

Curing system	**Factor**	**TypeIII sum of Square**	**Df**	**Mean square**	**Sig.**	**Conclusion**
TETA	Filler(A)	39.633	6	6.605	0.107	H_o(A)Accepted
	Time(B)	28.490	6	4.748	0.254	H_o(B)Accepted
DDS	Filler(A)	32.694	6	5.449	0.085	H_o(A)Accepted
	Time(B)	2.122	6	0.354	0.991	H_o(B)Accepted
TETA/DDS	Filler(A)	10.694	6	1.782	0.570	H_o(A)Accepted
	Time(B)	122.122	6	20.354	0.000	H_1(B)Accepted

4.3.2 Accelerated Condition

Under the natural sunlight, the plastic samples take several months or years to decompose. Therefore, the simulated artificial high energy sources known as accelerated weather is normally elected to replicate the decomposition time of GFRP in a shorter time. The system had been successfully used for studying the degradation of thermoplastic waste (Meekum and Kenharaj, 2002). In this study, the standard weatherometer, S3000 was employed as described in earlier in Chapter III, the experimental data obtained from this study was used to compare with the information gained from the normal exposure. By using the artificial chamber, the exposure period of 1964 hours is equivalent to a year explosion time under the natural atmosphere.

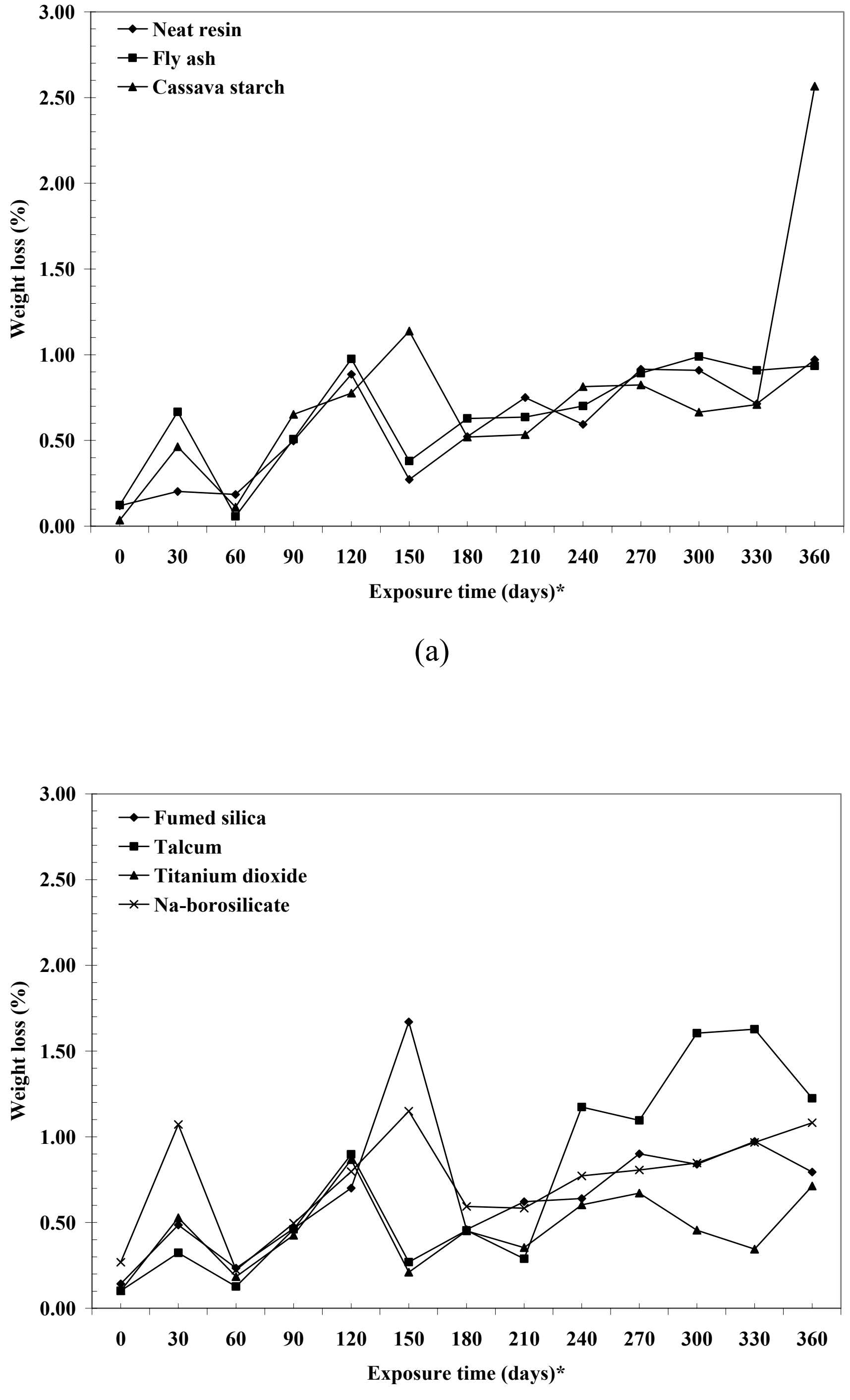
The progression of the GFRP degradation under accelerated condition was, again, monitored as the same manner as in the normal condition. Figure 4.8 to 4.9 are shown the % weight loss and hardness of the TETA cured system, respectively. From figure 4.8(a) and 4.8(b), the % weight loss of the sample within a year of the exposure times are totally scattered. In contrast, the hardness plots, as shown in figure 4.8s, are less scattered. Within the possible errors, the plots seem to indicate that the first step of weight reduction is started within the period of 30-60 days of explosion. Within a year of explosion, there is no further reduction. The similar trend is found for the plotted between hardness and times for all fillers used.

TETA/DDS cured system as reported in figure 4.10s - 4.11s and the DDS is shown in figure 4.12s to 4.13s, respectively. The same degradation pictures are repeated. These results would indicate that the epoxy systems filled with those fillers started to degrade within 1-2 months under the artificial conditions.

To verify and strengthen this initial conclusion, the SPSS with the applied significance of 0.05 were selected to prove that whichever the degradation of GFRP depend on the type of fillers and exposure time. Table 4.12 show the summarized result of the two ways ANOVA test on the weight loss under the accelerated condition. It is found that the calculated significance analyses by the filler factor of TETA cured system is greater than the given values, vice versa, the exposure time factor analysis is lower than the critical value. This lead to the conclusion that the degradation by mean of weight loss of the TETA cured composite does not depend on the type of fillers, otherwise it depends on the exposure time. Also, in table 4.13 shows the test obtained from hardness testing of TETA/DDS curing system. The change does depend on the exposure time.

Based on the weight loss analysis, table 4.12, the early conclusion could be represented that the degradation of the DDS and TETA/DDS cured composite systems under the accelerated condition are depend on the type of filler and the exposure time. On the other hand, it does depend on only the time for the TETA system. But, from the statistical data based on the hardness determination as illustrated in table 4.13, it is shown that the corrosion of GFRP derived from TETA and DDS curing systems are depend on the type of filler and the time. Conversely, the TETA/DDS cured does depend only the time.

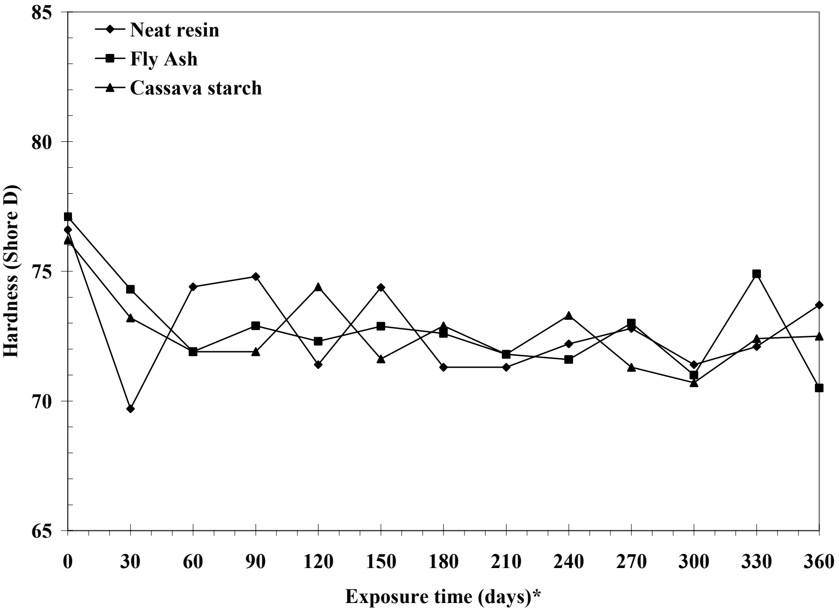
From the ANOVA test and weight loss and sample hardness observation, it can be reckon that the degradation of TETA, DDS and TETA/DDS cured reinforcements do degrade under accelerated condition. Moreover, the GFRP obtained from epoxy cured with DDS hardener also does degrade under accelerated and the time of degradation would depend on the filler used.



(a)

(b)

Figure 4.8 Weight loss of TETA system under accelerated condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass. *As equivalently calculated



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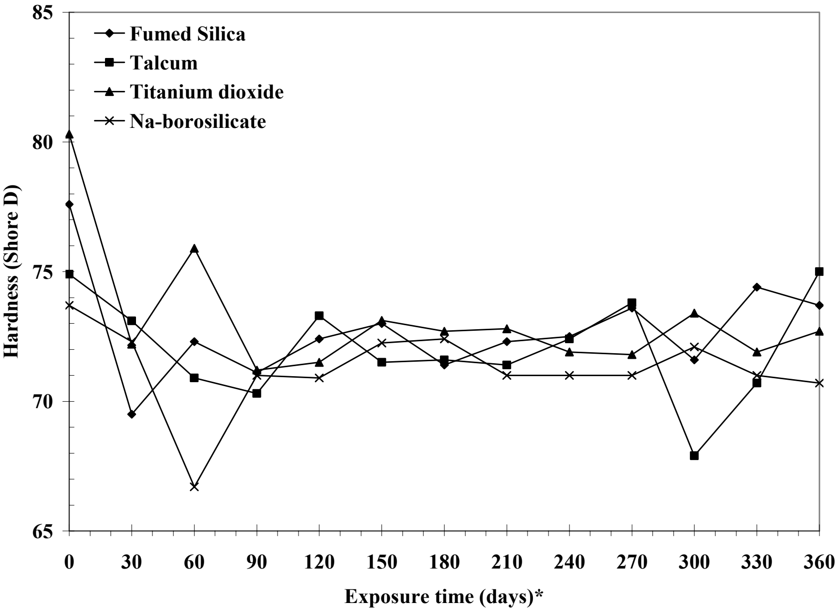
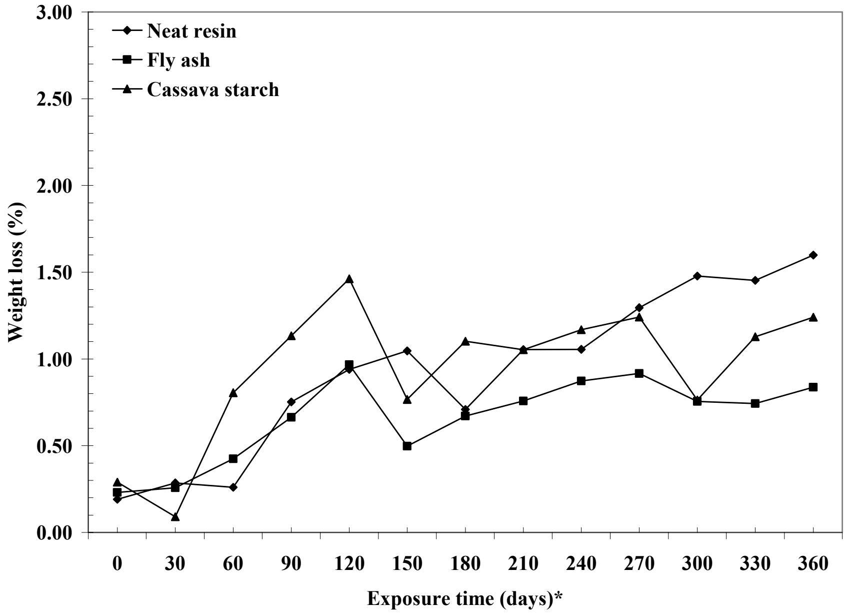


(b)

Figure 4.9 Hardness of TETA system under accelerated condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass. *As equivalently calculated



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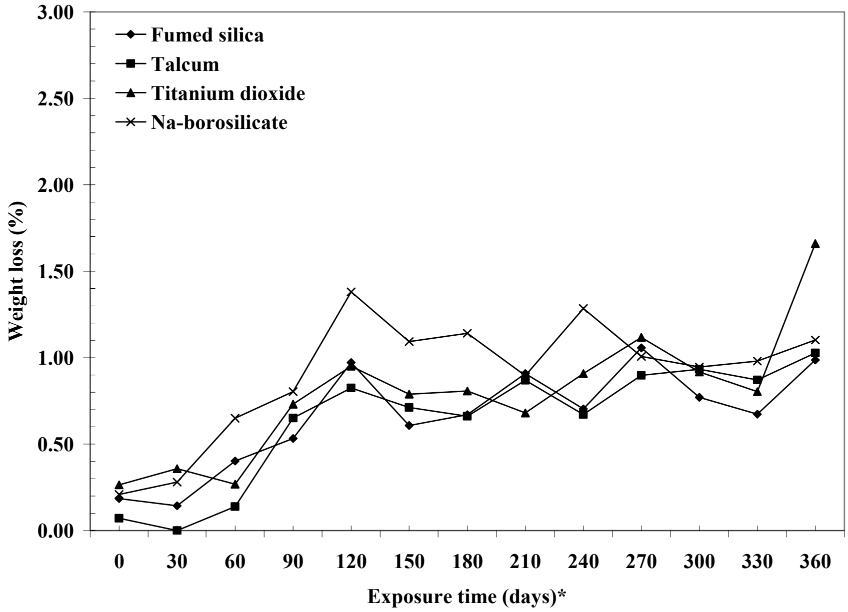
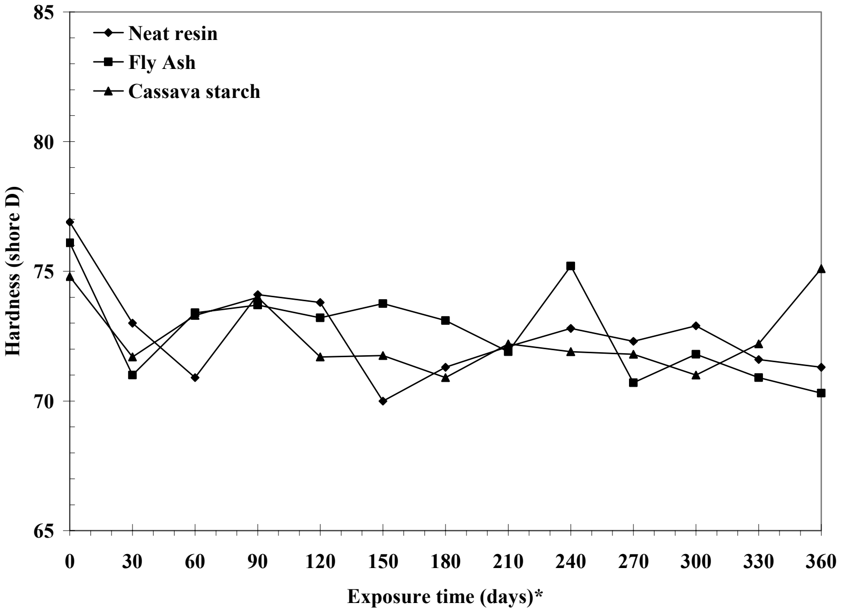


(b)

Figure 4.10 Weight loss of TETA/DDS system under accelerated condition with (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass. *As equivalently calculated



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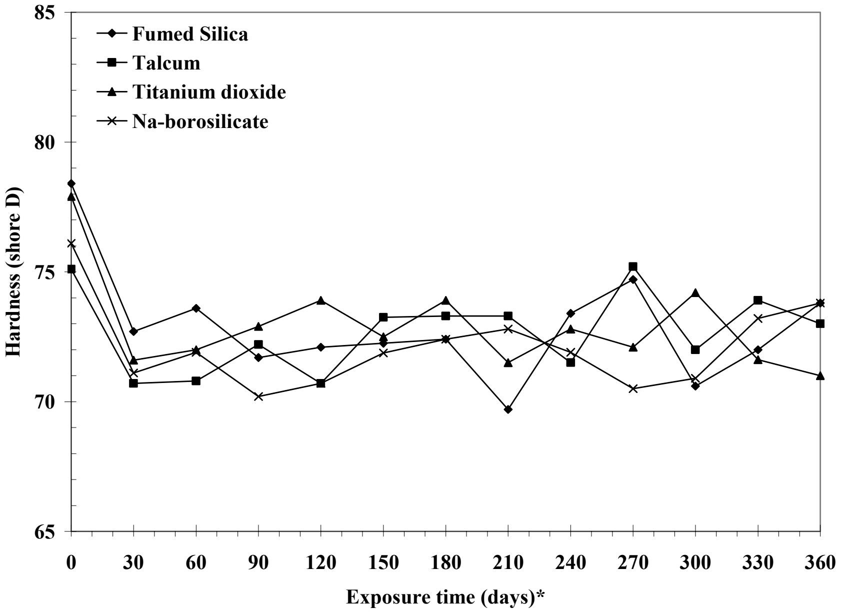
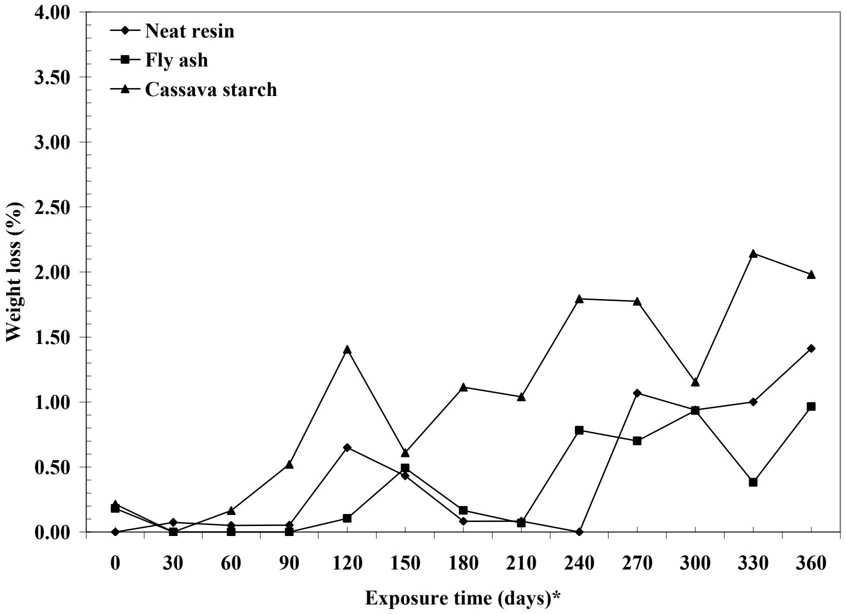


(b)

Figure 4.11 Hardness of TETA/DDS system under accelerated condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass. *As equivalently calculated



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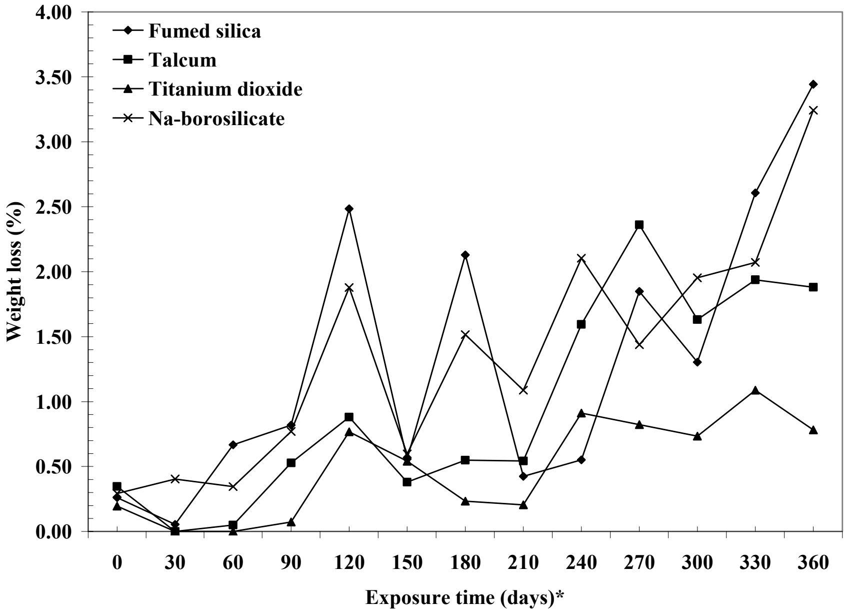

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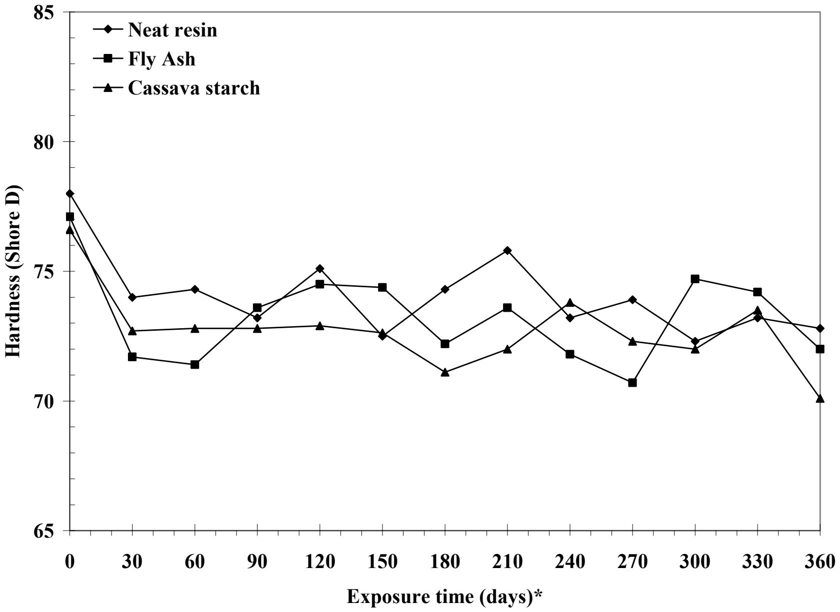
Figure 4.12 Weight loss of DDS system under accelerated condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass. *As equivalently calculated



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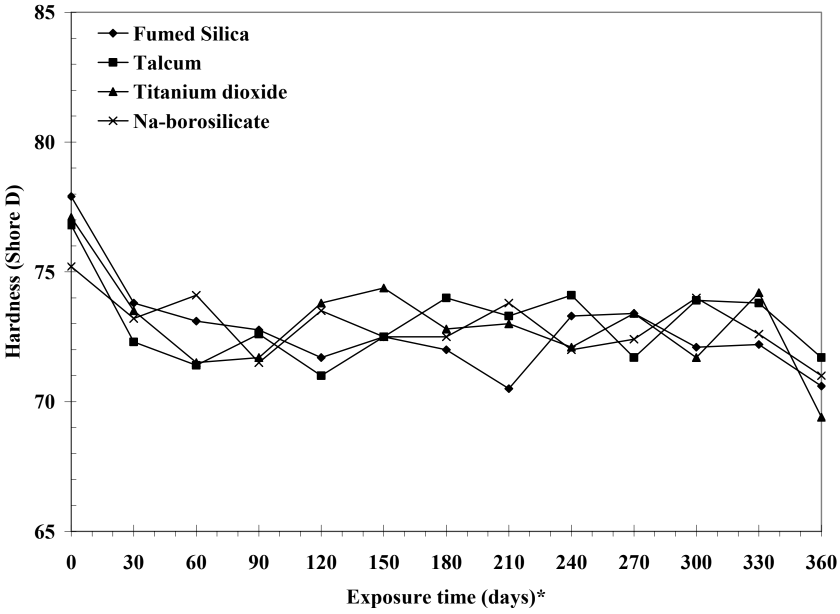


(b)

Figure 4.13 Hardness of DDS system under accelerated condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass. *As equivalently calculated

Table 4.12 Summary results of the two ways ANOVA test of % weight loss of the accelerated condition.

Curing system	**Factor**	**TypeIII sum of Square**	**Df**	**Mean square**	**Sig.**	**Conclusion**
TETA	Filler(A)	0.939	6	0.156	0.116	H_o(A)Accepted
	Time(B)	7.613	12	0.634	0.000	H_1(B)Accepted
DDS	Filler(A)	13.903	6	2.317	0.000	H_1(A)Accepted
	Time(B)	30.397	12	2.533	0.000	H_1(B)Accepted
TETA/DDS	Filler(A)	1.730	6	0.288	0.000	H_1(A)Accepted
	Time(B)	7.931	12	0.661	0.000	H_1(B)Accepted

Table 4.13 Summary results of the two ways ANOVA test of hardness of the accelerated condition.

Curing system	**Factor**	**TypeIII sum of Square**	**Df**	**Mean square**	**Sig.**	**Conclusion**
TETA	Filler(A)	34.132	6	5.689	0.013	H_1(A)Accepted
	Time(B)	152.747	12	12.729	0.000	H_1(B)Accepted
DDS	Filler(A)	88.440	6	14.740	0.004	H_1(A)Accepted
	Time(B)	253.099	12	21.092	0.000	H_1(B)Accepted
TETA/DDS	Filler(A)	6.901	6	1.150	0.662	H_o(A)Accepted
	Time(B)	114.725	12	9.560	0.000	H_1(B)Accepted

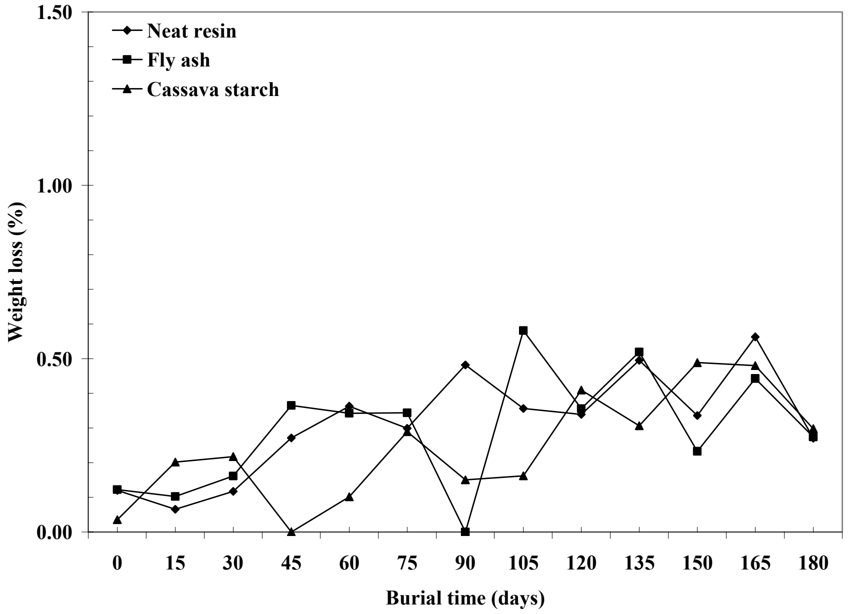
4.4 Degradation in Landfills

In order to study the degradation of GFRP in the intimidated landfills, the samples were buried in the constructed landfill site for a period of 180 days as described earlier in Chapter III. The progression of the GFRP degradation under this condition was monitored by calculated weight loss and sample hardness, shore D. From figure 4.14s show the plot of weight loss with buried time for the samples cured with TETA. Again, the points are scattered. The tendency of the change is difficult to be drawn. On the other hand the change in hardness with the exposure times shown in figure 4.15s are less scattered. Having a careful observation for both plots, they seem to manifest that the GFRP degradation is started within 30-60 days of burial time for all fillers used.

Figure 4.16s and 4.18s show the weight loss of the TETA/DDS and DDS cured sample with the buried times. The similar pattern as explained before is repeated. As well as the plots of hardness as shown in figure 4.17s and 4.19s where the changes are almost identical to those found in the previous experiments. Taking only the hardness results, it is very difficult when the GFRP degradation take place. It was expected that the GFRP sample filled with starch would be easily and rapidly degraded when compare with those organic fillers. To verify and strengthen the experimental conclusion that the degradation of the GFRP samples would depend on the type of fillers used and also the differences in the degradation. The statistical analysis had to be in placed. SPSS with the applied level of significance of 0.05 were chosen to prove that the degradation, using % weight loss and hardness, are depended on the type of filler and burial time. Table 4.14 summarized the results of the two ways ANOVA test of the weight loss for the landfill experiment. It is found that the calculated significance by the filler, factor A, of TETA, DDS cured system are higher than the given critical values. Vice versa the buried time, factor B, of DDS and TETA/DDS cured system, the calculated ones are higher than the given significance. These lead to the statistical conclusion that the degradation of GFRP, monitored by weight loss, of the epoxy/DDS and epoxy/TETA/DDS system does not depend on the type of fillers and also the burial time. The opposite conclusions are arisen for the epoxy/TETA system.

Table 4.15 is summarized the results of the two ways ANOVA test obtained by hardness experiment. The test reviewed that the calculated significance of the fillers and also the burial time factors for TETA and TETA/DDS cured systems less than the given significance. These indicate that the hardness of TETA and TETA/DDS curing system does depend on, again, both the type of fillers and burial time. In contrast, the calculated significance of the Epoxy/DDS system, for the burial time factor, is less than the given value. From the statistical analysis using hardness test, it could conclude that there is the degradation taken place for the Epoxy/DDS system.

According to the statistical resolution based on weight loss and sample hardness analysis, it is confident to pronounce that the degradation of GFRP cured with TETA hardener in landfill condition within 180 days is occurred and it not depend on the filler added. Vice versa, the degradation of the system cured with the DDS and TETA/DDS could not be occurred within the given experimental time in this study.



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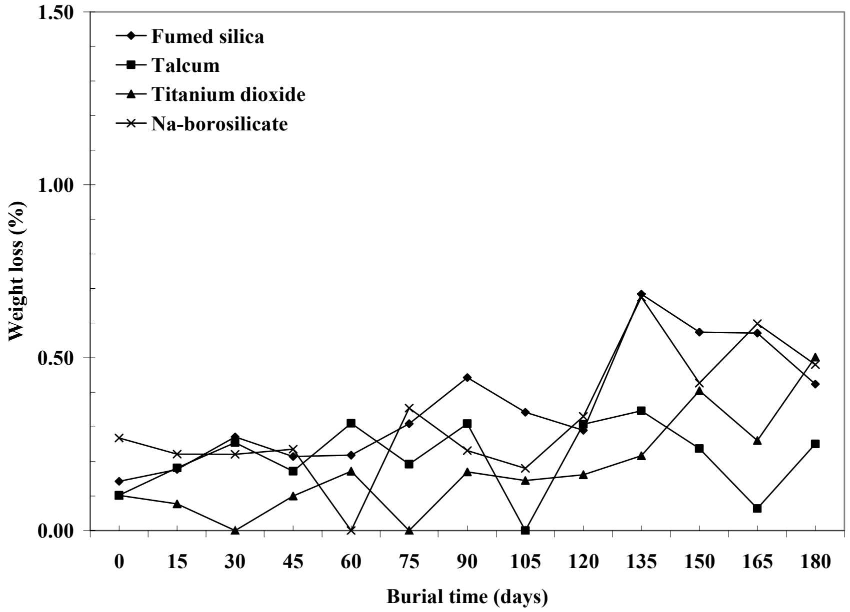
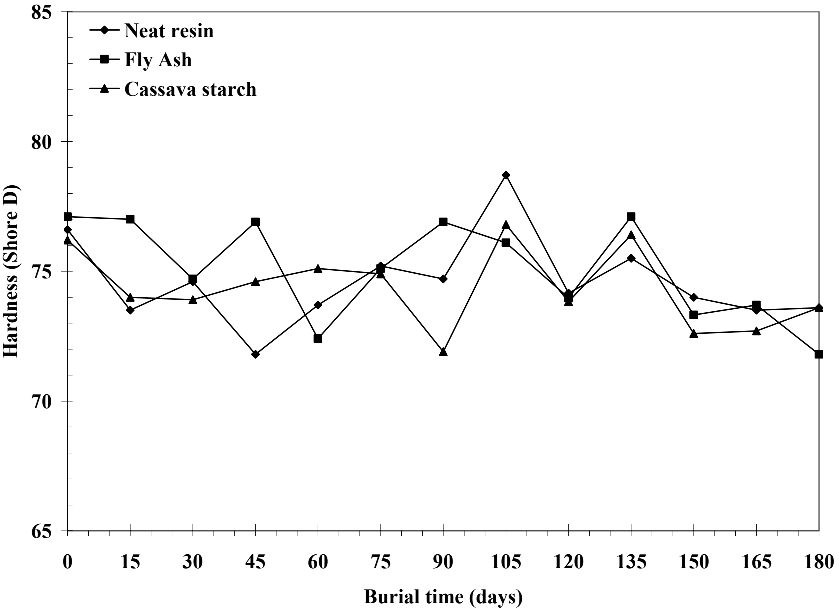


(b)

Figure 4.14 Weight loss of TETA system under landfill condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



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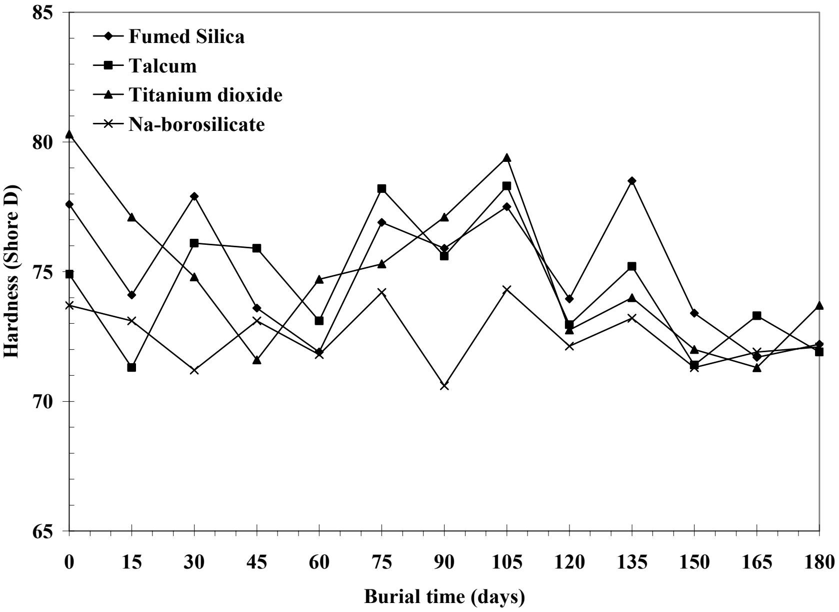
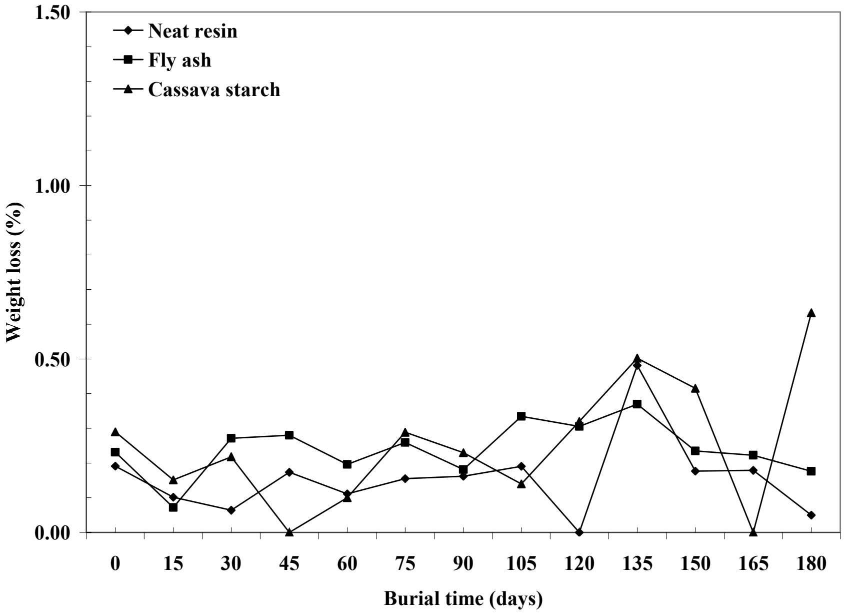


(b)

Figure 4.15 Hardness of TETA system under landfill condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



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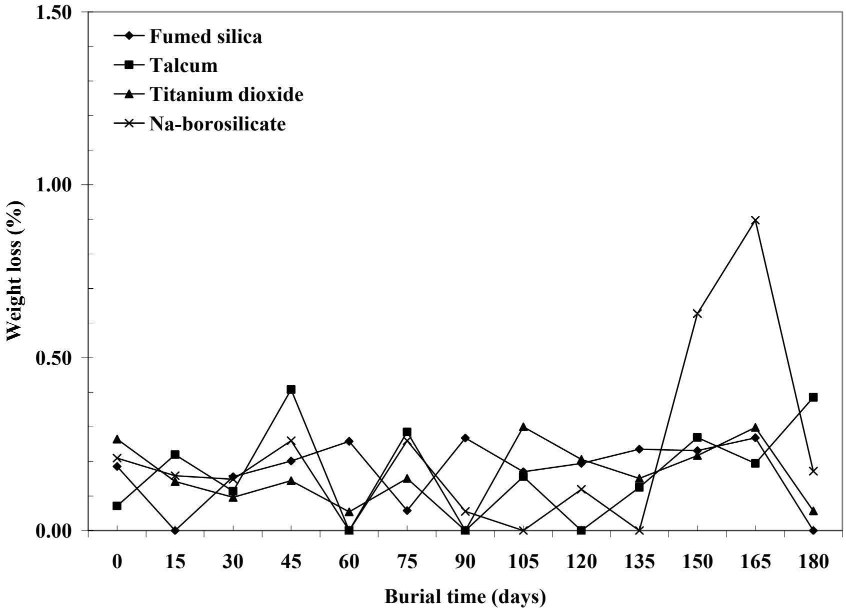

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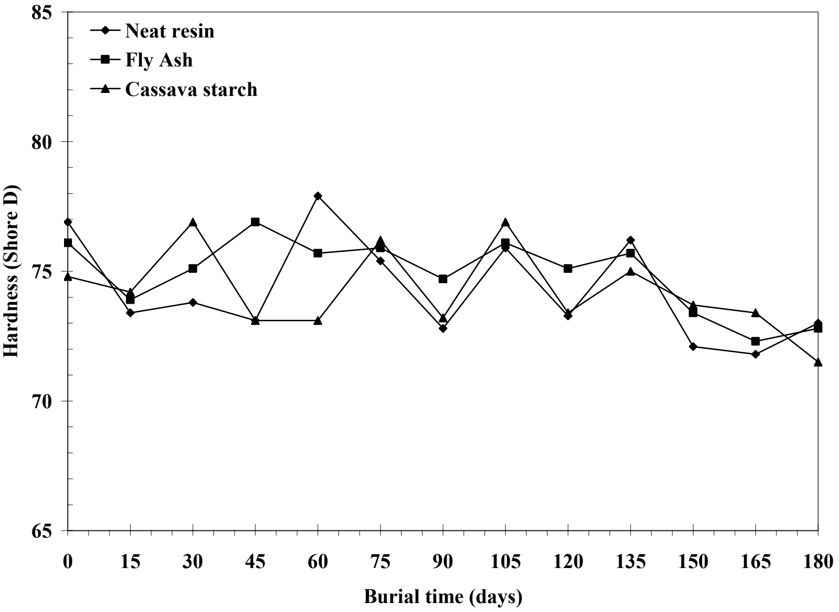
Figure 4.16 Weight loss of TETA/DDS system under landfill condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



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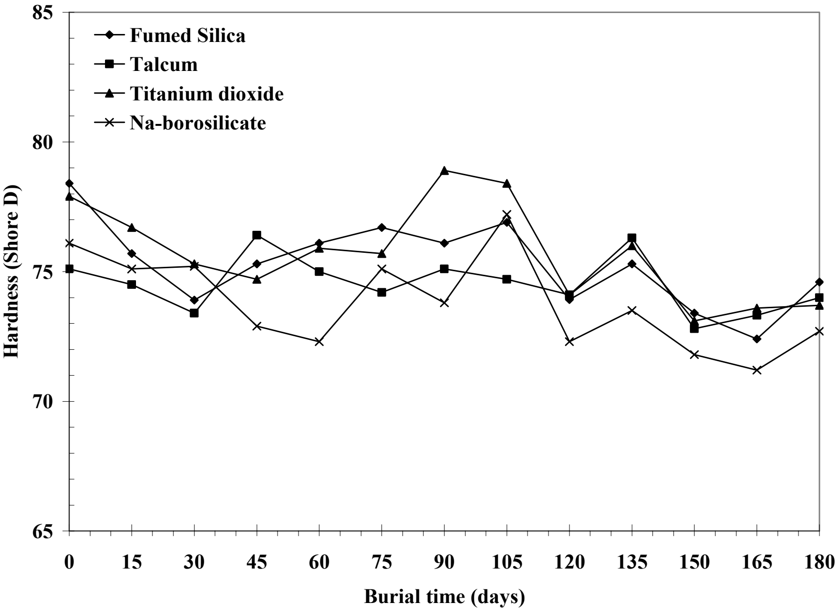

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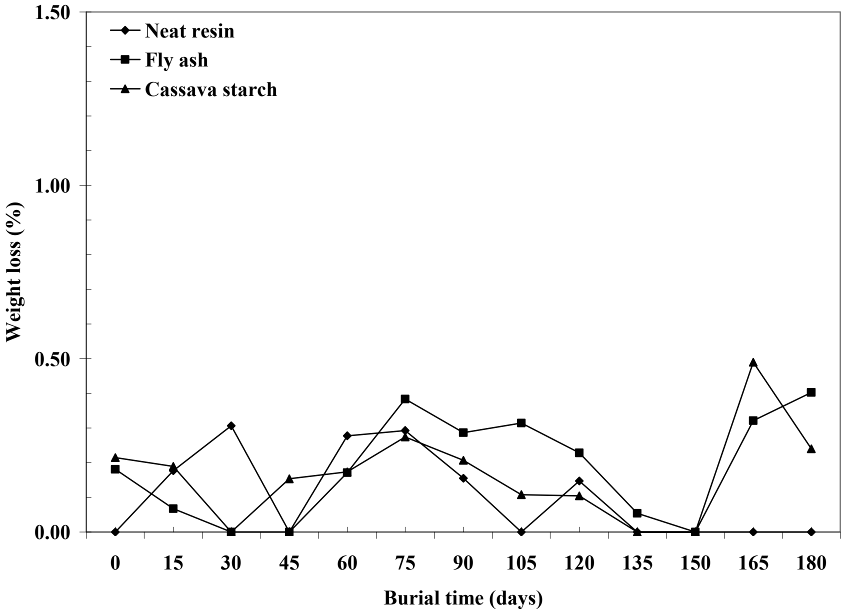
Figure 4.17 Hardness of TETA/DDS system under landfill condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



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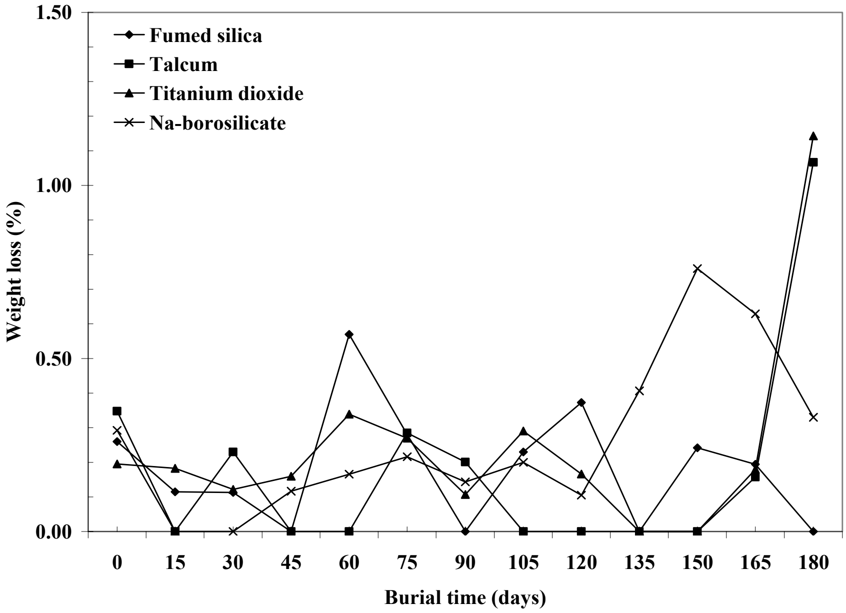

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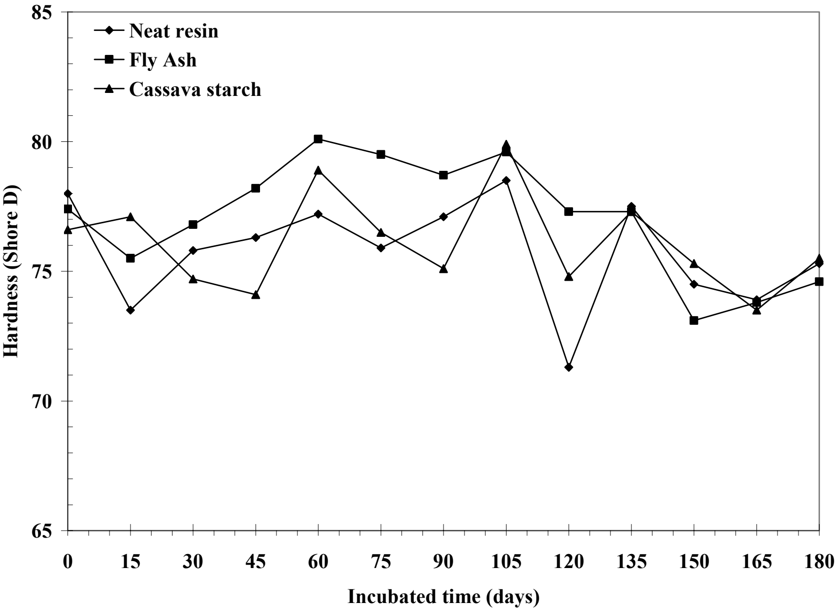
Figure 4.18 Weight loss of DDS system under landfill condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



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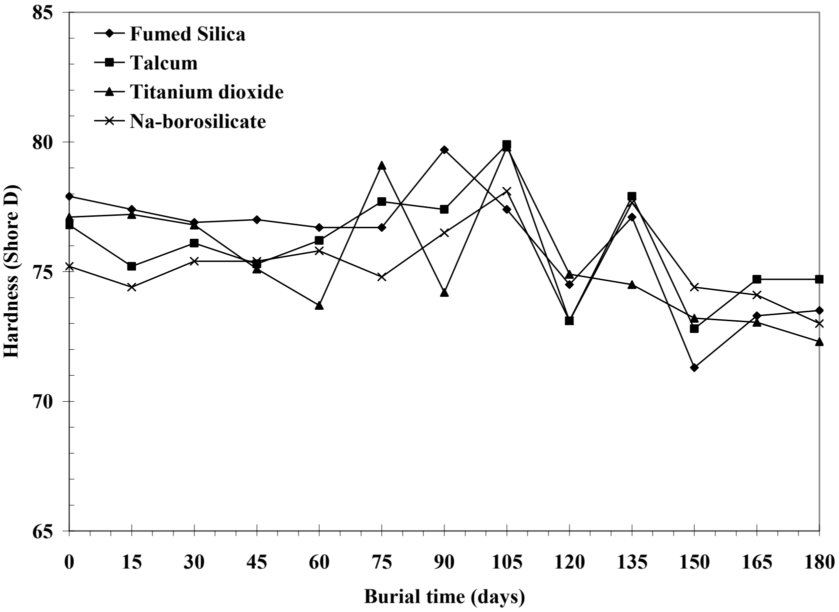


(b)

Figure 4.19 Hardness of DDS system under landfill condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

Table 4.14 Summary results of the two ways ANOVA test of % weight loss of the landfill condition.

Curing system	Factor	TypeIII sum of Square	Df	Mean square	Sig.	Conclusion
TETA	Filler(A)	8.238E-02	6	1.373E-02	0.421	H_o(A)Accepted
	Time(B)	0.382	6	6.363E-02	0.001	H_1(B)Accepted
DDS	Filler(A)	0.184	6	3.065E-02	0.789	H_o(A)Accepted
	Time(B)	0.562	6	9.363E-02	0.179	H_o(B)Accepted
TETA/DDS	Filler(A)	0.227	6	3.786E-02	0.034	H_1(A)Accepted
	Time(B)	0.199	6	3.320E-02	0.058	H_o(B)Accepted

Table 4.15 Summary results of the two ways ANOVA test of hardness of the landfill condition.

Curing system	Factor	TypeIII sum of Square	Df	Mean square	Sig.	Conclusion
TETA	Filler(A)	47.288	6	7.881	0.003	H_1(A)Accepted
	Time(B)	87.913	6	14.652	0.000	H_1(B)Accepted
DDS	Filler(A)	23.957	6	3.993	0.104	H_o(A)Accepted
	Time(B)	101.065	6	16.844	0.000	H_1(B)Accepted
TETA/DDS	Filler(A)	29.497	6	4.916	0.031	H_1(A)Accepted
	Time(B)	67.174	6	11.196	0.000	H_1(B)Accepted

4.5 Water Incubation Conditions

Degradation of solid waste in water resources is one of major concerns for the environment point of view. In the water sport goods made of polymers, the deterioration of the materials would induce in the mechanical failure of the equipment. The rate of ruin would depend on various factors. Fillers added into polymers would be one of them that could accelerate or retard the degradation. In order to determine the tendency of deterioration of the GFRP prepared in this research work, the degradation of experiment under water incubation conditions were designed for a period of 6 months. The experiments were set to imitate the condition where the GFRP would be disposed into waste water or used in the ocean. They were performed by immersion the samples in seawater and waste water as fully described in chapter III.

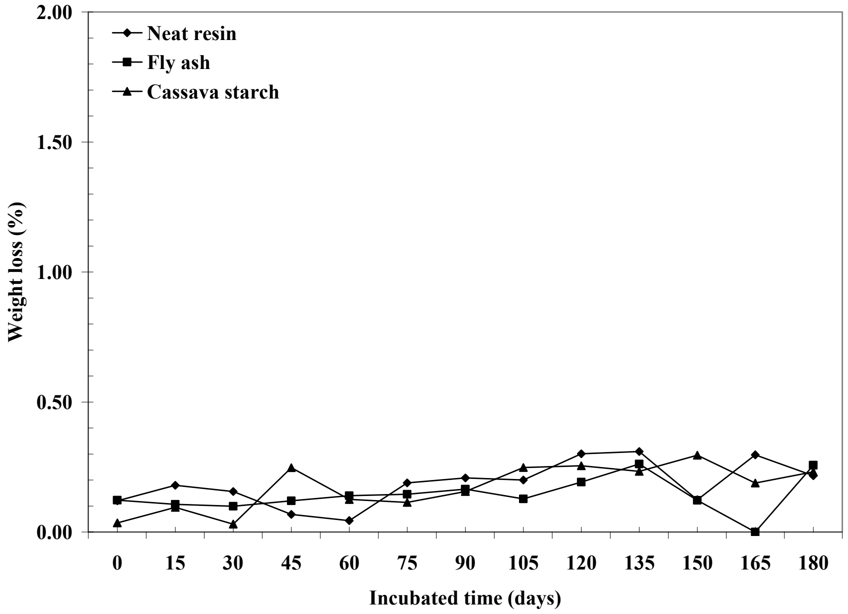
4.5.1 Wastewater Testing

The degradation under wastewater condition was monitored by both weight loss and sample hardness. Figure 4.20s, 4.22s and 4.24s show the plot of % weight loss of the GFRP cured with TETA, TETA/DDS and DDS against incubation time, respectively. Within the experimental errors, the plots of shows that the % weight loss are unchanged with the given incubation time. Moreover, when carefully consider the figure 4.21s, 4.23s and 4.25s shown the relationship of hardness with the incubation time of the same sample systems. It is difficult to draw the conclusion that when the degradation of the TETA and DDS cured GFRP are occurred. Again, the statistical analysis will be in placed to verify and strength this outcome.

As it has been done throughout this research work, the SPSS with the applied level of significance of 0.05 were used to prove that the degradation, performed by using weight loss and hardness, of the GFRP sample incorporated with the given fillers is actually occurred within the experimental time. Table 4.16 shows the test results of the two ways ANOVA of the % weight loss after immersion in wastewater for 180 days. It is shown that the calculated significance obtained from the fillers, factor A, and the time, factor B, of the TETA and DDS cured specimen, respectively, are higher than the given critical value. By using only the %weight loss experiment, these outcomes suggest that the TETA and the DDS/TETA cured GFRP might be degraded within the given incubation time and the degradation time might not depend on the type of fillers used, respectively. However, the degradation probably be not occurred for the DDS system and the dependency the fillers used could not be concluded.

Furthermore, the statistical testing based on the sample hardness, shown in table 4.17, the results review that the calculated significance of the time factor for the DDS and the TETA/DDS systems are higher than the assigned significance. This lead to suspect that there is no degradation for the DDS and TETA/DDS cured GFRP. According to the test results obtained it is difficult to verify the effect of fillers on the degradation. However in TETA curing system, where the calculated values are lower than the critical ones, they propose that the sample degradation is taken place and it depends on the fillers used.

From the above ANOVA test, based on weight loss and sample hardness, the recommendation may be illustrated that the degradation of TETA cured GFRP could be accomplished in the designed waste water but it is difficult to declare for the DDS and TETA/DDS systems. According to the outcomes obtained, the dependency of the fillers on the degradation would be ambiguously concluded.



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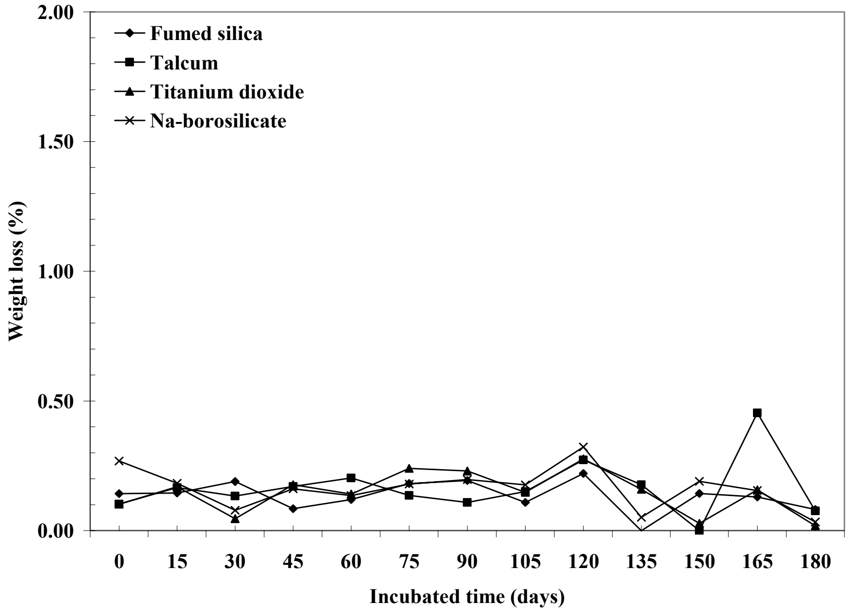

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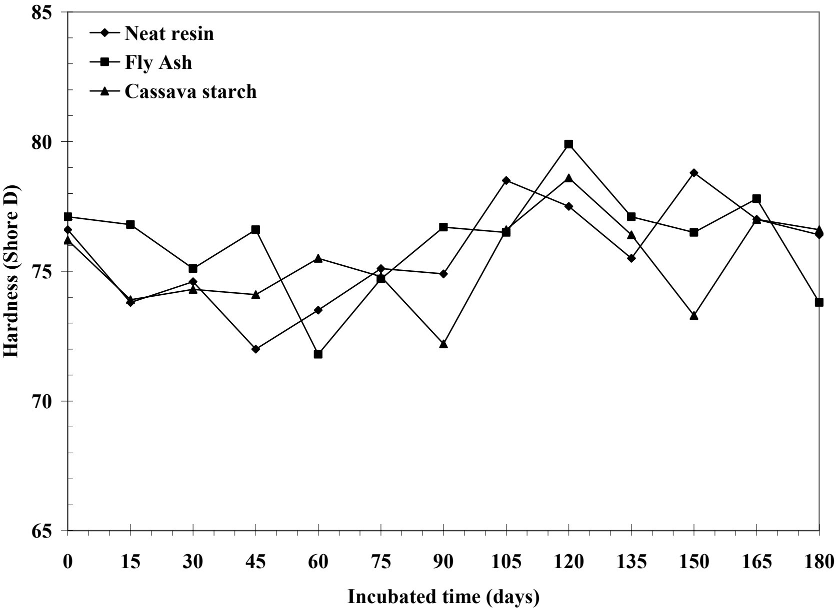
Figure 4.20 Weight loss of TETA system under waste water condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



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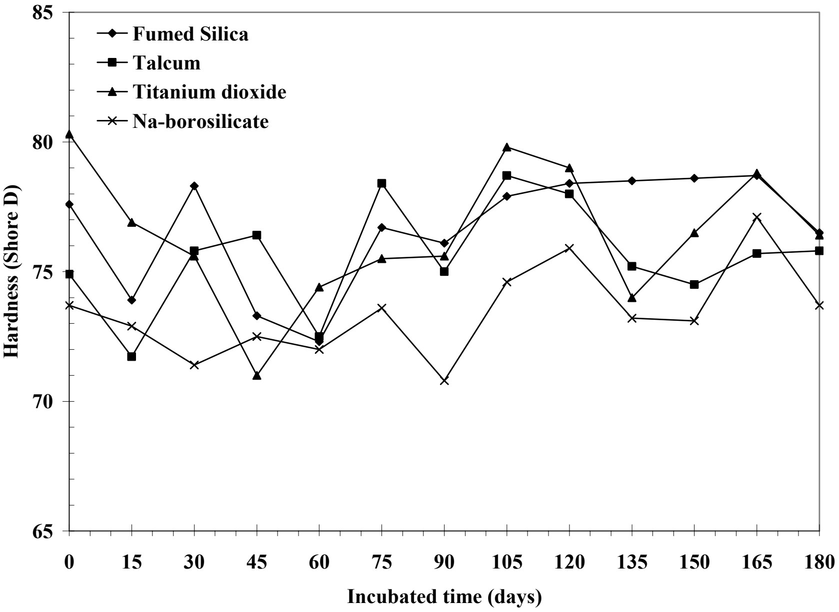
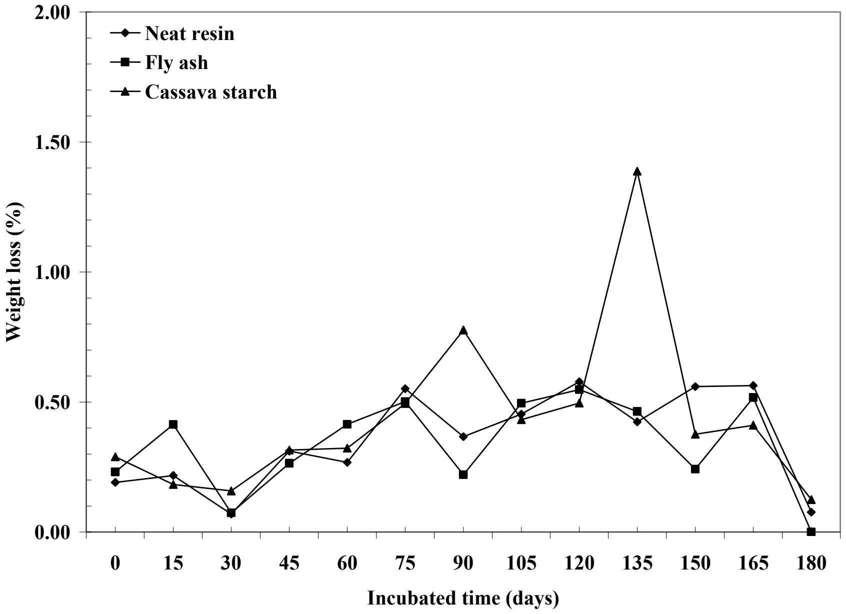
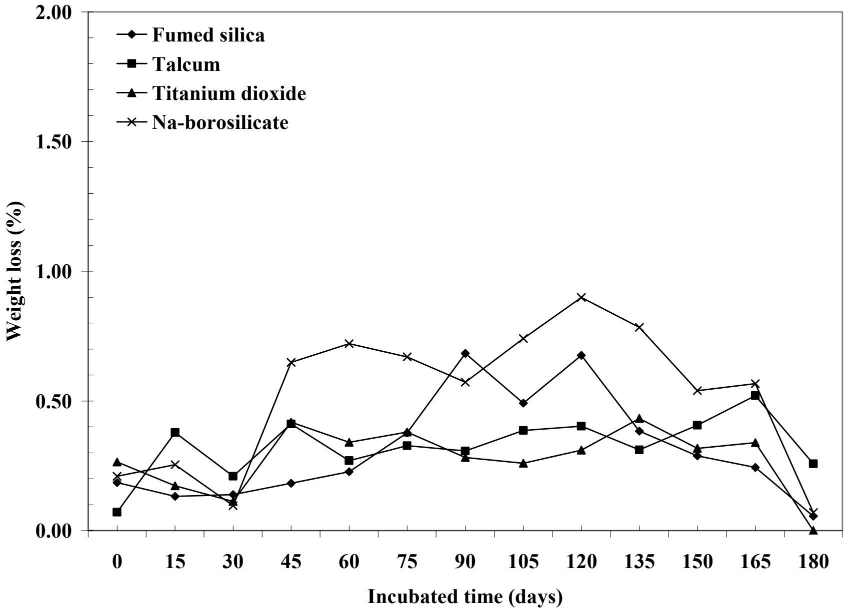


(b)

Figure 4.21 Hardness of TETA system under wastewater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

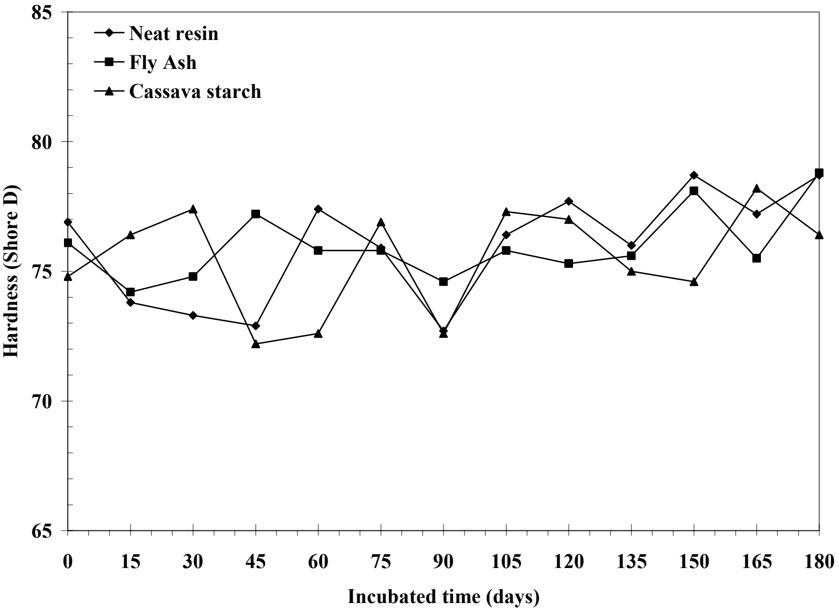


(a)



(b)

Figure 4.22 Weight loss of TETA/DDS system under waste water condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



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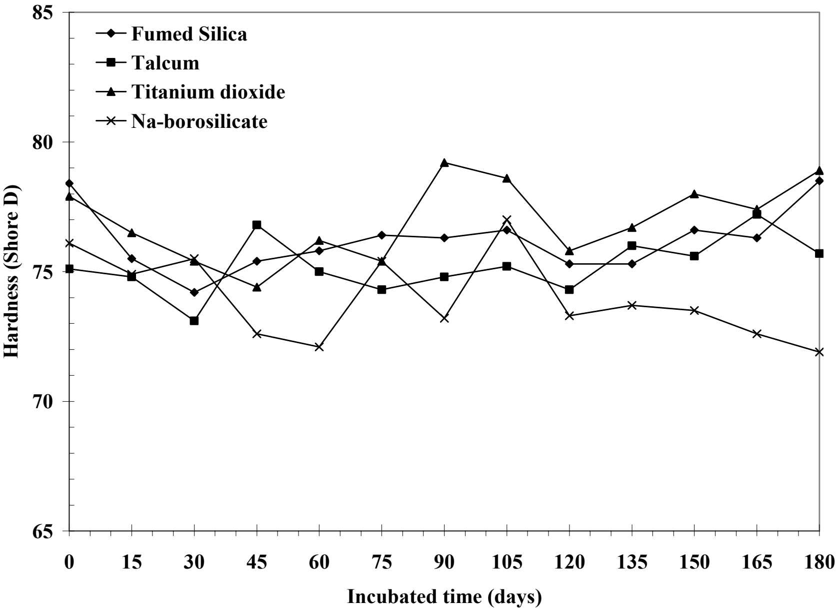
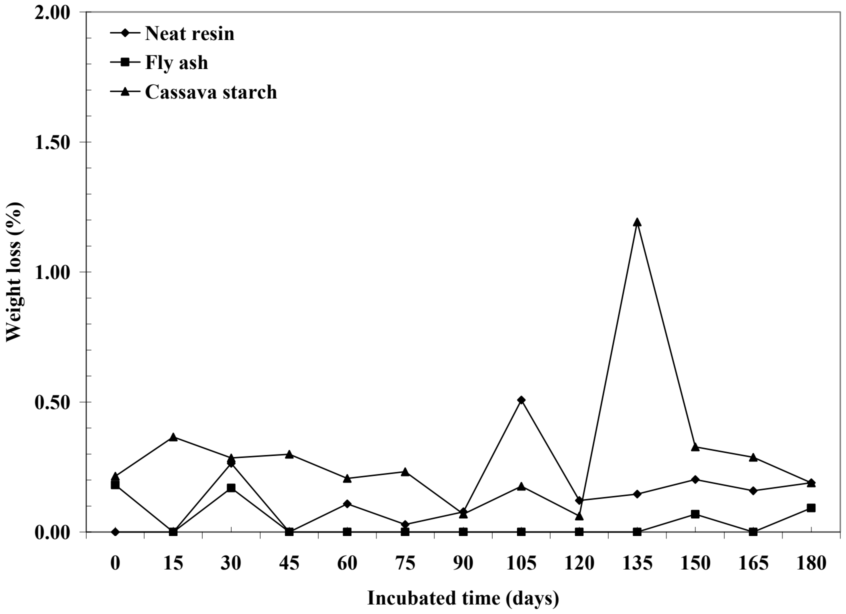


(b)

Figure 4.23 Hardness of TETA/DDS system under wastewater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



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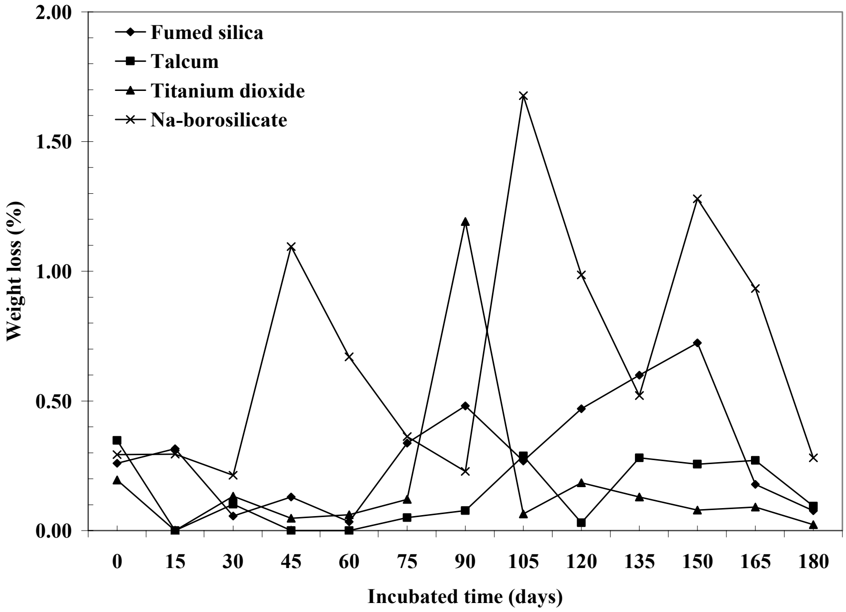
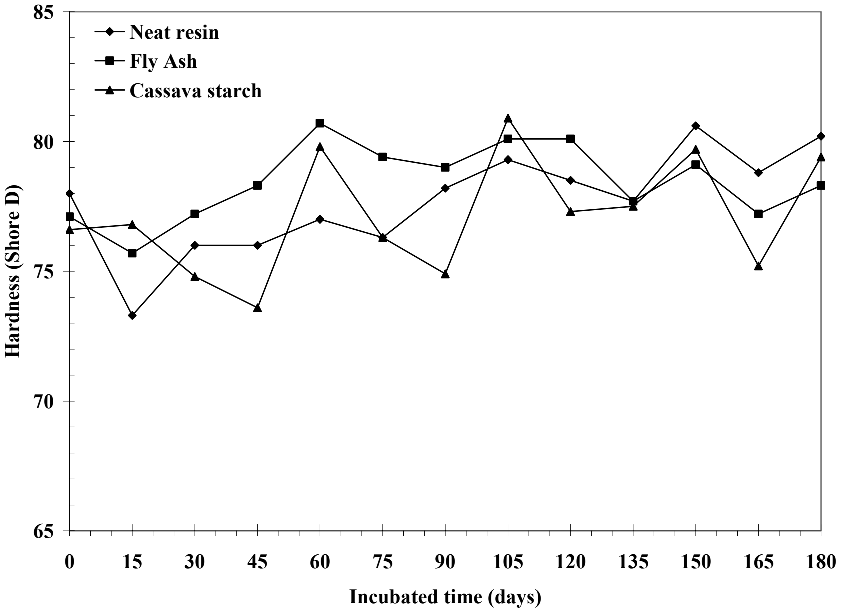
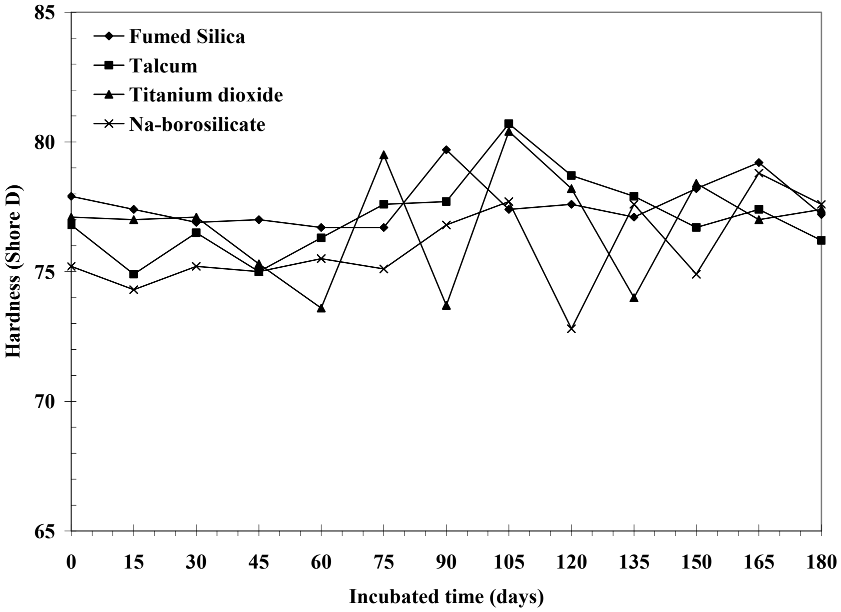


(b)

Figure 4.24 Weight loss of DDS system under waste water condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



(a)



(b)

Figure 4.25 Hardness of DDS system under wastewater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

Table 4.16 Summary results of the two ways ANOVA test of % weight loss of the wastewater condition.

Curing system	**Factor**	**TypeIII sum of Square**	**Df**	**Mean square**	**Sig.**	**Conclusion**
TETA	Filler(A)	1.737E-02	6	2.895E-03	0.767	H_o(A)Accepted
	Time(B)	0.119	6	1.980E-02	0.005	H_1(B)Accepted
DDS	Filler(A)	1.136	6	0.189	0.021	H_1(A)Accepted
	Time(B)	0.426	6	7.099E-02	0.389	H_o(B)Accepted
TETA/DDS	Filler(A)	0.469	6	7.822E-02	0.001	H_1(A)Accepted
	Time(B)	0.805	6	0.134	0.000	H_1(B)Accepted

Table 4.17 Summary results of the two ways ANOVA test of hardness of the wastewater condition.

Curing system	**Factor**	**TypeIII sum of Square**	**Df**	**Mean square**	**Sig.**	**Conclusion**
TETA	Filler(A)	74.208	6	12.368	0.000	H_1(A)Accepted
	Time(B)	108.351	6	18.059	0.000	H_1(B)Accepted
DDS	Filler(A)	54.754	6	9.096	0.005	H_1(A)Accepted
	Time(B)	19.629	6	3.271	0.249	H_o(B)Accepted
TETA/DDS	Filler(A)	66.694	6	11.116	0.002	H_1(A)Accepted
	Time(B)	34.894	6	5.816	0.053	H_o(B)Accepted

4.5.2 Seawater Incubation

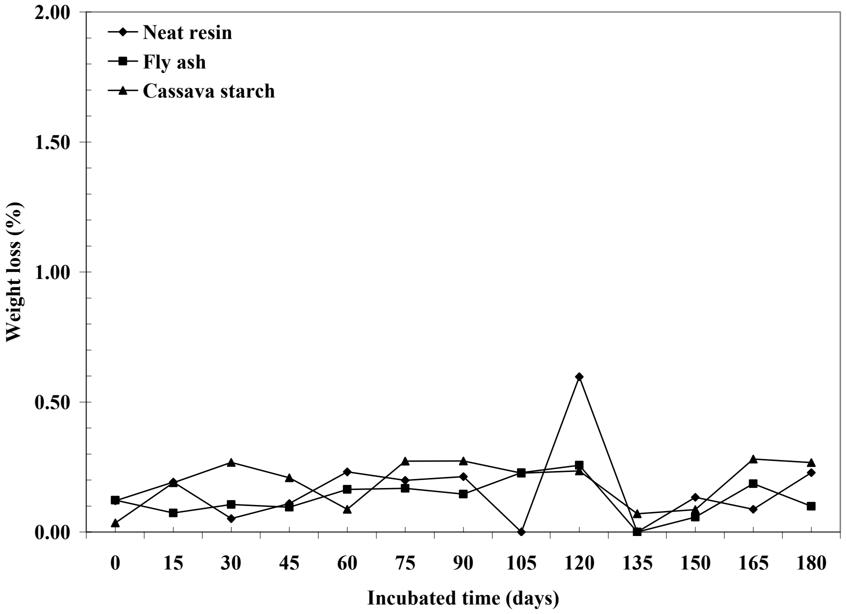
The degradation studies of GFRP incubated in seawater, monitored by weight loss and hardness, are reported in figure 4.26s to 4.31s, respectively. In figure 4.26s, 4.28s and 4.30s illustrate the plot of the weight loss and incubation times of the sample obtained from TETA, TETA/DDS and DDS curing system, respectively. The changes of the sample loss with times of all systems are similar to those found previously. There is slightly increased in the loss after around 30 days of incubation period.

Nevertheless, the plots of the hardness as shown in figure 4.27s, 4.29s and 4.31s, respectively, are almost unchanged with the times. Within the acceptable errors, it seems that there is no degradation observed for the GFRP under seawater within 180 days of incubation period.

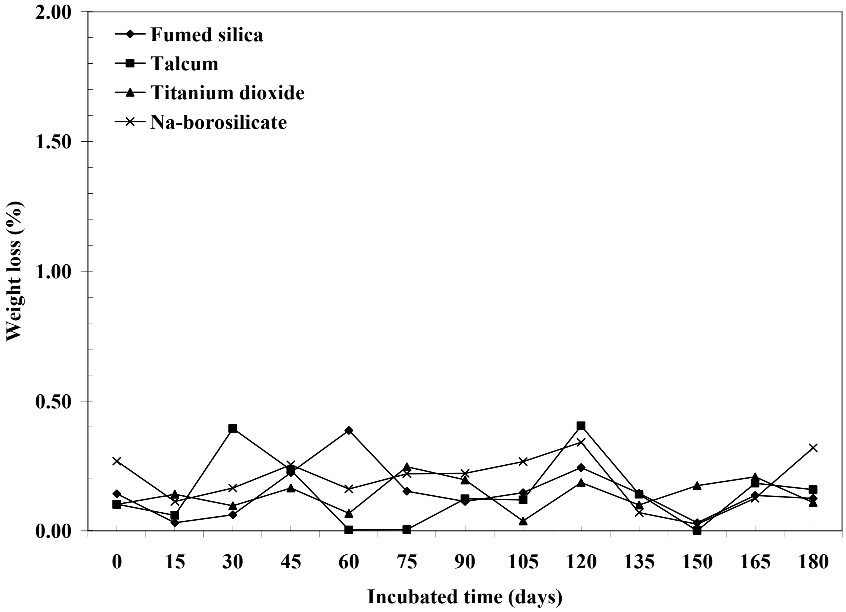
To strengthen the statement indicated above, SPSS with the applied level of significance of 0.05 were again used to prove either there is a degradation of GFRP after soaking in sea water for 6 months or not. The statistic test results are reported in table 4.18 and 4.19. Considering the incubation time factor, the results review that the calculated significances are lower than the critical value, 0.05, for all systems and for both testing experiment. Therefore, the H_1 is accepted. It means that the samples are probably degraded after soaking in sea water for 6 months. However, in order to investigate the dependency of the fillers on the degradation, factor A, the test results shown that the same agreement obtained from both experiments is found only for the TETA/DDS system. The rests are ambiguous.

Taken only the ANOVA two ways testing for the GFRP samples degradation under seawater, it could be pronounced that degradation may be occurred when TETA, TETA/DDS and DDS used as curing agents. Moreover, the degradation rate would be effected by the filler used for the TETA/DDS system.

According to the results obtained in this research work, they suggest, with difficulty, that the degradation of GFRP prepared by three curing systems and using both inorganic and natural abundant fillers, under typical environments might be occurred. But by looking at the fillers dependency test results, it is ambiguously to say that either the bio-filler, starch, would effectively induce the degradation or not.

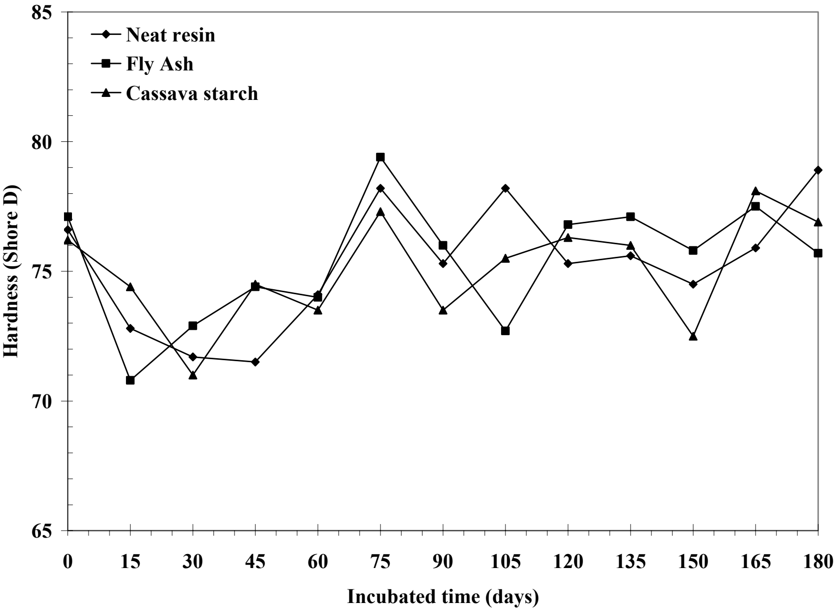


(a)

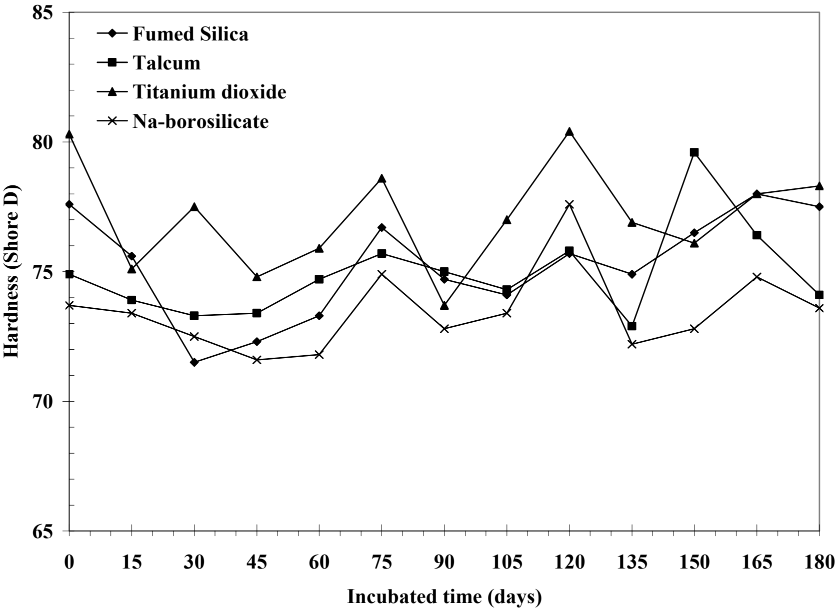


(b)

Figure 4.26 Weight loss of TETA system under seawater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

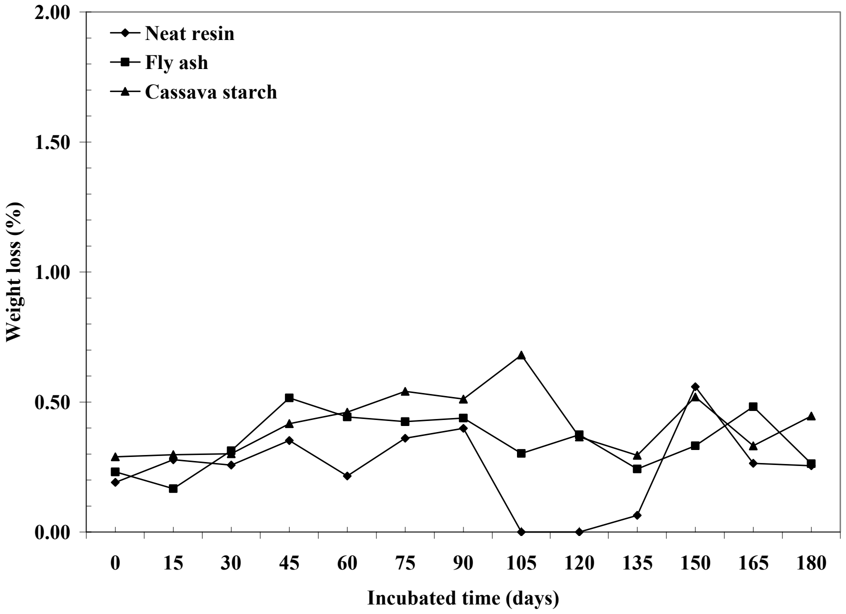


(a)

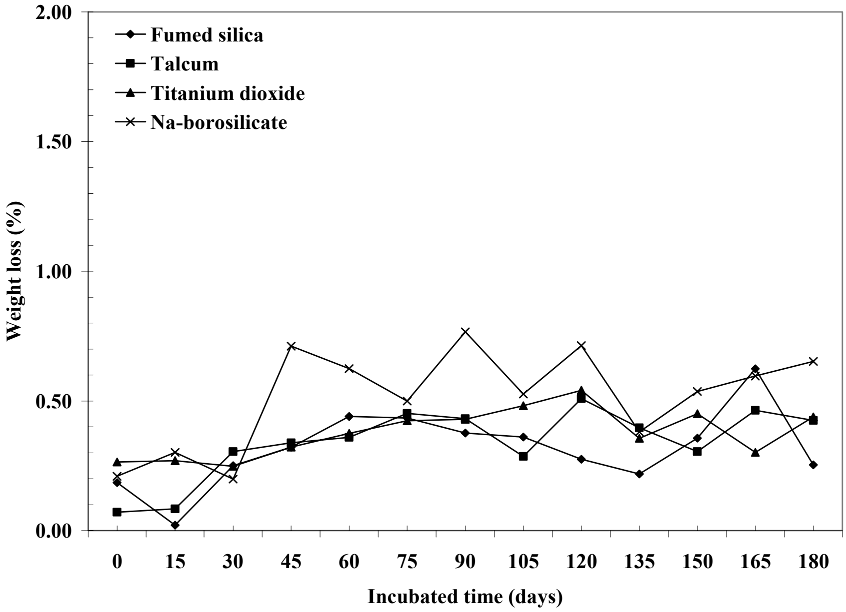


(b)

Figure 4.27 Hardness of TETA system under seawater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

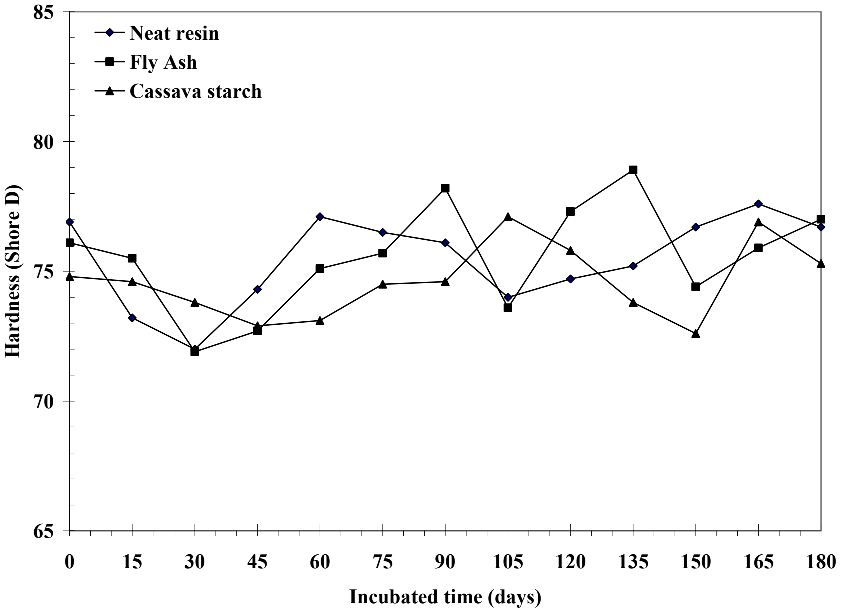


(a)

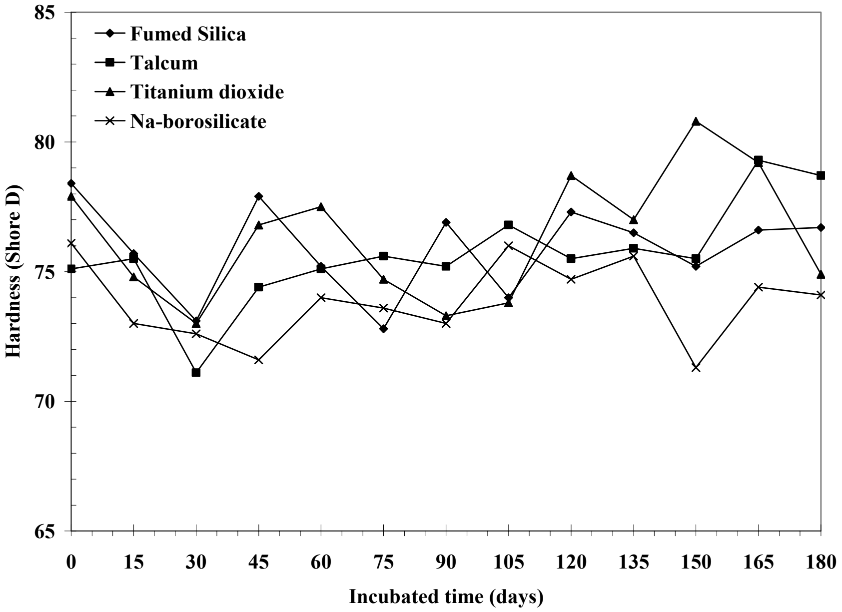


(b)

Figure 4.28 Weight loss of TETA/DDS system under seawater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

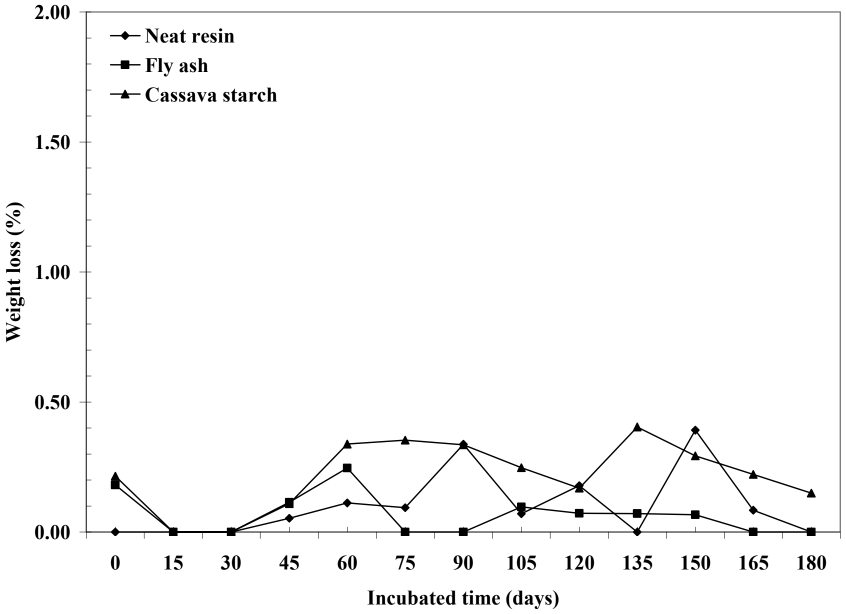


(a)

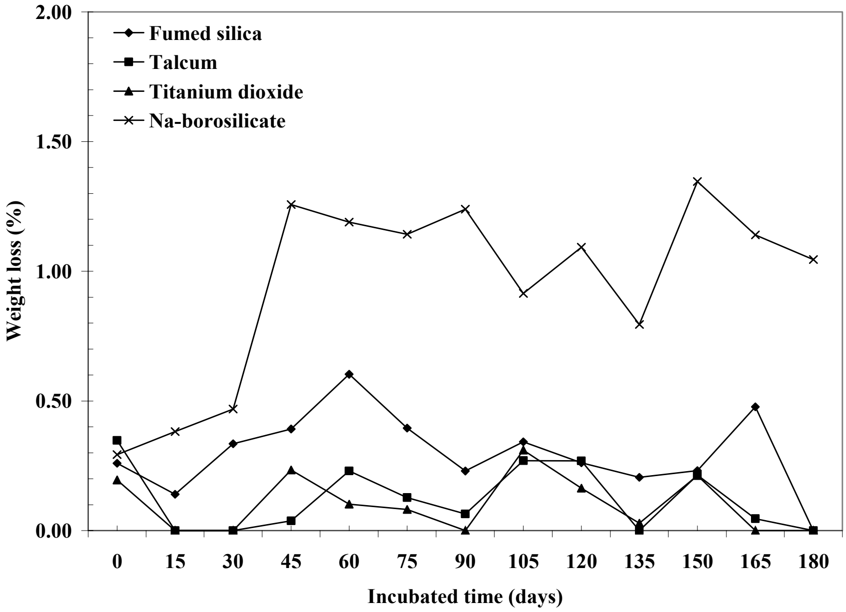


(b)

Figure 4.29 Hardness of TETA/DDS system under seawater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

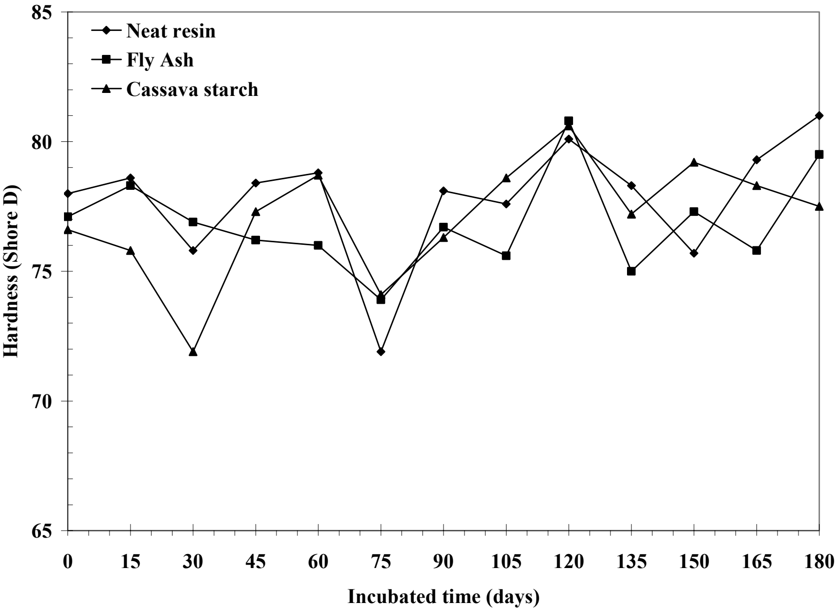


(a)

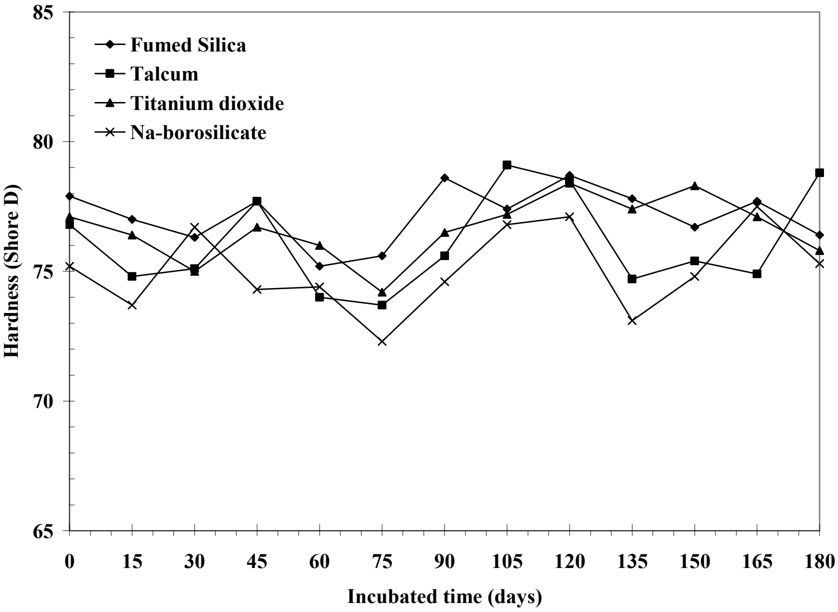


(b)

Figure 4.30 Weight loss of DDS system under seawater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.



(a)



(b)

Figure 4.31 Hardness of DDS system under seawater condition of (a) neat resin, fly ash and cassava starch and (b) fumed silica, talcum, titanium dioxide and sodium borosilicate glass.

Table 4.18 Summary results of the two ways ANOVA test of % weight loss of the seawater condition.

Curing system	**Factor**	**TypeIII sum of Square**	**Df**	**Mean square**	**Sig.**	**Conclusion**
TETA	Filler(A)	5.265E-02	6	8.776E-03	0.542	H_o(A)Accepted
	Time(B)	0.250	6	4.161E-02	0.003	H_1(B)Accepted
DDS	Filler(A)	3.939	6	0.657	0.000	H_1(A)Accepted
	Time(B)	1.149	6	8.651E-02	0.028	H_1(B)Accepted
TETA/DDS	Filler(A)	0.302	6	5.041E-02	0.003	H_1(A)Accepted
	Time(B)	0.403	6	6.719E-02	0.000	H_1(B)Accepted

Table 4.19 Summary results of the two ways ANOVA test of hardness of the seawater condition.

Curing system	**Factor**	**TypeIII sum of Square**	**Df**	**Mean square**	**Sig.**	**Conclusion**
TETA	Filler(A)	52.531	6	8.755	0.010	H_1(A)Accepted
	Time(B)	91.388	6	15.231	0.000	H_1(B)Accepted
DDS	Filler(A)	33.633	6	5.605	0.084	H_o(A)Accepted
	Time(B)	43.918	6	7.320	0.030	H_1(B)Accepted
TETA/DDS	Filler(A)	42.816	6	7.136	0.039	H_1(A)Accepted
	Time(B)	76.531	6	12.755	0.002	H_1(B)Accepted

CHAPTER V

CONCLUSIONS

The goals of this research work include the investigation of the cassava starch and fly ash as the potential fillers in fiber reinforced composites industries. The four common industrial fillers were used as references. DGEBA cured with three typical curing systems, aliphatic amine, TETA, aromatic amine, DDS and their mixtures, TETA/DDS were chosen as the matrix of the glass fiber reinforced polymer(GFRP). Rheological and also the basic cure properties of DGEBA filled with six types of filler were investigated. Moreover the mechanical properties by means of tensile properties, impact strength, flexural properties and heat distortion temperature of the GFRP samples were examined. In order to study the effect of fillers on how long would it take for those samples to be degraded or to retain their optimal service mechanical properties, the environmental conditions for degradation of the GFRP filled with those six fillers were manipulated; the landfill condition, water incubated, open-air and accelerated exposure.

From the viscosity measurement by mean of thixotropic index, fly ash and cassava starch could not be used as the thixotropic fillers in the epoxy. Especially when compare with the common industrial thixotropic filler, fumed silica.

The cure data of the filled epoxy resin were ambiguous. The statistical analysis had been used to verify the experimental results. The study revealed that the $t_{50^\circ C}$ and t_{cure} of the epoxy systems were affected by only the type of filler but did not change with the fillers content.

The mechanical properties indicated that cassava starch and fly ash enhanced the tensile properties of the GFRP derived from TETA and TETA/DDS as curing agents. However, the fracture and, perhaps, thermal properties of the reinforcement samples were incompetence by adding fillers especially fly ash and starch. Those mechanical properties were fluctuated by the type of filler used.

When the filled GFRP had been exposed under the natural sunlight, the statistical calculation shown that the degradation of TETA/DDS cured reinforcements did degrade under natural exposure condition. Vice versa, the degradation of the systems cured with the TETA and DDS could not be observed within the given experimental time, 180 days, in this study.

In the accelerated condition, using the standard weatherometer chamber, the GFRP specimens were exposed to the artificial atmosphere. From the statistical analysis based on the experimental data, it was found that the degradation of TETA, DDS and TETA/DDS cured reinforcements did occur under accelerated condition. This outcome had partially confirmed the results obtained from the natural exposure. Ambiguously, the GFRP obtained from epoxy cured with DDS hardener also did degrade under accelerated and the degradation time would depended on the filler used.

When the GFRP samples were buried under the landfill doping with the inorganic bacteria nutrition, nitrate and sulfate. According to the statistical resolution, it was confident to pronounce that the degradation of GFRP cured with TETA hardener was occurred within 180 days and the fillers added did not have an effect on degradation. Vice versa, the degradation of the system cured with the DDS and

TETA/DDS were not be observed within the given experimental time in this study.

To imitate the degradation of the GFRP when it was dumped and also used in the water resources, the reinforcements were soaked into the seawater and waste water. From the statistical calculation, they illustrated that the degradation of TETA cured GFRP could be accomplished in the designed wastewater but it was difficult to declare for the DDS and TETA/DDS systems. Under the seawater, it could be pronounced that degradation might be occurred when TETA, TETA/DDS and DDS used as curing agents. Moreover, the degradation rate would be affected by the fillers used for the TETA/DDS system.

Recommendation For Further Work

The main interesting objectives for the further studied related to this research study should be followed:

(i) To investigate the mechanical properties of the carbonised rice husk as filler in the GFRP

and (ii) Degradation of the GFRP in the longer period, for example 1 – 2 years, must be observed in accelerated chamber.

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APPENDIX A

CONVERSION TABLE OF BROOKFIELD VISCOMETER AND THIXOTROPIC INDEX OF FILLERS

Table A1 Conversion table of Brookfield Viscometer Models RV

Spindles number													
1		**2**		**3**		**4**		**5**		**6**		**7**	
Speed	**Factor**	**Speed**	**Factor**	**Speed**	**Factor**	**Speed**	**Factor**	**Speed**	**Factor**	**Speed**	**Factor**	**Speed**	**Factor**
0.5	200	0.5	800	0.5	2M	0.5	4M	0.5	8M	0.5	20M	0.5	80M
1	100	1	400	1	1M	1	2M	1	4M	1	10M	1	40M
2	50	2	200	2	500	2	1M	2	2M	2	5M	2	20M
2.5	40	2.5	160	2.5	400	2.5	800	2.5	1.6M	2.5	4M	2.5	16M
4	25	4	100	4	250	4	500	4	1M	4	2.5M	4	10M
5	20	5	80	5	200	5	400	5	800	5	2M	5	8M
10	10	10	40	10	100	10	200	10	400	10	1M	10	4M
20	5	20	20	20	50	20	100	20	200	20	500	20	2M
50	2	50	8	50	20	50	40	50	80	50	200	50	800
100	1	100	4	100	10	100	20	100	40	100	100	100	400

Table A2 Thixotropic Index of fillers

Filler	Spin number	Speed	Reading value	Factor	Viscosity	Thixotropic index
Fumed silica[a]	7	1	3.6	400000	144000	2.71
	7	10	18.9	4000	75600	
Fly ash[b]	4	1	4.8	2000	9600	1.11
	4	10	43.2	200	8640	
Talcum[b]	4	1	3	2000	6000	1.05
	4	10	28.5	200	5700	
Titanium dioxide	4	1	5.6	2000	9600	1.05
	4	10	44.5	200	9100	
Cassava starch[b]	4	1	4.6	2000	9200	1.07
	4	10	42.9	200	8580	
Na- borosilicate[b]	4	1	6.2	2000	12400	1.06
	4	10	58.5	200	11700	

Remark : [a]phr=5, [b]phr=10

APPENDIX B

CALCULATION FOR CONVERTS NATURAL EXPOSURE TIME TO XENON ARC LAMP WEATHEROMETER TIME

The calculation to convert the natural exposure time to the Xenon arc lamp weatherometer equivalent time.

Calculation concept:

The concept of converting the natural exposure time to the weatherometer time is, the dosing of energy that produced from the weatherometer to the the specimen must be equaled to the energy that the sample was received from the natural sunlight.

Meteological data:

The total solar radiation in one year exposure (from Table 3.4) = 6898.5 MJ/m^2

The UV energy (λ<295) that could be damaged the plastic

was about 5% of the solar radiation obtained (Mustafa, 1993).

Therefore, total UV energy obtained from the Solar radiation = 344.9 MJ/m^2

Weatherometer data:

From the instrument specification;

For the Boro-Borosilicate inner filter, the factor to convert the total natural UV energy to the equivalent energy at λ= 340 nm = 0.01025

The UV energy (@340 nm) produced by using the weatherometer at 0.7 W/m^2 irradiation setting = 2.52 kJ/m^2-hour

Calculation:

From the data above, to convert the natural exposure time to the weatherometer time, the total UV energy @ 340 nm dosage per year are divided by the value of energy produced by the weatherometer as show follow.

$$Weatherometer\ time = \frac{The\ natural\ UV\ energy\ dosage\ per year \times 0.01025}{The\ UV\ energy\ produce\ by\ weatherometer}$$

$$= \frac{344.9\ MJ/m^2 \times 0.01025}{2.52\ kJ/m^2 - hour}$$

= 1403 hours

So, one year in natural exposure correspond to **1403 hours** in the weatherometer.

APPENDIX C

TIME TEMPERATURE PLOTS

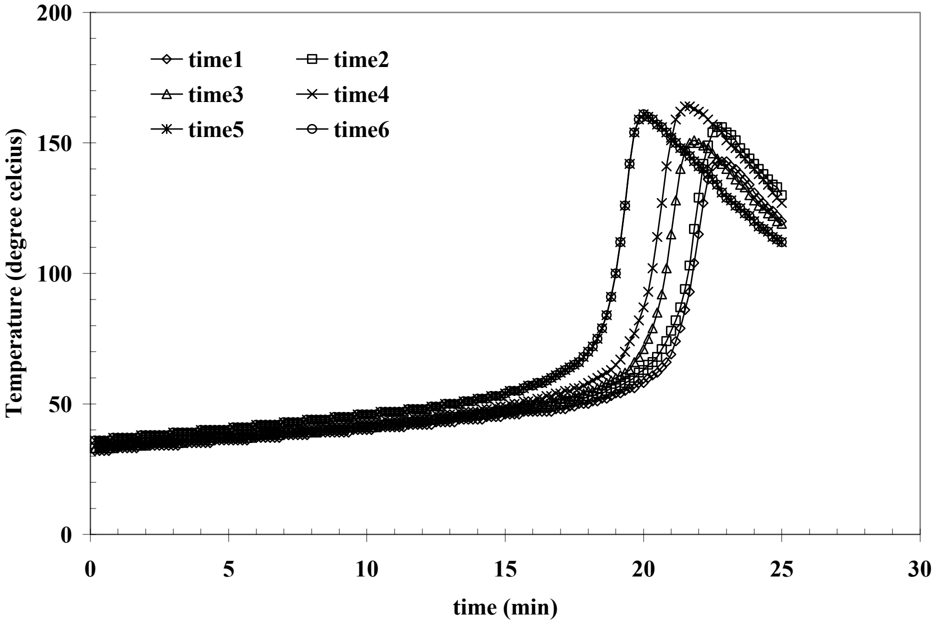

Figure C1 Time-temperature plotted of DGEBA cured with TETA

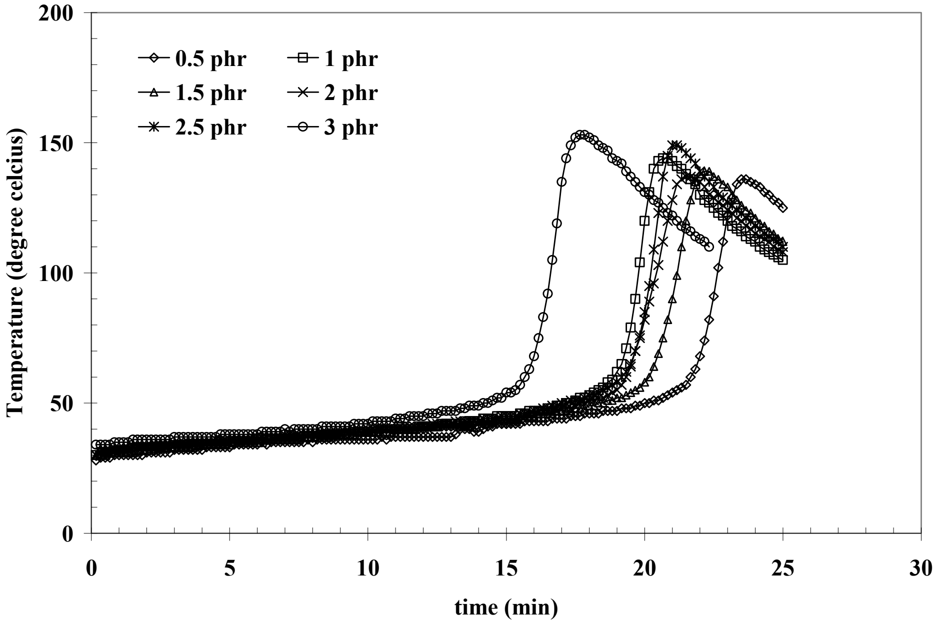

Figure C2 Time-temperature plotted of DGEBA cured with TETA and filled fumed silica

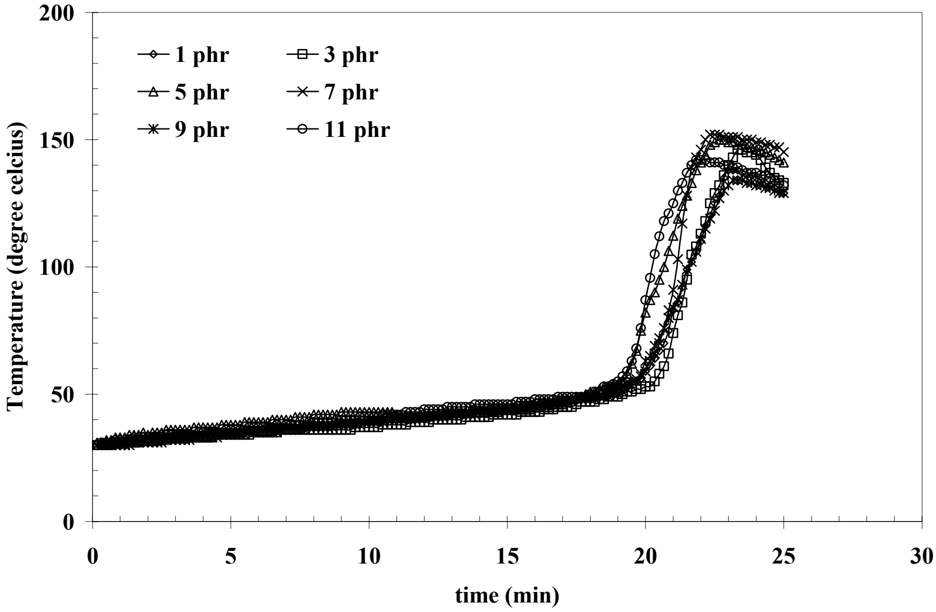

Figure C3 Time-temperature plotted of DGEBA cured with TETA and filled fly ash

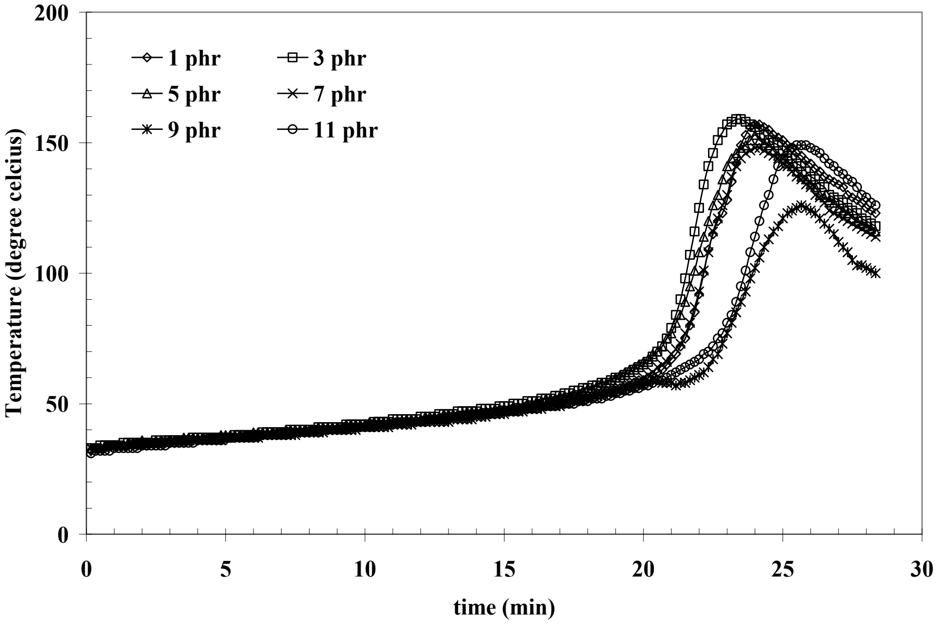

Figure C4 Time temperature plotted of DGEBA cured with TETA and filled talcum

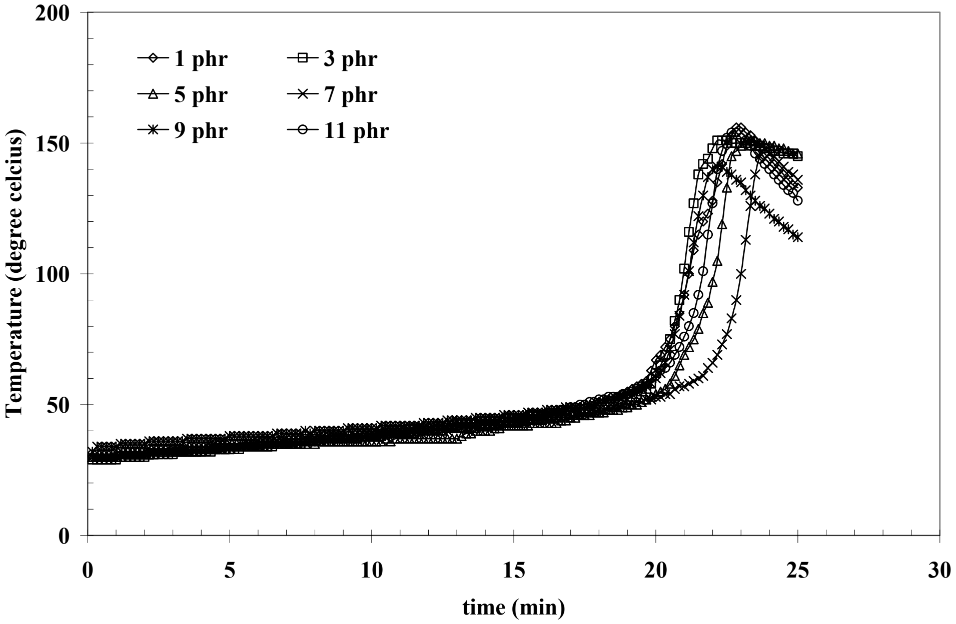

Figure C5 Time temperature plotted of DGEBA cured with TETA and filled titanium dioxide

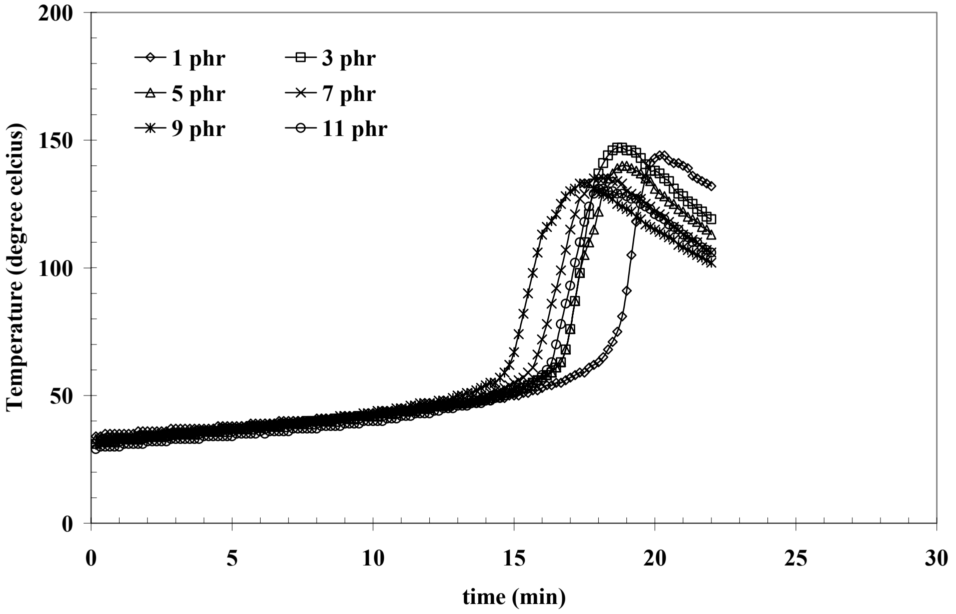

Figure C6 Time-temperature plotted of DGEBA cured with TETA and filled cassava starch

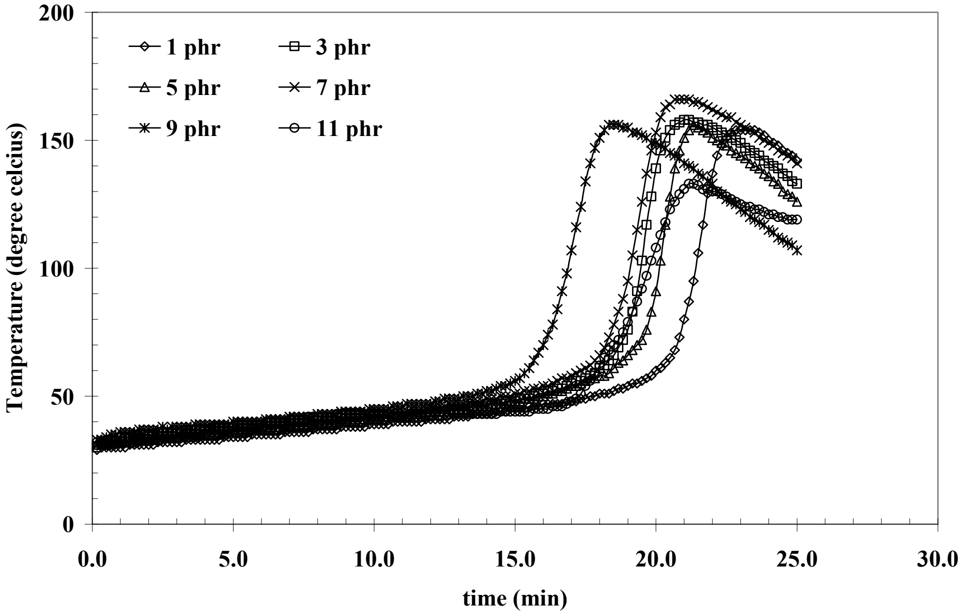

Figure C7 Time-temperature plotted of DGEBA cured with TETA and filled sodium borosilicate glass

APPENDIX D

STATISTICAL TABLES

Table D1 The F distribution with ν_1 and ν_2 degree of freedom (0.95 quantiles)

ν_1 ν_2	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.06	6.00
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.91	2.90
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04
120	3.92	3.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.98

Source: Conover(1999)

Table D2 Chi-Squared distribution[a]

	p=0.750	**0.900**	**0.950**	**0.975**	**0.990**	**0.995**	**0.999**
k = 1	1.323	2.706	3.841	5.024	6.635	7.879	10.83
2	2.773	4.605	5.991	7.378	9.210	10.60	13.82
3	4.108	6.251	7.815	9.348	11.34	12.84	16.27
4	5.385	7.779	9.488	11.14	13.28	14.86	18.47
5	6.626	9.236	11.07	12.83	15.09	16.75	20.51
6	7.841	10.64	12.59	14.45	16.81	18.55	22.46
7	9.037	12.02	14.07	16.01	18.48	20.28	24.32
8	10.22	13.36	15.51	17.53	20.09	21.96	26.13
9	11.39	14.68	16.92	19.02	21.67	23.59	27.88
10	12.55	15.99	18.31	20.48	23.21	25.19	29.59
11	13.70	17.28	19.68	21.92	24.73	26.76	31.26
12	14.85	18.55	21.03	23.34	26.22	28.30	32.91
13	15.98	19.81	22.36	24.74	27.69	29.82	34.53
14	17.12	21.06	23.68	26.12	29.14	31.32	36.12
15	18.25	22.31	25.00	27.49	30.58	32.80	37.70
16	19.37	23.54	26.30	28.85	32.00	34.27	39.25
17	20.49	24.77	27.59	30.19	33.41	35.72	40.79
18	21.60	25.99	28.87	31.53	34.81	37.16	42.31
19	22.72	27.20	30.14	32.85	36.19	38.58	43.82
20	23.83	28.41	31.41	34.17	37.57	40.00	45.32
21	24.93	29.62	32.67	35.48	38.93	41.40	46.80
22	26.04	30.81	33.92	36.78	40.29	42.80	48.27
23	27.14	32.01	35.17	38.08	41.64	44.18	49.73
24	28.24	33.20	36.42	39.37	42.98	45.56	51.18
25	29.34	34.38	37.65	40.65	44.31	46.93	52.62
26	30.43	35.56	38.89	41.62	45.64	48.29	54.05
27	31.53	36.74	40.11	43.19	46.96	49.64	55.48
28	32.62	37.92	41.34	44.46	48.28	50.99	56.89
29	33.71	39.09	42.56	45.72	49.59	52.34	58.30
30	34.80	40.26	43.77	46.98	50.89	53.67	59.70
40	45.62	51.81	55.76	59.34	63.69	66.77	73.40
50	56.33	63.17	67.50	71.42	76.15	79.49	86.66
60	66.98	74.40	79.08	83.30	88.38	91.95	99.61
70	77.58	85.53	90.53	95.02	100.4	104.2	112.3
80	88.13	96.58	101.9	106.6	112.3	116.3	124.8
90	98.65	107.6	113.1	118.1	124.1	128.3	137.2
100	109.1	118.5	124.3	129.6	135.8	140.2	149.4

Source: Conover (1999)

[a] The entries in this table are quantiles W_p of a chi-Squared random variable W with k degree of freedom, selected so $P(W \le W_p) = p$ and $P(W > W_p) = 1-p$.

Table D3 Quantiles of the Kruskal-Wallis test statistic for small sample sizes[a]

Sample Sizes	**$W_{0.90}$**	**$W_{0.95}$**	**$W_{0.99}$**
2, 2, 2	3.7143	4.5714	4.5714
3, 2, 1	3.8571	4.2857	4.2857
3, 2, 2	4.4643	4.5000	5.3571
3, 3, 1	4.0000	4.5714	5.1429
3, 3, 2	4.2500	5.1389	6.2500
3, 3, 3	4.6000	5.0667	6.4889
4, 2, 1	4.0179	4.8214	4.8214
4, 2, 2	4.1667	5.1250	6.0000
4, 3, 1	3.8889	5.0000	5.8333
4, 3, 2	4.4444	5.4000	6.3000
4, 3, 3	4.7000	5.7273	6.7091
4, 4, 1	4.0667	4.8667	6.1667
4, 4, 2	4.4455	5.2364	6.8727
4, 4, 3	4.7730	5.5758	7.1364
4, 4, 4	4.5000	5.6538	7.5385
5, 2, 1	4.0500	4.4500	5.2500
5, 2, 2	4.2933	5.0400	6.1333
5, 3, 1	3.8400	4.8711	6.4000
5, 3, 2	4.4946	5.1055	6.8218
5, 3, 3	4.4121	5.5152	6.9818
5, 4, 1	3.9600	4.8600	6.8400
5, 4, 2	4.5182	5.2682	7.1182
5, 4, 3	4.5231	5.6308	7.3949
5, 4, 4	4.6187	5.6176	7.7440
5, 5, 1	4.0364	4.9091	6.8364
5, 5, 2	4.5077	5.2462	7.2692
5, 5, 3	4.5363	5.6264	7.5429
5, 5, 4	4.5200	5.6429	7.7914
5, 5, 5	4.5000	5.6600	7.9800

Source: Conover (1999)

[a] The null hypothesis may be rejected at the level α if the Kruskal-Wallis test statistic, given by equation E5 in Appendix E, exceeds the 1-α quantile given in the table.

Table D4 The *t* distribution[a]

Degree of Freedom	p=0.6	0.75	0.90	0.95	0.975	0.99
1	0.325	1.000	3.078	6.314	12.706	31.821
2	0.289	0.816	1.886	2.920	4.303	6.965
3	0.277	0.765	1.638	2.353	3.182	4.541
4	0.271	0.741	1.533	2.132	2.776	3.747
5	0.267	0.727	1.476	0.215	2.571	3.365
6	0.265	0.718	1.440	1.943	2.447	3.143
7	0.263	0.711	1.415	1.895	2.365	2.998
8	0.262	0.706	1.397	1.860	2.306	2.896
9	0.261	0.703	1.383	1.833	2.262	2.821
10	0.260	0.700	1.372	1.812	2.228	2.764
11	0.260	0.697	1.363	1.796	2.201	2.718
12	0.259	0.695	1.356	1.782	2.179	2.681
13	0.259	0.694	1.350	1.771	2.160	2.650
14	0.258	0.692	1.345	1.761	2.145	2.624
15	0.258	0.691	1.341	1.753	2.131	2.602
16	0.258	0.690	1.377	1.746	2.120	2.583
17	0.257	0.689	1.333	1.740	2.110	2.567
18	0.257	0.688	1.330	1.734	2.101	2.552
19	0.257	0.688	1.328	1.729	2.093	2.539
20	0.257	0.687	1.325	1.725	2.086	2.528
21	0.257	0.686	1.323	1.721	2.080	2.518
22	0.256	0.686	1.321	1.717	2.074	2.508
23	0.256	0.685	1.319	1.714	2.069	2.500
24	0.256	0.685	1.318	1.711	2.064	2.492
25	0.256	0.684	1.316	1.708	2.060	2.485
26	0.256	0.684	1.315	1.706	2.056	2.479
27	0.256	0.684	1.314	1.703	2.052	2.473
28	0.256	0.683	1.313	1.707	2.048	2.467
29	0.256	0.683	1.311	1.699	2.045	2.462
30	0.256	0.683	1.310	1.697	2.042	2.457
40	0.255	0.681	1.303	1.684	2.021	2.423
60	0.254	0.679	1.296	1.671	2.000	2.390
120	0.254	0.677	1.289	1.658	1.680	2.358
∞	0.253	0.674	1.282	1.645	1.960	2.326

Source: Conover (1999)

[a] The entries in this table are quantiles W_p of the t distribution for various degrees of freedom. Quantiles W_p for $p<0.5$ may be computed from the equation

$$W_p = -W_{1-p}$$

Note that $W_{0.50} = 0$ for all degrees of freedom.

APPENDIX E

THE KRUSKAL-WALLIS TEST MANNER

The nonparametric statistical methods are used for this experiment. They are based on some of the same assumption on which parametric methods are based, such as the assumption that the sample is a random sample. According to Conover, 1999, nonparametric methods are perfectly robust for distribution assumptions on the population because they are equally valid for all distributions. Although a parametric test does not depend critically on an assumption that samples come from a distribution in a particular family, when in doubt they may prefer a nonparametric test which needs weaker assumptions. In addition, nonparametric methods are often the only ones available for data that simply specify order, ranks or count of numbers of events or of individuals in various categories. They are also not assumption-free. Mostly, statistical problems what can deduce, by either parametric or nonparametric methods, depends upon what assumptions can validly be made (Sprent and Smeeton, 2001).

The procedure for the Kruskal-Wallis test is conducted in the following manner:

1. Data

The data consist of k random samples of possibly different sizes. Denote the ith random sample of size n_i by X_{i1}, X_{i2}, …, X_{in_i}. Then the data may be arranged into columns.

Sample 1	Sample 2	……	Sample 3
$X_{1,1}$	$X_{2,1}$		$X_{k,1}$
$X_{1,2}$	$X_{2,2}$		$X_{k,2}$
…..	…..		…..
X_{1,n_1}	X_{2,n_2}		X_{k,n_k}

Let N denote the total number of observations

$$N = \sum_{i=1}^{k} n_i \tag{E1}$$

Assign rank 1 to the smallest of the totality of N observations, rank 2 to the second smallest, and so on to the largest of all N observations, which receives rank N. Let $R(X_{ij})$ represent the rank assigned to X_{ij}. Let R_i be the sum of the ranks assigned to the *i*th sample.

$$R_i = \sum_{j=1}^{n_i} R(X_{ij}),\ i = 1, 2, \ldots, k \tag{E2}$$

Compute R_i for each sample.

If the ranks may be assigned in several different ways because several observations are equal to each other, assign the average rank to each of the tied observations.

2. Assumptions

1. All samples are random samples from their respective populations.
2. In addition to independence within each sample, there is mutual independence among the various samples.
3. The measurement scale is at least ordinal.
4. Either the *k* population distribution functions are identical, or else some of the populations tend to yield large values than other

populations do.

3. Test Statistic

The test statistic T is defined as

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right) \tag{E3}$$

where N and R_i are defined in equation E1 and E2, respectively, and where

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\Ranks}} R(X_{ij})^2 - N\frac{(N+1)^2}{4}\right) \tag{E4}$$

If there are no ties S^2 simplifies to N(N+1)/12, and the test statistic reduces to

$$T = \frac{12}{N(N+1)}\sum_{i=1}^{k}\frac{R_i^2}{n_i} - 3(N+1) \tag{E5}$$

If the number of ties is moderate there will be very little difference between equation E3 and E5, so the simpler equation E5 may preferred.

4. Null Distribution

The exact distribution of T is given by table D3 in appendix D for k=3 and $n_i \leq 5$, but in general the exact distribution is too cumbersome to work with. Therefore the chi-squared distribution with k-1 degrees of freedom is used as an approximation to the null distribution of T.

5. Hypotheses

H₀ : All of the *k* population distribution functions are identical

H₁ : At least one of the populations tends to yield larger observations than at least one of the other populations

Reject ***H₀*** at the level α if T is greater than its 1-α quantile from the null distribution. If k=3, all of the sample sizes are 5 or less, and there are no ties, the exact quantile may be obtained from table D3 in Appendix D. When there are ties, or when exact tables are not available, the approximate quantiles may be obtained from table D2 in appendix D, the chi-squared distribution with k-1 degree of freedom. Reject H_o at the level α if T exceeds the $1-\alpha$ quantile thus obtained. The p-value is approximately the probability of a chi-squared random variable with k-1 degrees of freedom the observed value of T.

6. Multiple Comparisons

If, and only if, the null hypothesis is rejected, we may use the following procedure to determine which pairs of populations tend to differ. We can say that populations *i* and *j* seem to be different if the following inequality is satisfied:

$$\left|\frac{R_i}{n_i}-\frac{R_j}{n_j}\right\rangle t_{1-(\alpha/2)}\left(S^2\,\frac{N-1-T}{N-k}\right)^{1/2}\left(\frac{1}{n_i}+\frac{1}{n_j}\right)^{1/2} \qquad \text{(E6)}$$

where R_i and R_j are the rank sums of the two samples, $t_{1-\alpha/2}$ is the $(1-\alpha/2)$ quantile of the t distribution obtained from table D4 in Appendix D with N-k degree of freedom, S^2 comes from equation E4, and T comes from equation E3 or E5. This procedure is repeated for all pairs of populations. The same α level is usually used here as in the Kruskal-Wallis test.

APPENDIX F

RESEARCH PUBLICATION

Research Publication

Parts of this work were published and being presented in the following conferences;

Thananowan, P. and Meekum, U. (2003). Effect of fillers on rheological and degradation properties of epoxy systems. In **An international conference on advance in petrochemicals and polymers in the new millennium.** Bangkok, Thailand.

Thananowan, P. and Meekum, U. (2004). Study of cassava starch and fly ash as thixotropic materials in epoxy resin systems. In **The 4th national symposium on graduate research.** Chiang Mai, Thailand.

BIOGRAPHY

Pacharapol Thananowan was born in Bangkok, Thailand. He obtained his undergraduate degree in Polymer Engineering from Suranaree University of Technology, Nakorn Ratchasima. He had two year experience as a sales executive at Channel Chemicals Co., Ltd. before continued his graduate degree in Polymer Engineering at the same university. During graduate study he presented three papers entitled of “Controlling the cure time of epoxy resin in hand lamination process for windsurf manufacturing” in the 3rd national symposium on graduate research on July 18-19, 2002 in Nakorn Ratchasima, Thailand , “Effect of Fillers on Rheological and Degradation Properties of Epoxy Systems” in An International Conference on “Advance in Petrochemicals and Polymers in the New Millennium” on July 22-25, 2003 in Bangkok, Thailand, “Study of cassava starch and fly ash as Thixotropic materials in epoxy resin systems” in the 4th Grad Research Conference on August 10-11, 2004 in Chiang Mai, Thailand.