PREPREG FORMULATION FOR WINDSURF AND SURFBOARD MANUFACTURING

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สูตรพรีเพคสำหรับกระบวนการผลิตกระดานโต้คลื่นและกระดานโต้ลม

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โดยใช้พื้นฐานผลทางด้านคุณสมบัติทางความร้อนและคุณสมบัติเชิงกลและการยืนยันโดยใช้การทดสอบทางสถิติแบบ ANOVA พบว่า อัตราส่วนเหมาะสมระหว่างอีพอกซี YD115 กับ YD127 ที่ทำให้คุณสมบัติเชิงกลมีค่าสูง คือ ที่สัดส่วน 80:20 โดยน้ำหนัก ซึ่งสวนทางกับผลทางกระแสวิทยา พบว่า ที่สัดส่วนของอีพอกซี 20:80 โดยน้ำหนัก ให้ค่าของอุณหภูมิการบิดงอ (HDT) และค่าความหนืดที่สามารถยอมรับได้ แต่ให้ค่าคุณสมบัติเชิงกลปานกลาง ซึ่งสอดคล้องอย่างดีกับกฎของสารผสมและความต้องการของกระบวนการผลิต พบว่าที่สัดส่วน 20:80 โดยน้ำหนัก ได้รับการยอมรับสำหรับเป็นอีพอกซีเรซินสำหรับสูตรของพรีเพค ผลการศึกษายังบ่งชี้ว่า ขนาดอนุภาคของไดซี (DICY) ไม่มีผลอย่างมีนัยสำคัญต่อคุณสมบัติเชิงกลและคุณสมบัติทางความร้อนของวัสดุเชิงประกอบที่ซึ่งเตรียมมาจากสูตรพรีเพค สาร Ancamine 2165 ไม่เพียงแต่ทำให้คุณสมบัติทางด้านแรงดึงเพิ่มขึ้นแต่ยังเพิ่มความเหนียวของวัสดุเชิงประกอบที่เตรียมจากสูตรพรีเพคให้มีค่าสูงขึ้น แต่ให้ค่า HDT มีค่าต่ำลงเล็กน้อย นอกจากนี้พบว่า ตัวเร่งปฏิกิริยาชนิดสารประกอบยูเรีย Dyhard UR200 ที่เติมในสัดส่วน 10 โดยน้ำหนัก ให้คุณสมบัติของวัสดุเชิงประกอบที่สูงขึ้นด้วย

เวลาการเหนียวตัว B-stage (t_B) ที่อุณหภูมิ 20°C คำนวณจากสมการ Arrhenius พบว่า ค่า t_B ของพรีเพคที่ได้จากการใช้ Ancamine 1618 กับ Ancamine 2165 ที่สัดส่วน 20:30 โดยน้ำหนัก มีค่าเท่ากับ 12 ชั่วโมง และยอมรับได้อย่างดีสำหรับกระบวนการผลิต จากการศึกษาพบว่า สูตรพรีเพคที่ดีที่สุดสำหรับการผลิตกระดานโต้คลื่นและกระดานโต้ลม ประกอบด้วย อีพอกซีเรซินที่เตรียมจากการผสมของ YD115 กับ YD127 ที่สัดส่วน 20:80 โดยน้ำหนัก และตัวทำแข็งที่ได้จากการผสมของ Ancamine 1618, Ancamine 2165, Dyhard 100 และ Dyhard UR 200 ในสัดส่วน 25:25:40:10 โดยน้ำหนัก ตามลำดับ

สภาวะของการบ่มแข็งที่ดีที่สุดคือ การบ่มแข็งขั้นต้น (pre-cure) ที่ 150°C เป็นเวลา 10 นาที และบ่มแข็งขั้นสุดท้าย (post-cure) ที่ 150°C เป็นเวลา 8 ชั่วโมง จากผลการทดลองและการประเมินโดยวิธีทางสถิติพบว่า ตัวทำละลายที่ใช้ผสมในสูตรพรีเพคและชนิดของเส้นใยเสริมแรงไม่มีความสัมพันธ์กับความแข็งแรงของวัสดุเชิงประกอบที่เตรียมได้

สาขาวิชาวิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา วรรณพร ณ ไทร
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EPOXY RESIN/ PREPREG/ COMPOSITE MATERIALS/ CURE CONDITIONS/ SOLVENTS/ REINFORCEMENTS

Based on the thermal and mechanical properties justification and also confirmation by the statistical testing using the ANOVA, the results showed that optimal ratio between YD115 and YD127, which gave rise to the superior mechanical properties, was 80:20 by weight. On the other hand from the rheological points of view, the epoxy ratio at 20:80 provided the acceptable HDT and viscosity values but moderate in mechanical properties. According to the well verified rule of mixture and also the manufacturing constrain the ratio of 20:80 was accepted as the base epoxy resin for the prepreg formulation. The results indicated that the particle size of DICY did not have the significant influence on the mechanical and thermal properties of the composite product prepared from the prepreg formulation. Ancamine 2165 was not only used to enhanced the tensile property but also improved the toughness of cured prepreg composite but inferior in HDT. It was found that urea substituted catalyst, Dyhard UR200, at 10 part of weight ratio provided the distinguish performance properties.

The B-stage time at 20°C was calculated based on the Arrhenius's equation. It was found that t_B of the prepreg derived from the mixture of Ancamine 1618 and Ancamine 2165 at 20:30 weight ratio was 12 hrs. and successfully accepted for the manufacturing. The conclusion found that the optimal prepreg formulation for windsurf and surfboard production was the combination of the R2 epoxy resin mixture, 20:80 of YD115 and YD127, and the hardener derived from 25:25:40:10 of Ancamine 1618, Ancamine 2165, Dyhard 100 and Dyhard UR200, respectively.

The optimal cure conditions were pre-cure at 150°C for 10 mins and post cure at 150°C for 8 hrs. The strong recommendation on the solvents used for the prepreg and assigned reinforcement systems could not be drawn either by experiment or statistical evaluation.

School of Polymer Engineering

Academic Year 2006

Student's Signature WANNAPORN NASAI

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SYMBOLS AND ABBREVIATIONS

% = Percent

η = Viscosity

η_{mix} = Viscosity of Mixture

ρ = Density

α = Conversion

A = Arrhenius's Constant

σ_u = Ultimate Tensile Stress

σ_{fM} = Flexural Strength

a_{iN} = Impact Strength

µm = Micrometer

°C = Degree Celsius

E = Young's Modulus

E_a = Apparent Activation Energy

E_f = Flexural Modulus

GPa = Giga Pascal

H_0 = Null Hypothesis

H_1 = Alternative Hypothesis

hrs = Hours

J = Joule

kgf = Kilogram Force

kJ = Kilo Joule

SYMBOLS AND ABBREVIATIONS (Continued)

kPa = Kilo Pascal

mins = Minutes

mm = Millimeter

MPa = Mega Pascal

mPa.s = Milli Pascal Second

N = Newton

phr = Parts per Hundred Parts of Resin

psi = Pound per Square Inch

R = Universal Gas Constant

r = Correlation Coefficient

R^2 = Coefficient of Determination

T = Absolute Temperature

t_B = B-Stage Time

T_g = Glass Transition Temperature

W = Impact Energy

w_i = Weight Fraction

wt.% = Percent by Weight

CHAPTER I

INTRODUCTION

1.1 General Introduction

At present, Thai composite industries are small compared to the global scale. However, they are extremely diverse with the production ranging from automotive, sport goods, housing and infrastructure products for both local use and overseas export. The market for composite products made in Thailand is sizable and it is expected to increase considerably in coming years.

One of the most well known components used in the industry is prepreg that is important composite material. Prepreg is often used to produce various composite products. It is the fiber reinforcing materials impregnated with resin, which is to be molded to desired shape according to the needs of the final products and cured by application of heat and pressure. The excellent handle ability of prepreg makes it very desirable to the composite industry, where lightweight parts can be manufactured with high temperature capabilities. Moreover, prepreg material will be used in place of the common wet methods because its can be solved many of the critical and problems associated with traditional processing method of composites. For instance, resin-rich or fiber rich that it is poor distribution or uniformity, labor of rolling the lay up or spray up to wet out the fiber and volatile vapor problems.

Most of typical thermosetting resins and some thermoplastic resins are commonly used in prepreg material. The most common thermoset resin is epoxy because it is the major markets for prepreg materials and also it is widely used for composite materials. The epoxy resin was chosen as matrix in several applications due to many advantages. It has superior heat resistance, corrosion resistance, low shrinkage, excellent adhesion, and relative better mechanical properties among thermosetting resins. In addition, epoxy prepreg is produced according to their end uses and applications. Several factors such as epoxy resins, curing agents, reinforced fibers, modifiers such as solvents and cure cycle have important effects on the properties of prepreg and their final products.

In this thesis focus on prepreg formulation that will be applied for windsurf and surfboard application is preliminary concerned. The effects of epoxy matrix materials, reinforcements, solvents prepreg and cure cycles on the mechanical and thermal properties will be interested. Hopefully, the outcome of this study could bring the clear understanding about the influence on epoxy prepreg formulation and processing parameters required to optimal the requirement of the final properties. In addition, the results obtained from this research could be used as basic information to improve and develop the other properties of composite materials for other applications as well.

1.2 Research Objectives

The research problem is arisen from the industrial cooperation work. The windsurf and surfboard manufacturer, Cobra International Co. Ltd., has keen on having its own technology for prepreg manufacturing to reduce the dependency of importing the material. Therefore, the prime objectives of the research work will mainly rely on the industry requirements that include;

(1) To study the effect of epoxy resins and curing agent components on the mechanical and thermal properties of fiber glass reinforced composite prepared from the prepreg formulation.

(2) To observe the effect of cure cycles on the final properties in order to optimize the properties of the final product.

(3) To investigate the influence of fiber reinforcement and solvents on the properties of cured prepreg.

1.3 Scope of Work

The main study of this research was to prepare the prepreg formulation for windsurf and surfboard manufacturing with optimum properties. The purpose of this studied was to investigate the effect of epoxy ratio, curing agent ingredients, reinforcing materials, cure cycles and solvents used in prepreg on the properties. The processability, mechanical and thermal properties were used as bench mark to evaluate these effects. The tensile, flexural and impact testing were employed to obtain the mechanical properties. Also, the thermal property by means of heat distortion temperature (HDT) has been reviewed which indicate the maximum service temperature. In the processability parameter; resin viscosity, cure conditions and B-stage time were also tested. The main reinforcement used in this study was glass fiber. The carbon fiber was also employed in order to compare the compatibility of the prepreg formulation with the reinforcements. Two solvents, metyl ethyl ketone (MEK) and ethyl acetate (EA) as the diluent for the prepreg formulation were also studied.

CHAPTER II

LITERATURE REVIEW

2.1 General Background

The term “prepreg” contracted from “pre-impregnated materials” and originated well known in 1954 (Kelly and Zweben, 2001). Prepreg consisted of unidirectional fiber or woven fabrics with the resin matrix to produce a uniform laminate structure that it is of uncured composites. The reinforcing fibers may be glass, Kevlar, carbon, polyester, nylon and ceramic fiber, but the most commonly used one is glass fiber (Morley, 1987). The polymer matrix can be prepared from either thermoplastic or thermosetting resins. The advantages of thermosets lie in their low molecular weight and low glass transition temperature prior to reaction. These enable thermosetting composites to conform to different shapes easily and to allow stacks of plies to stick together.

For years, prepregs have been successfully used as precursors in the manufacture of high performance composites. This is mainly attributed to their ease of handing, uniform fiber alignment, accurate control of the resin content, and their readiness to use with on further treatment. Specifically, epoxy matrix based prepregs have desirable tack and drape that allow more complicated shapes than flat panels to be formed. Besides, epoxy prepregs possess various excellent properties such as high tensile strength and modulus, good thermal and chemical resistance and dimension stability.

In this chapter, the background of research is briefly discussed. This includes the epoxy systems, epoxy prepregs, curing reactions and properties of epoxy resins and composites that are reviewed from the research works published in various scientific documents.

2.2 Epoxy Systems

Epoxy is a class of thermosetting materials used extensively in the structural and special composite applications. Because its offer the unique properties that is unattainable with other thermoset resins. The applications of epoxy are found in many fields such as aerospace applications and are now being used to produce lightweight bicycle frames, golf clubs, snowboards, racing cars, and musical instruments. To support these applications, epoxy resins are formulated to generate specific physical and mechanical properties. While, the simplest formulations may combined epoxy resins with curing agents and/or include modifiers for toughness or flexibility. The three basic elements of epoxy resin formulation that must be understood when selecting. It is necessary to known what each of these components contributes to the physical and mechanical performance. In this section, the background and research works about epoxy resins, curing agents and modifiers will be discussed.

2.2.1 Epoxy Resins

Epoxy resins were first used for composite applications in the early 1950s (Jang, 1994). The first liquid epoxy resin is the reaction product from bisphenol A (BPA) with an excess epichlorohydrine (ECH). This resin commonly is called the diglycidyl ether of bisphenol A (DGEBA). Other types of epoxy resins are glycidyl ethers of novolac resins, phenoxy epoxy resins, and (cyclo) aliphatic epoxy resins. Glycidyl ethers of novolac resins and phenoxy epoxy resins usually have high viscosity and better high temperatures properties while (cyclo) aliphatic epoxy resins have low viscosity and low glass transition temperatures.

The commercially available DGEBA has a large distribution of chain lengths. Epoxy resins are characterized by epoxy equivalent weight (EEW). The equivalent weight of epoxy is used to calculate the stiochiometric ratio between epoxy and curing agent in order to optimize the cured properties. The present of the glycidyl units in these resins enhances the processability but reduces thermal resistance. The glass transition temperature (T_g) of the cured resin is relatively low (<120°C) (Lin and Pearce, 1993). This is a limitation of these resins in high performance applications. Higher T_g and improvement in thermal and mechanical properties can be achieved by either introducing thermally stable rigid rings in the backbone or by increasing crosslink density (Chen et al., 1982).

2.2.2 Curing Agents

Epoxy resins are usually used in conjunction with a curing agent to achieve desirable hard solid products. Curing agents are important role in the curing process of epoxy resin because they relate to the curing kinetics reaction rate, gel time, degree of cure, viscosity, curing cycle, and the final properties of cured products. The properties such as chemical resistance, thermal stability and glass transition temperature are controlled by curing agents (Jang, 1994). The choice of curing agents depends on processing method, curing cycle, curing temperature and time, physical and chemical properties desired, toxicological and environmental limitations and cost.

Curing agents for epoxies are available with a wide range of cure characteristics, from rapid, room temperature and high temperature. The curing agents are of three basic types including amine, anhydride and catalysts. This study would be focus on amine curing agents and catalysts. Amine curing agents are further divided into aliphatic, cycloaliphatic, and aromatic amine (May, 1988).

Aliphatic amines such as diethylene triamine (DETA) and triethylene tetramine (TETA) have a short pot life about 30 minutes and result in a completely cure in a few day.

Cycloaliphatic amines, they can be gelled at room temperature. Isophorone diamine (IPDA) is the principle commercial and largest volume cycloaliphatic amines. The properties of epoxies cured with this amine are intermediate between those cured with aliphatic and those cured with aromatic amines.

Diamino diphenyl methane (DDM) and diamino diphenyl sulfone (DDS) are principal commercial aromatic amines. They are used mainly for high performance composites. Epoxies cured with the aromatic amines have excellent overall properties, but required cure high temperature.

Catalytic curing agents will be used in conjunction with other curing agents to accelerate the cure rate. A commonly materials used as catalysts are Boron trifluoride amine complexes (Lewis acids), imidazole and substituted urea. They are inert at low temperature but vigorously trigger the process when heated above a critical threshold temperature (Mallick, 1997). Dicyandiamide (DICY) is used together with co-curing catalysts because the uncatalyzed reactions begin above 150°C (Kelly and Zweben, 2001).

2.2.3 Modifiers

The general modifiers such as reactive diluents, rubbers, thermoplastics, solvents, etc are used to provide specific physical and mechanical performance. Reactive diluents and solvents are used primarily in epoxy formulations to reduce viscosity and they may be selected to alter the final properties of cured system. Rubbers and thermoplastic are used as resin modifiers to improve mechanical and thermal resistance, increase elongation, and obtained higher flexibility and impact strength (Kelly and Zweben, 2001).

Oliveira, Azevedo and Machado (1995) investigated the structure properties of epoxy diluted with xylene. The DGEBA was diluted in concentration range 0 to 20% and was cured with ethylene diamine. It was found that the chain length of the polymer gets larger when diluted with xylene.

2.3 Epoxy Prepreg

Epoxy prepreg is of the composite materials in which the fibers have been pre-impregnated with the epoxy resin and/or with solvent, with a catalyst under heat and pressure. The process of combining fibers with epoxy is usually applied by hand or by automated machines. The manufacturing processes for prepreg, dominated in the market, are hot melt process and solvent process. The choice between these processes depends on raw materials characteristic and their properties used in formulations. In this section focused on the prepreg processing and formulations.

2.3.1 Prepreg Processing

The process for resins which are liquids at room temperature or which can be made liquid by some minor resin preheating in the resin mixing pot where all of the resin components are combined. The general term for this process is “hot melt or solventless process”. For resins that are solids at room temperature and cannot be easily melted, a slightly different process may be used. It is called “solvent process”. The resin is dissolved in a solvent to transform into liquid. Then the resin solution is coated onto the backing material or directly onto the fibers using a nip-roll system and then mated with the backing material. In the solvent application system, most of the solvent is removed during the heating stage so that the B-staged resin is relatively dried of solvent. The description of B-stage will explained in curing reaction section. For some applications, a minor amount of solvent can be left in the prepreg so that the prepreg material will be softer and tackier when it is laid up.

Hong and Wu (1998) studied the effect the solvents on the curing behaviors of epoxy (DGEBA) and Dicyandiamide/2-methyl imidazole system. Three different solvents, acetone, tetrahydrofuran (THF) and toluene were used in studied. The results showed that the reaction exotherm, the time of maximum curing rate, the glass transition temperature (T_g), and the reaction order of epoxy system decrease in the presence of solvents. The changes were in the order of toluence> tetrahydrofuran> acetone and which are consistent with the order of their boiling points. The heat absorbed during the solvent evaporation consumed the curing exotherm and resulted in a change in temperature dependent curing mechanisms.

Solvents are not environmentally friendly and contribute to voids in prepreg and laminates. Casto (2004) investigated the development of solventless process for electronic prepregs. Voids cause the product variability, which is a major source of scrap in board shops. To eliminate these drawbacks, solventless process, based no the concept of injection pultrusion, has been developed. The impregnation is performed in a die under pressure to minimize voids. A microscope has been used to observe the void contents of the prepregs. The solventless prepregs had been compared against standard prepregs and shown qualitatively to have fewer voids.

Hayes and Seferis (1997) investigated the effect of fabric tension and number of impregnation rollers used during hot melt prepreg processing. The results showed that fabric tension had a large influence on the prepreg characteristics due to more cylindrical tow shapes and a ridged fiber bed. The number of impregnation rollers was found to affect only the characteristics of the prepreg manufactured with no tension prepreg. The void content was negligible for all laminates cured at higher consolidation pressure.

2.3.2 Prepreg Formulations

A common epoxy prepreg is typically formulated from a blend of epoxy resins, with curing agents and catalytic curing agents. The raw materials used in prepreg formulations mostly depend on processes, required properties and the applications. Although a great variety of epoxy materials, the number of prepreg materials based on epoxy resins available for prepreg manufacture in particular is limited.

Banks et al. (2004) had studied the development of new structural prepreg. Based on this research, a new type of prepreg was produced in the commercial quantities in Australia. The resin used in the prepreg was a solvent-free DGEBA epoxy premixed with 10% Ethacure 100^{TM}.

Rhee et al. (2003) reviewed the non-woven graphite/epoxy prepreg. The matrix material was an epoxy based on the DGEBA resin (43%) and phenolic novlac resin (50%). The curing agents are Dicyandiamide (5%) and aromatic urea compound (2%).

Timmerman et al. (2002) studied the formulation of carbon/epoxy prepreg. The resin used EPON® 828, 836, 817 and D.E.R. 661. The epoxy equivalent weights of these materials were 187, 315, 430 and 530 g/epoxy, respectively. D.E.R. 661 and EPON® 828 and 836 are based on DGEBA and only differ in their backbone lengths. EPON® 871 was aliphatic epoxy resin. Two commonly and commercially available for aerospace prepreg curing agents and, diaminodiphenyl sulfone (DDS), and dicyandiamide (DICY) was used in conjunction with Diuron as accelerator. Nipol 1472, solid butadiene/acrylonitrile rubber, was included in the formulations as toughening agent. Chromium (2%) naphthenate was used as a catalyst for the epoxy/carboxyl etherification reaction (Martin and Seferis, 1998).

Glibert et al. (2003) investigated the carbon prepreg. The formulation consisted of two difunctional epoxies, Epon® 828 and Epon® 836, both based on DGEBA. The resin was cured with Dicyandiamide and Diuron. This formulation contained 67.1 wt.% Epon 836, 23.5 wt.% Epon® 828, 6.0 wt.% Amicure® CG 1400, and 3.4 wt.% Diuron.

2.4 Curing Reaction of Epoxy Resins

The Curing reaction of epoxy resin can be carried out by addition reaction to yield a highly crosslinked three dimensional network structure which is infusible and insoluble. Unreacted resins are usually referred to as A-stage resin. A partially reacted resin, usually a vitrified system below gel point is called a B-stage resin, while completely cured resin is called a C-stage resin. The essential condition to B-stage is verification prior to gelation and achieved by keeping the reaction temperature below the curing temperature. Ease in processability is achieved by using B-stage resin (Kelly and Zweben, 2001).

The B-stage resin is a partially cured resin where crosslinks exist at widely spaced points. The hardness and tackiness of such resin depend on the degree of cure advancement. By lowering temperature, the curing reaction can be slowed down. The B-staged resin and prepreg can be stored at low temperature and can later transformed into a hard insoluble cure resin/laminate by completing the cure at elevated temperature.

The curing of epoxy resin is associated with a change in state from a low molecular weight liquid mixture to a highly crosslinked network. The molecular mobility in the system decreases as the cure proceeded due to the crosslinking of several chains into network of infinite molecular weight. The sudden and irreversible transformation from a viscous liquid to an elastic gel is known as gel point. Gelation typically occurs between 55-80% conversion. Beyond the gel point, reaction proceeds towards the formation of one infinite network with substantial increase in crosslink density, T_g, and ultimate physical properties. Wingrad (1999) have found that epoxy/fiberglass prepreg in advanced composites piping systems had a gel point at 63% conversion.

Curing time depends on the amount and type of curing agent. Thus, curing time is less than an hour at ambient temperature when DETA or TETA are used for DGEBA resin, while it takes more than 6 hrs with m-phenylene diamine. DICY with liquid/solid epoxy resins gives a curing time of 6 months and it is considered as latent epoxy resin curing agent. This is due to its insolubility in the resin at room temperature.

The transformation from solution to gel and to glass has been followed by variety techniques, such as viscosity (Younes et al., 1994), calorimetry (Shim et al., 1997), dielectric and mechanical relaxations (Casalini et al., 1997), dilatometry, and ultrasonic measurements (Alig et al., 1992). Several spectroscopic methods including Infrared (Min, Stachurski and Hodgkin, 1993; Nigro and Ishida, 1989; Schiering et al., 1987) and Raman spectroscopy had also been used. Amongst all the techniques described above, differential scanning calorimetry and gel point determination have been widely used to study kinetics and mechanism of curing of epoxy resins.

2.5 Properties of Cured Epoxy Resins and Composites

In a cured epoxy resin, there is distribution of molecular weights or segments lengths between the crosslinking points. Also, there is a distribution of unreacted functional groups and monomers that are trapped or fixed in spatial arrangements throughout the network. The T_g of a crosslink polymer may be related to the overall conversion, stiffness of the crosslinked chain, and the free volume entrapped in the network (Grillet et al., 1989).

Changing the stiochiometry of epoxy amine also leads to unreacted epoxy or amino functionalities and results in lowering the T_g drastically (Almeida and Monteiro, 1998). Thus, the T_g of DGEBA cured with DDS has been reports as 128°C, 184°C and 169°C when the epoxy amine ratio was 2.0, 1.0 and 0.5, respectively. In order to describe the shift in T_g with stiochiometry, it was convenient to classify networks as rigid (high T_g) or flexible. For rigid networks, Neilson's equation can be used to predict the shift in the T_g with stiochiometry by taking concentration of elastic network chains. While for flexible networks, T_g depends on changes in chemical composition (Vallo et al., 1991). The T_g along with some other characteristics of DGEBA epoxy cured with m-PDA at 75°C for 2 hrs in an inert gas environment for epoxy amine ratios of 1.90, 1.00 and 0.56. It was noteworthy that the stiochiometric sample, which has the highest crosslink density and the lowest M_c, showed the highest T_g.

The thermal properties of cured epoxies are determined by the structure of epoxy, cross-linking density and the functionality of epoxy and curing agent. If the chemical structures of cured epoxy resins are constituted with aromatic rings, heterocyclic rings, or both, their thermal properties is superior to those of constituents with flexible or aliphatic chains (Potter, 1970).

Su et al. (2002) investigated the different of thermal properties between rigid and flexible bisphenol A (DGEBA) epoxies. The rigid rod epoxies of azomethine (AM), bisphenol (BP) and tetramethyl bisphenol (TMBP) were cured with diaminodiphenylsulfone (DDS) and dicyandiamide (DICY), respectively. The DDS cured epoxies had higher glass transition temperature (T_g) and decomposition temperature than the DICY cured epoxies due to the high functionality and rigid structure of DDS. The AM, BP and TMBP had higher T_g than DGEBA due to the low molecular motion and high thermal stability of rigid rod structure. The bulky methyl substitution on the BP main chain of TMBP epoxy decreased the order of polymer packing and reduced the T_g. The AM epoxy has the longest rigid rod structure, thus the AM epoxy has a higher T_g than that of BP and TMBP epoxies.

The mechanical properties of cured epoxy resins depend on chemical structure of curing agents (Grillet et al., 1991) and epoxy resin, epoxy and amino stiochiometry, or crosslink density (Plamese and McCullough, 1992) of the cured network, cure schedule (Ellis et al., 1996), test temperature, and strain rate (Won et al., 1990), Urbacewski et al., 1991; Sind et al., 1996). The tensile strength and tensile modulus of cured epoxy resin lied in the range of 40 - 130 MPa and 2.0 - 4.1 GPa, respectively (Mallick, 1993). The elongation at break lied in the 2 - 9% range. Cure shrinkage was low in these resins about 1 - 5% and specific gravity was around 1.2 - 1.3.

Although epoxy have been used as matrix materials for many advance composites. The intrinsic brittleness, poor resistance to crack propagation and low fracture toughness associated with their highly crosslinked structure remain a major drawback. The toughness of epoxy resins has been increased by blending with reactive liquid rubbers such as carboxyl terminated butadiene acrylonitrile rubbers (CTBN) or terminally functionalized engineering thermoplastics.

More recently, engineering thermoplastics are interesting materials as modifiers for epoxy resins from the viewpoint of the maintenance of mechanical and thermal properties for the matrix resins. Modifications of epoxy resins with various types of ductile thermoplastics have been studied as alternatives to reactive rubbers for improving the toughness of epoxy resins. For example, polysulfone containing pendant amino groups had been reported as effective modifiers.

Epoxy composites are composed of reinforcing fiber and epoxy matrix. Epoxy resins have high heat resistance and great structural durability while reinforcing fibers can provide strength and stiffness. The combination of reinforcing fibers and the epoxy matrix gives composites many desirable chemical and physical properties. They have high strength and can meet specific strength requirement in engineering applications.

2.6 Cure Cycle

The optimum cure cycle of epoxy resins depends on the type of epoxy resins and curing agents. The cure temperature is the important factor in determining the application of epoxy resins. Epoxy formulations do not have naturally definable cure temperatures. The rate of reaction of given mixture of epoxy and curing agent is dependent on the temperature. If the temperature was not reached or the time at given temperature was insufficient, the resin will not completely react to full conversion.

Min et al. (1993) studied the influence of cure temperature and cure cycle; one-step or two step cure, on the properties of epoxy system. The glass transition temperature (T_g), fracture toughness, and tensile properties of DGEBA cured with DDS were studied as a function of cure conditions. The glass transition showed a linear increase with increasing cure temperature and levels off toward the cure temperature at 200°C. Fracture toughness, tensile strength, strain at break, and tensile fracture energy also increased significantly with increasing final cure temperature regardless of cure cycle. In contrast, the modulus, yield stress, and yield strain were not influenced greatly by cure temperature and cure cycle.

Prepreg based composites required the application of heat and pressure to bring the individual prepreg plies and consolidate them together into one uniform material. Additionally, elevated temperatures are necessary to initiate and complete the curing reaction of thermosetting prepreg materials. Several techniques, such as compression or autoclave operations, are available to conduct this manufacturing operation.

Sun et al. (2002) analyzed the isothermal cure process of epoxy prepreg. The commercial prepreg used in the study was the commercial 8552 epoxy matrix, which was the amine cured system. It contained about 33% resin with reinforcement of carbon fiber. The curing process was studied by differential scanning calorimeter analysis. The epoxy prepreg was isothermally measured from 110°C to 220°C. The results showed that the heat of isothermal cure reaction increased with increment of temperature. The complete cure reaction could be achieved at 220°C within a very short cure time.

From the literature review, it is strongly suggested that there are many influence factors contributed to the final properties of the laminated product prepared from prepreg materials. Therefore, the study in the specific prepreg formulation that will be used in the windsurf and surfboard manufacturer is an interesting issue. The result data from this study are not only directly applied into the product line but also could be used as the fundamental information for proper developing the prepreg and another composite in the future.

CHAPTER III

EXPERIMENTAL METHODOLOGY

3.1 General Background

The main topics of this research study include the epoxy matrix and hardener formulations, cure conditions, reinforcements and solvents for used in epoxy prepreg which was mainly applied for windsurf and surfboard manufacturing. Processing parameters such as viscosity, cure conditions and B-stage time were also investigated. The mechanical properties by mean of tensile, flexural and impact testing were also observed. In order to certify the maximum service temperature of the formula, heat distortion temperature (HDT) was measured. The descriptions of the materials, experimental procedures and performance testing are given in detail as follows.

3.2 Materials and Chemical Reagents

The main materials used in this research can be classified into 3 categories (i) the resin and hardener ingredients (ii) the reinforcement materials and (iii) the miscellaneous solvents used in the prepreg formulations.

The resin was consisted of bisphenol A based epoxy resins and amine curing agents. The two difunctional epoxies resins supplied from the Thai Epoxy and Allied Products Co., Ltd. The Epotec YD115 and Epotec YD127 based on diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight (EEW) of 198.2 and 183 g/mol, respectively were used. They were used without further purification.

The curing agent ingredients were mainly comprised of dicyandiamide, amine curing agents and catalysts. Triethylene tetramine (TETA) and diethylene triamine (DETA), aliphatic amine, supplied from Witco Co. Ltd. Isophorone diamine (IPDA) was cycloaliphatic amine which supplied from Vantico Pte., Ltd. The properties of epoxies cured with cycloaliphatic amines were intermediate between those cured with only aliphatic and those cured with aromatic amines. Ancamine 1618 and Ancamine 2165, the mixture of the cycloaliphatic and aromatic amines in benzyl alcohol, respectively, supplied from Air Products and Chemicals Co., Ltd. Ancamine 1618 is a mixture of IPDA and benzyl alcohol at ratio approx. 80:20 by weight. Ancamine 2165 is mixture of m-xylene diamine and benzyl alcohol at ratio approx. 60:40 by weight. Dyhard 100 and Dyhard 100s are Dicyandiamide having the average gains size of 40 µm and 10 µm, respectively. Dyhard UR200, Dyhard UR300 and Dyhard UR500 are used as catalysts. The Dyhard series were obtained from the Deggussa Co., Ltd. All the chemicals are commercially supplied and they are used without further purification. The chemical structures of those chemicals mentioned are shown in Table 3.1 and their general characteristics are summarized in Table 3.2.

The reinforcements were plain woven E-glass fabric, LT800-E, and carbon fabric, GV-125 U, with an area weight density of 821±3% g/m^2 and 123±5% g/m^2 and supplied from Chrong Yi Company and G. Angloni Company, respectively.

Methyl ethyl ketone (MEK) and ethyl acetate (EA) were used as diluent solvents for prepreg formulation. The boiling point of MEK and EA are 80°C and 77°C, respectively. These solvents were supplied from Use Well Development Company and used as received.

Table 3.1 Chemical structure of the materials used in prepreg formulations.

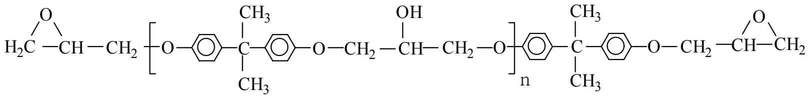
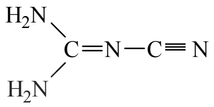
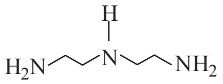
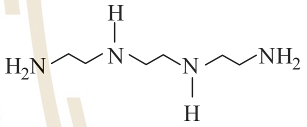
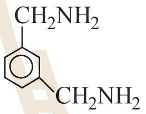
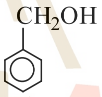
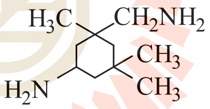
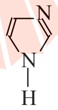
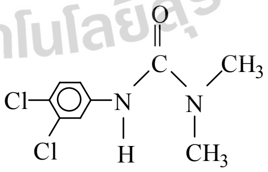
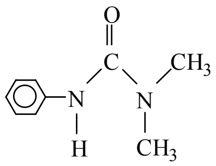
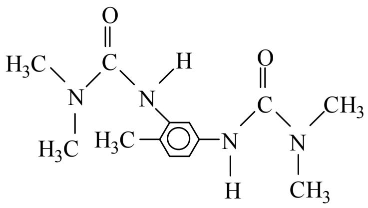
Resin	**Chemical Structure**
DGEBA	
Curing Agents	**Chemical Structure**
DICY	
DETA	
TETA	
M-xylene diamine	
Benzyl alcohol	
IPDA	
Imidazole	
Substituted urea (Dyhard UR200)	
Substituted urea (Dyhard UR300)	
Substituted urea (Dyhard UR500)	

Table 3.2 General characteristic of epoxy resins, curing agent ingredients and catalyst used for the prepreg formulations.

Trade Name	**Chemical Name**	**EEW**	**Viscosity (mPa.s)**	**Boiling Point (°C)**
Resin:				
Epotec YD115	DGEBA	198	413	-
Epotec YD127	DGEBA	183	8175	-
Trade Name	**Chemical Name**	**AHEW**	**Viscosity (mPa.s)**	**Boiling Point (°C)**
Curing Agent:				
Ancamine 2165	M-xylene diamine in benzyl alcohol	48	7.85	> 200
Ancamine 1618	Isophorone diamine in benzyl alcohol	115	61.83	> 205
D.E.H. 24	Triethylene tetramine	24.4	25.99	277.4
D.E.H. 20	Diethylene diamine	20.6	6.08	206.7
ARADUR 42	Isophorone diamine	42.5	10.89	247
Trade Name	**Chemical Name**	**AHEW**	**Particle Size (µm)**	**Melting Point (°C)**
Curing Agent:				
Dyhard 100	Dicyandiamide	21	33.5	210
Dyhard 100S	Dicyandiamide	21	8.9	209
Catalyst:				
Dyhard UR200	3-(3,4-dichlorophenyl)-1,1-dimethylurea	233	7.9	157
Dyhard UR300	3-phenyl-1,1-dimethylurea	164	8.8	133
Dyhard UR500	3,3’-(4-methyl-1,3-phenylene)bis(1,1-dimethylurea	132	8.8	171
XU-3123	Imidazole	68.08	-	90

3.3 Experimental Procedures

3.3.1 Preparation of Formulations

The designated prepreg formulations conducted in this study are summarized in Table 3.3 to 3.6. Each formulation is the combination mixtures of epoxy and curing agents in stiochiometric ratio, phr, based on the functionality of the ingredients. The stiochiometric relation between the epoxy resin and curing agent calculated by mean of active hydrogen equivalent weight (AHEW) of hardener and epoxy equivalent weight (EEW) of epoxy resin are given by the following equations;

$$\text{phr} = \frac{\text{AHEW}}{\text{EEW}} \times 100 \qquad (3.1)$$

where $$\text{AHEW} = \frac{\text{Molecular weight of amine (g/mol)}}{\text{Number of active hydrogen}} \qquad (3.2)$$

$$\text{EEW} = \frac{\text{Molecular weight of epoxy resin (g/mol)}}{\text{Number of epoxide group}} \qquad (3.3)$$

Table 3.3 Rs series of prepreg formulations with different in epoxy ratio.

Formula	**Resin (wt.%)**		**Curing agent (wt.%)**				phr
	DGEBA		DICY	Catalyst	Amine curing agent		
	YD 115	YD 127	Dyhard 100	Dyhard UR200	Ancamine 1618	Ancamine 2165	
R1	**0**	**100**	40	10	25	25	20
R2	**20**	**80**	40	10	25	25	20
R3	**40**	**60**	40	10	25	25	20
R4	**60**	**40**	40	10	25	25	19
R5	**80**	**20**	40	10	25	25	19
R6	**100**	**0**	40	10	25	25	19

Table 3.4 Ds series of prepreg formulations with different particle of DICY curing agents.

Formula	**Resin (wt.%)**		**Curing agent (wt.%)**					phr
	DGEBA		DICY		Catalyst	Amine curing agent		
	YD 115	YD 127	Dyhard 100	Dyhard 100s	Dyhard UR200	Ancamine 1618	Ancamine 2165	
D1	20	80	**0**	**40**	10	25	25	20
D2	20	80	**40**	**0**	10	25	25	20

Table 3.5 Cs series of prepreg formulations with different type and amount of Dyhard catalysts.

Formula	**Curing agent(wt.%)**							phr
	DICY	Catalyst				Amine curing agent		
	Dyhard 100	Imidazole	Dyhard UR200	Dyhard UR300	Dyhard UR500	Ancamine 1618	Ancamine 2165	
C1	40	0	0	0	0	25	25	19
C2	40	**5**	0	0	0	25	25	19
C3	40	0	**5**	0	0	25	25	19
C4	40	0	0	**5**	0	25	25	19
C5	40	0	0	0	**5**	25	25	19
C6	40	**10**	0	0	0	25	25	20
C7	40	0	**10**	0	0	25	25	20
C8	40	0	0	**10**	0	25	25	20
C9	40	0	0	0	**10**	25	25	20
C10	40	**15**	0	0	0	25	25	21
C11	40	0	**15**	0	0	25	25	21
C12	40	0	0	**15**	0	25	25	21
C13	40	0	0	0	**15**	25	25	21

Footnote: Epoxy resin used in Cs formulation is YD127 and YD115 at 80:20 weight ratio.

Table 3.6 Bs series of prepreg formulations with different type and amount of amine components.

Formula	**Curing agent(wt.%)**							phr
	DICY	Catalyst	Amine curing agent					
	Dyhard 100	Dyhard UR200	Ancamine 1618	Ancamine 2165	TETA	DETA	IPDA	
B1	40	10	**50**	0	0	0	0	23
B2	40	10	0	**50**	0	0	0	18
B3	40	10	0	0	**50**	0	0	13
B4	40	10	0	0	0	**50**	0	12
B5	40	10	0	0	0	0	**50**	17
B6	40	10	**40**	**10**	0	0	0	22
B7	40	10	**30**	**20**	0	0	0	21
B8	40	10	**20**	**30**	0	0	0	20
B9	40	10	**10**	**40**	0	0	0	19

Footnote: Epoxy resin used in Bs formulation is YD127 and YD115 at 80:20 weight ratio.

According to formulation shown in Table 3.3 to Table 3.6, they can be classified into four categories of interest. The first group of formulations design to study the influence of the different epoxy having different in EEW and viscosity on the properties of the final product. They are assigned as Rs series. The second group is formulated to investigate the effect of DICY curing agent, which are differed in particle size on the properties of the cured prepreg. The Ds series are called. The influence of catalysts used in the prepreg on the cure parameter and mechanical properties of the final product were the prime interest. They are named as Cs series. The last set of formula derived from different types and amount of amines in curing agent and they are designed as Bs series.

3.3.2 Prepreg Processing

The process used to prepare prepreg sheet in this study was adopted from the procedures employed at Cobra International Co., Ltd. The prepreg was prepared on double size backing silicon coated paper. The woven fabric was throughout impregnated with the mixed resin at room temperature by using hand lay-up. In fiber to matrix ratio were controlled at 50±5% by weight. After lamination, the prepreg were sealed by zip lock polyethylene bag and stored in refrigerator which has the temperature approximately 18-20°C for 12 hrs. The B-stage cure was obtained. Upon removing the prepreg from the storage, they were allowed to equilibrate at room temperature before the seal was released in order to prevent the moisture condensation on the prepreg. A silicon paper was peeled off and the imprepregnated sheet was placed into the compression mold. The left over silicone sheet was then removed. The stacking procedures were repeated until the number of the required piles was achieved. During the sheet laid up process, touching the surface of the prepreg by bare hand should be avoid.

3.3.3 Solvent Prepreg

Solvents were used to reduce the viscosity of the mixed epoxy mixture. Two different solvents, methyl ethyl ketone and ethyl acetate were employed. The solvent prepreg was prepared by mixing epoxy resin with 1% and 5% by weight of solvent at ambient temperature using hand mixer. The R2 was adopted to study the effect of solvents. Glass and carbon fiber were used as reinforcement. The preparation the prepreg sheet was similar to those described above.

3.3.4 Curing Condition

Most of prepregs were cured at referee condition, 150°C for 10 mins by using compression machine. In order to study the effect of cure conditions on the properties of the final product, the cures were performed at the assigned time and temperature. The prepreg was placed into a rectangular preheated two plate metal mold laid by two Teflon™ sheets on the top and bottom cavity. The consolidation pressure used during the cure was constant at 150 psi. The cured reinforced composite was machine sawing cut into the required dimensions for the testing. The samples were polished using water proof sanding paper. After that the specimens were post cured at 150°C for 8 hrs prior to be tested. In order to minimize the effect of thermal stresses, specimens were allowed to slowly cool down inside the oven.

3.3.5 Cure Cycle

The prepreg formulations investigated in this research were high temperature curing epoxy system. Therefore, pre-cured and post-cured practices were required. In this study, temperature of the pre-cure condition, in order to study the effect of pre-cured temperature was chosen at 120°C, 150°C and 180°C, respectively. Meanwhile, in post-cured temperature was also investigated at 150°C and 180°C, respectively. Also, at 120°C cure temperature, the curing time was varied from 20, 25 and 30 mins, respectively. At higher cure temperature, 150°C, the cure times were examined at 10, 15 and 20 mins. However, at 180°C of cure, the time was lowered to 5, 10 and 15 mins, respectively. In the study, two post cured systems were evaluated. There were the systems with and without post cure processes. For the system with post cure, two post-cure temperature, 150°C and 180°C for 8 hrs were established. The experimental conditions are summarized in Table 3.7.

Table 3.7 Summary of isothermal cure cycle of prepreg formulations.

Series	Cure Condition		Series	Cure Condition		Post Cure Condition		Series	Cure Condition		Post Cure Condition	
	T (°C)	t (mins)		T (°C)	t (mins)	T (°C)	t (hrs)		T (°C)	t (mins)	T (°C)	t (hrs)
N1	120	20	P1	120	20	120	8	P11	120	20	150	8
N2	120	25	P2	120	25	120	8	P12	120	25	150	8
N3	120	30	P3	120	30	120	8	P13	120	30	150	8
N4	150	10	P4	150	10	120	8	P14	150	10	150	8
N5	150	15	P5	150	15	120	8	P15	150	15	150	8
N6	150	20	P6	150	20	120	8	P16	150	20	150	8
N7	180	5	P7	180	5	120	8	P17	180	5	150	8
N8	180	10	P8	180	10	120	8	P18	180	10	150	8
N9	180	15	P9	180	15	120	8	P19	180	15	150	8

Footnote: T is temperature and t is time

3.4 Measurement and Instrumentations

There were three main properties employed to evaluate the prepreg formula in this study. The viscosity and B-stage time as processability variables were tested. The mechanical properties by mean tensile, flexural and impact were observed. The heat distortion temperature (HDT) as thermal property was also reported. The experimental procedures to obtain these properties are described.

3.4.1 Viscosity Measurement

The viscosity of epoxy resin was measured by using the Falling Ball Viscometer in accordance with DIN 53015 from Haake Company. The test was conducted at 25°C in water circulator bath. The resin was filled into the measurement tube and the appropriate ball was placed. The ball used to determine the viscosity depends on the resin viscosity range. The ball constants factors are shown in

Table 3.8. The viscometer was allowed to equilibrate at measuring temperature for approximately 10 mins. The falling times, *t*, were recoded three times. The average value was calculated. The viscosity is calculated according to equation 3.4;

$$\eta = K(\rho_1 - \rho_2)\,t \tag{3.4}$$

where η = Viscosity in mPa.s

K = Constant calculation factor

ρ_1 = Density of ball

ρ_2 = Density of liquid

t = Falling time (sec.)

Table 3.8 The ball constant factor (*K*) and recommended viscosity ranges.

Ball Number	Type of Ball	Diameter of Ball (mm)	Weight of Ball (g)	Density (g/ml)	*K* (m.Pa.ml/g)	Range of Viscosity (mPa.s)
1	Borosilicate Glass	15.83	4.610	2.222	0.00449	0.2-2.5
2	Borosilicate Glass	15.67	4.480	2.224	0.0455	2.0-20
3	Nikel-iron Alloy	15.63	16.525	8.144	0.0719	15-200
4	Nikel-iron Alloy	15.25	15.081	8.128	0.540	100-1,200
5	Stainless Steel	124.28	11.723	7.709	4.54	800-10,000

3.4.2 B-Stage Time Measurement

The B-stage time (t_B) is the time that imprepregnated resin manifests the tacking characteristic. Without B-stage cure or before, the adhesion between the piles and therefore required shape cannot be succeed. There is, so far, no literature and standardized document reported on the B-stage time measurement. Only manual tacking observation is recommended. In this study, the hardness measurement was adopted and applied for the B-stage time measurement. The ASTM D2240 hardness testing were followed. The shore D hardness series M202 from DuroTech^{TM} was employed. Specimens of the impregnated prepreg with 50x50 mm^2 were stacked into 5 layers and placed on the surface of heating plate controlled by PID controller. The testing was performed at constant temperature of 80°C, 100°C and 120°C, respectively. The hardness was recorded for every 5 mins at 80°C and 100°C. However, it was measured for every 2 mins for the test conducted at 120°C.

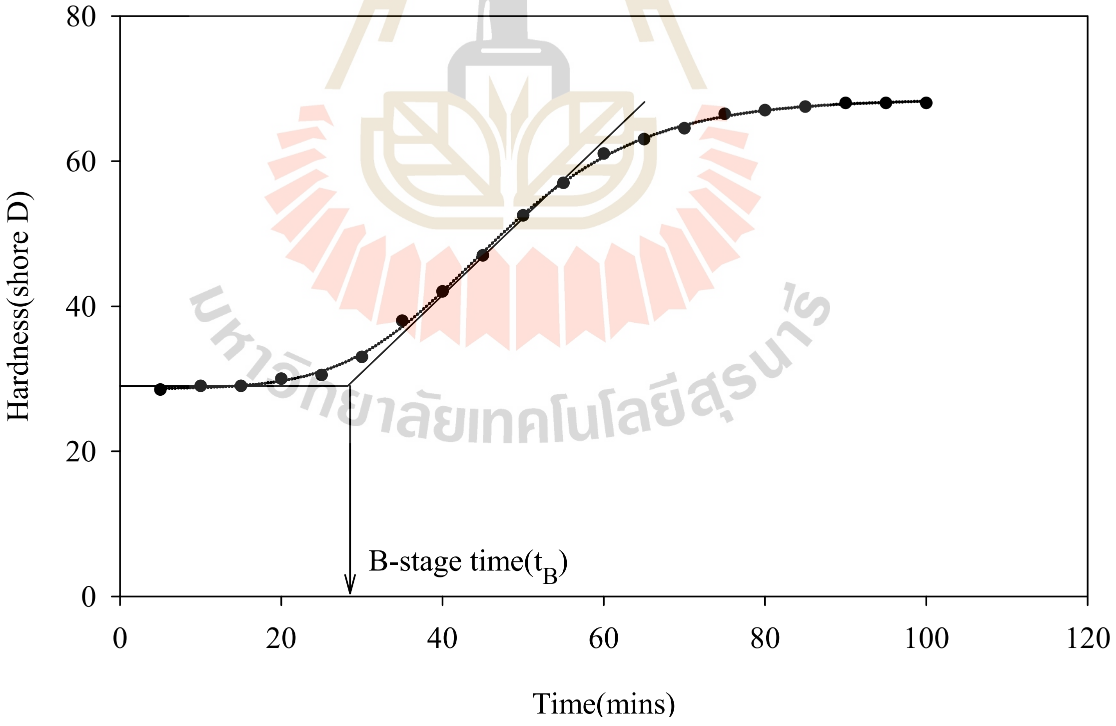


Figure 3.1 Relationship between sample hardness and time at 100°C.

Figure 3.1 illustrates the experiment result from the hardness determination with time at 100°C. B-stage time is then defined as onset the hardness where it becomes exponentially risen.

3.4.3 Tensile Testing

The tensile testing was conducted according to the ASTM D3039 using the Instron^{TM} 5565 tensile tester equipped with 5 kN static load cell and jaw face grips. The tests were carried out at room temperature, 25°C. At least five specimens were tested for each formulation. The tensile properties were measured on the rectangular specimens with a length of 250 mm, width of 25 mm and thickness of 2.5 mm that prepared from 10 layers of pile. All tests were performed under displacement control. The crosshead displacement rate was 2.0 mm/min. The grip lengths of all specimens were approximately 55 mm and gage length of 140 mm. The tensile parameters, ultimate tensile strength (σ_u) and tensile modulus (E) were recorded.

3.4.4 Flexural Testing

The apparent flexural properties of the prepregs were investigated by mean of bending stiffness. The three-point bending configuration and Instron^{TM} 5565 Universal Testing Machine with 5 kN load cell were employed. The ASTM D5943 was followed. Five prepreg samples with 15 layers of stacking pile were bended for each condition. Flexural specimens with an average geometry of 100 mm length, 10 mm width, and 3 mm thickness were prepared and polished using sand papers. The length to thickness ratio of 20 was calculated in order to minimize the shear effects at the neutral axis and to nucleate failure on the tensile side. The span length, L, was measured as 60 mm. The specimens were bended to failure under constant displacement control. The loading nose displacement rate of 2 mm/min was electrically controlled. Five specimens were needed for tested. The flexural strength (σ_{fM}) and flexural modulus (E_f) were calculated and reported.

3.4.5 Impact Testing

Izod pendulum impact testing of laminated cured prepreg was measured according to ASTM D5941 using Atlas Pendulum Impact Tester from Atlas Electric Devices Company. The test was conducted at room temperature. The rectangular specimen prepared from 15 layers of stacking pile with the dimension of 63.5 mm in length, 12.7 mm in width, and 3 mm in thickness, was cut and polished. The V-shaped notch with the depth of approximately 3 mm was marked using the notching machine. The notches were carefully sharpened by using a razor blade. Five specimens for each formulae were tested and the average value of impact strength (a_{iN}), kJ/m^2, was calculated. The Izod impact strength was computed according to the equation 3.5.

$$a_{iN} = \frac{W}{h \times b_N} \times 10^3 \qquad (\mathrm{kJ/m^2}) \tag{3.5}$$

where W = Impact energy, J

h = Thickness of specimen, mm

b_N = Width of specimen at notched mark, mm

3.4.6 Heat Distortion Temperature Determination

Heat distortion temperature (HDT) of fiber reinforced cured prepreg was measured according to ASTM 648 using HDV-1 tester from Atlas Electric Devices Company. It is defined as temperature at which a standard specimen is defected to 0.25 mm under standard load. The test specimen of 10 layers of woven pile was compressed and cut into rectangular bar of 127 mm in length, 13 mm in width and 2.5 mm in thickness or depth. The specimens were polished and post-cured. The standard load of 1820 kPa was applied. The loading weigh to obtained the required standard load was calculated according to the equation 3.6 and 3.7, respectively.

$$P = \frac{2Sbd^2}{3L} \tag{3.6}$$

$$P' = \frac{P}{9.80665} \tag{3.7}$$

where P = Load, N

S = Standard stress required on the specimen

B = Width of specimen, m

d = Depth of specimen, m

L = Span length between the supports (0.1 m)

and P' = Loading mass , kgf

The specimens were immersed under given load in the silicon oil bath fitted with a heating chamber and controller that raise the temperature at the rate of 2±0.2°C/min. After applying the load for five minutes, the pointer is adjusted to zero. The HDT was immediately read when the specimen was deflected to 0.25 mm.

CHAPTER IV

RESULTS AND DISCUSSION

The main aspiration of this thesis study is to formulate the epoxy prepreg that suit for the windsurf and surfboard manufacturing. Four main research topics were investigated. There were the exploring an effect of epoxy resins and curing agents on the properties of cured prepreg. The investigating of the optimal cure conditions on the properties of cured composites was also experimented. Finally, the observation of the reinforcing fibers and the solvents used as diluent on the properties of the final laminated. The tensile, impact, flexural, hardness and HDT testing and also rheological properties by mean of falling ball viscosity are employed. Those results will be used for evaluation. In this chapter, all the tested results will be presented and discussed.

4.1 Epoxy Resins

According to rule of mixture for the fiber reinforced composites, they are typically depended on both matrix and fiber reinforcement. The former material acts as adhesive to bond the fibrous phase together. Epoxy resins are mainly used in high performance composites. They are commonly formulated from epoxy resin and curing agent or hardener. In this study, two commercial DGEBA based epoxy resins, differ in viscosity and EEW, are investigated. Commercially, the amine curing agent is made by incorporating of various chemical ingredients. In particularity for prepreg

In this study, the ratio of the DGEBA epoxy resins, the influent of particle size of the high temperature catalysts or latent catalysts, dicyandiamides, the effect of chemical characteristic amine curing agents and, finally, the role of urea catalysts were observed. The fiber glass woven was used to prepare the prepreg samples. The mechanical and thermal properties and curing parameters were obtained.

4.1.1 Effect of Resins on the Mechanical and Thermal Properties

The resins used as matrix were formulated from two commercial based DGEBA resins, Epotec YD115 and YD127. These resins differ in their EEW and viscosity. The general characteristics of the resins are previously shown in Table 3.2. Epotec YD127 had significantly higher viscosity than Epotec YD115 but lower in EEW. Typically, increasing the molar mass of resin will increase the EEW and also rise in viscosity. Vice versa, adding the very low molecular weight active diluent, such as aliphatic epoxy resin or commercially know as bisphenol R resin, will lower the EEW and the viscosity. However, mixing bisphenol R resin into the resin formulation will enhance the fracture toughness but deteriorate the thermal properties such as HDT. According to the manufacturer data sheet, it would indicate the difference between YD115 and YD127 is mainly contributed from active diluent added.

In order to determine the optimal properties, both the mechanical and rheological, of the prepreg formulations derived from these two resins mixture, the mechanical and thermal properties of the cured composites samples were investigated. Moreover, the viscosity of the formula, which is an important property for composite manufacturing processes, was also determined. The six formula differed in % weight ratio of Epotec YD115 and YD127 from 0, 20, 40, 60, 80 and 100% by weight were prepared. The test results by mean of tensile, flexural, impact strength and HDT are summarized in Table 4.1 and also graphically presented in Figure 4.1 to Figure 4.3.

From Table 4.1 and Figure 4.1 to 4.3, the results show that the tensile properties, ultimate tensile stress (σ_u) and Young's modulus (E), are not obviously corresponded with the resin ratios. The R5 formulation give rise to the maximum values at 305±13 MPa and 6.8±0.2 GPa but the R4 show the lowest at 240±13 MPa and 6.2±0.1 GPa, respectively. The toughness properties by mean of flexural strength and modulus are also reported. The similar trend is also observed. As expected that increasing in the YD115 ratio would increase the fractural properties of the prepreg but the results showed an ambiguous. The highest strength (σ_{fM}) and modulus (E_f) obtained are 496±11 MPa and 19.8±0.9 GPa for R5 and the lowest are 454±15 MPa and 18.3±0.1 GPa for the R4, respectively. Again, the best of all formula in this category is found for R5 and the worst is R4.

However, the fracture impact strengths (a_{iN}) are slightly increased with increasing the amount of YD115 except for the R4 where the values are out of trend. These results suggest that using active diluent as in YD115 would enhance the toughness of resin and hence the reinforced composite. This statement is strengthen by the HDT where there obviously decreased from 127±0.6°C down to 71±0.6°C with increasing the YD115 ratio 0% to 100%. These outcome can be repetitively explained by the fact that incorporating the active diluent, such as bisphenol R, into epoxy resin not only reducing the resin viscosity but also enhancing the fracture properties but inferior the service temperature.

Taken only the effect of the epoxy ratio on the mechanical and thermal mechanical properties of the fiber glass reinforced composite obtained from the prepreg formulations, the general conclusion could be drawn that increasing in the YD115 composition will slightly increase in the mechanical properties of the composite. Vice versa, the thermal property by mean of HDT is decreased. The changes in the properties can be explained by the contribution of the active diluent presented in the resin YD115. According to the results found, the optimal mixture composition, YD115 and YD127, is 80:20 by weight. The incompetence properties will be found when the ratio is reduced to 60:40.

Table 4.1 Mechanical and thermal properties of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

Formula	**Resin**		**Properties**					
	YD115	YD127	σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
	(wt.%)	(wt.%)	(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(^oC)
R1	0	100	265±23	6.4±0.2	467±17	19.9±0.5	158±17	127±0.6
R2	20	80	281±17	6.6±0.1	484±14	18.6±0.9	176±14	113±0.6
R3	40	60	240±13	6.2±0.1	465±12	19.3±0.3	179±12	105±1.0
R4	60	40	252±9	6.2±0.2	455±15	18.2±0.6	172±15	76±1.0
R5	80	20	305±13	6.8±0.2	496±11	19.8±0.9	178±11	73±0.6
R6	100	0	279±11	6.3±0.2	465±15	19.3±0.9	185±15	71±0.6

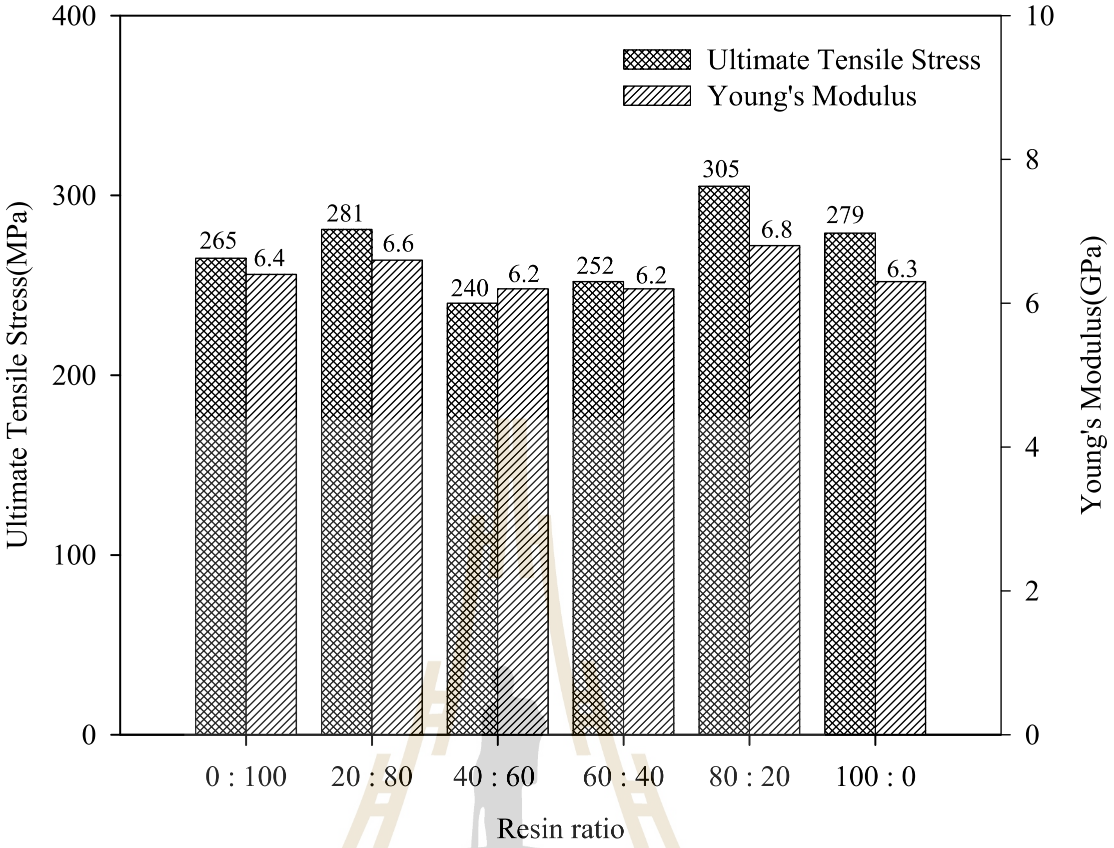


Figure 4.1 Ultimate tensile stress and Young's modulus of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

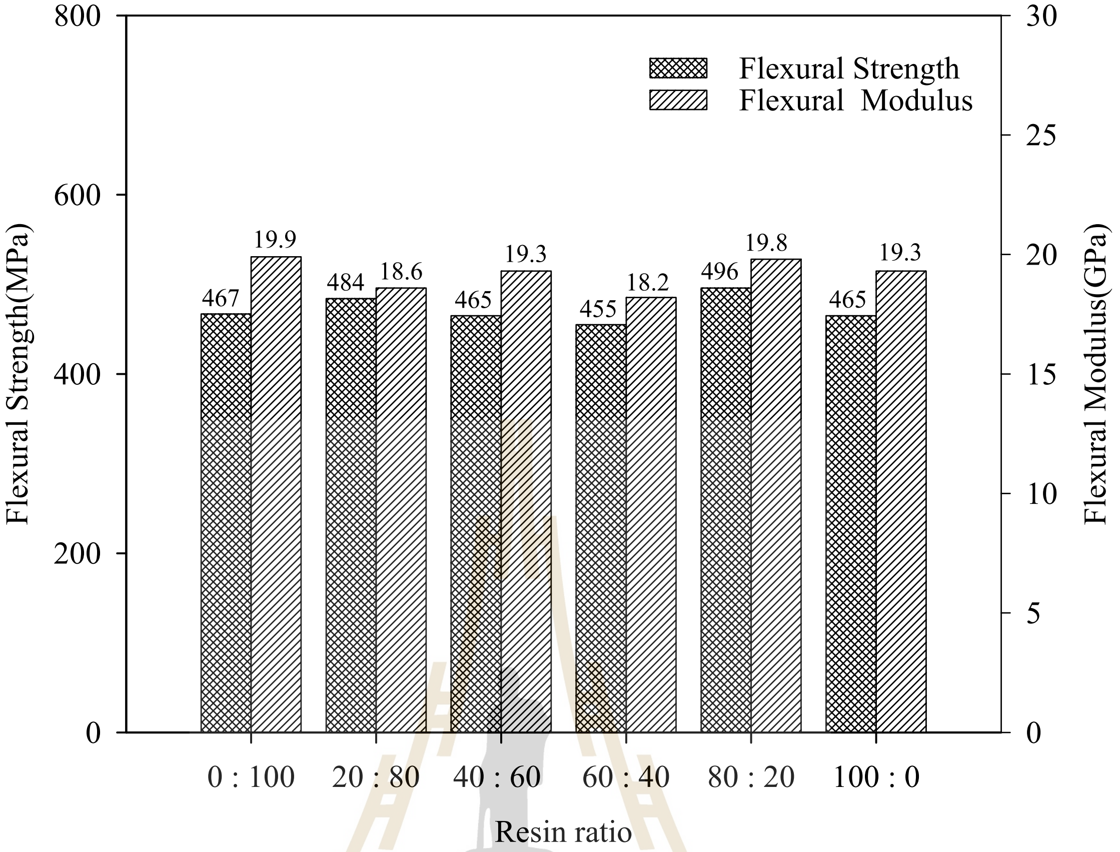


Figure 4.2 Flexural strength and flexural modulus of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

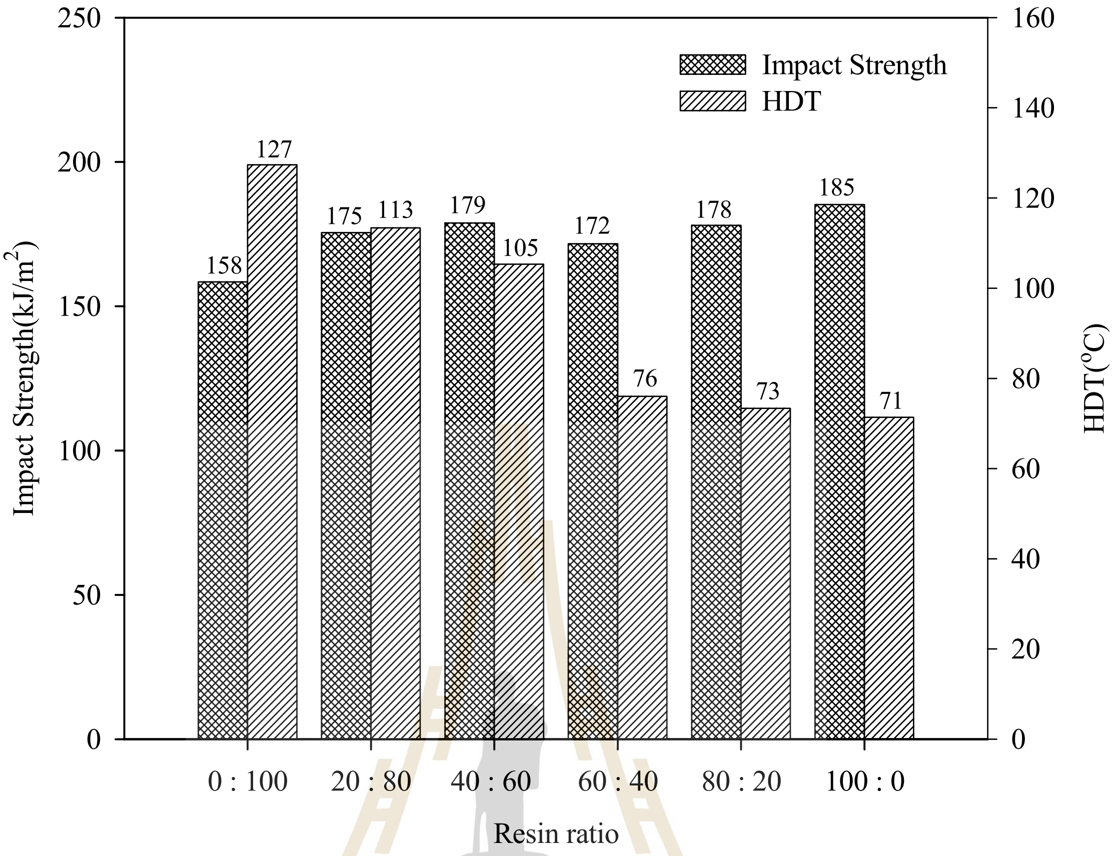


Figure 4.3 Impact strength and HDT of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

In order to verify and strengthen the dependency of resin ratio on the mechanical properties of cured composites derived from the prepreg formulations, the single factor analysis of variance or one-way ANOVA test, as summarized in Appendix A, is applied. In general, two statistical hypothesizes, null (H_0) and alternative (H_1) will be identified as show below:

H_0 : the six formulations, differed in resin ratio, can not be differentiated by means value of the properties

H_1 : one way or another, six formulations differed in resin ratio can be Differentiated by means value of the properties

If H_0 is accepted, it means that the property of the cured prepreg does not depend on the resin ratio. Vice versa, accepting H_1 means that the property of the cured does depend on the resin ratio used.

In this study, the level of significant (α) for accepted H_0 is set at 0.05 or 95% confidential. The calculated $\boldsymbol{f}$ value ($\boldsymbol{f}_{\text{cal}}$) and level of significant (α) of the experimental data was obtained by using SPSS$^{\text{TM}}$ Version 11.5 for windows, which is commercial computer programming to assist the statistical calculation.

According SPSS calculation, if the calculated $\boldsymbol{f}$ is less than critical $\boldsymbol{f}$ value ($\boldsymbol{f}_{\text{crit}}$) obtained, as shown in the statistical table in Appendix B, or else, if the level of significant(α) is higher than the given value, 0.05, then the hypothesis H_0 will be accepted. Vice versa, the would be rejected.

Table 4.2 show the one-way ANOVA table of ultimate tensile stress analysed from those six formula. The statistical test result indicates the $\boldsymbol{f}_{\text{cal}}$ value of 11.78 which is more than the $\boldsymbol{f}_{\text{crit}}$ of 2.62. It means that the H_1 is accepted or on another word H_0 is rejected. Taken this statistical conclusion, it can be pronounced that the ultimate tensile property of the resin formulation is depended on the epoxy mixture ratio.

Table 4.2 One way ANOVA table of the ultimate tensile stress of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

Source of Variation	Sum of Square	df	Mean Square	Calculated *f*	Critical *f*	Sig.
Between Groups	13318.60	5	2663.72	11.78	2.62	0.00
Within Groups	5426.49	24	226.10			
Total	18745.09	29				

Table 4.3 summarizes the ANOVA results for tensile modulus, flexural strength, flexural modulus and impact strength obtained from those resin formula The statistical test results show that all the f_{cal} values are higher the f_{crit} ones. Hence, all H_1 are accepted. Consequently, they are suggested that the mechanical properties of the cure prepreg composites manufactured using DGEBA resin mixture are influenced by the ratio of epoxy resins used, YD115 and YD117. For the HDT, the dependency of result was clearly observed. Therefore, the ANOVA test is not required.

Taken both experimental results and statistical testing, the preliminary conclusion can be made that the properties of cured composites obtained from the prepreg are depended on mixing ratio of resin used. In this study, the optimal ratio between YD115 and YD127 which give rise to the superior properties is 80:20 by weight. These two base DGEBA epoxy resins are differences in the basic characteristic, EEW and viscosity, by mean of active diluent concentration.

Table 4.3 Summary of one-way ANOVA test of mechanical properties of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

Test properties	**Calculated *f* (f_{cal})**	**Critical *f* (f_{crit})**	**Level of significant (α)**	**Conclusion**
Ultimate tensile stress	11.781	2.62	0.000	H_1 Accepted
Young's modulus	6.916	2.62	0.000	H_1 Accepted
Flexural strength	5.854	2.62	0.001	H_1 Accepted
Flexural modulus	4.342	2.62	0.006	H_1 Accepted
Impact strength	5.202	2.62	0.002	H_1 Accepted

4.1.2 Effect of Epoxy Resins on Rheological Property

In the actual commercial applications, not only the superior mechanical properties are concerned but the rheological property by mean of the resin viscosity is also greatly important. Lower in the viscosity will create the resin drainage while applying and prolong storage. On the other hand, deficient impregnation and require human or machine force will be taken place for high viscous resin. As mentioned earlier that the main guide line of the properties regarding to the prepreg formulation studied in this research work is followed from the windsurf and surfboard manufacturer, Cobra International Co. Ltd.. According to the physical data sheet, the viscosity of 2500-3000 mPa.s has been successfully used for both unidirectional (UD) winding and fabric impregnation processes.

As presented in 4.1.1, the optimal overall properties the cured laminated sample was derived from the prepreg formula using 80:20 weight ratio of YD115 and YD127, respectively. By using the falling ball viscometer, as previously described in Chapter III, the viscosity of the resin mixtures will be discussed in this section. To retain the processing ability and also mechanical properties is the main concerned. As well as, the validity of the rule of mixture applied for this mixture system will be verified.

Table 4.4 and Figure 4.4 show the viscosity of the YD115 and YD127 mixtures with their composition gradually increased from 0:100 to 100:0. As expected, the result reviews that the viscosity is exponentially decreased with increasing the amount of low viscosity YD115. It is acted as viscosity diluent for the resin formulations. Regarding to only viscosity data provided from the windsurf industry and actual onsite trial, the R2 and R3 will be the most applicable formula for the industry. This conclusion is contradicted to the mechanical point of view where the R5 is preferred. Furthermore in this research work, it will be demonstrated that the optimal viscosity value of the resin is retained for the R2, 4920 mPa.s. Whereas, the mechanical properties will be improved by redesign the hardener.

Table 4.4 The viscosity of the YD115 and YD127 resin mixture determined by falling ball viscometer

Formula	**Resin (wt.%)**		**Viscosity**[a]	**Viscosity**[b]
	YD115	YD127	(mPa.s)	(mPa.s)
R1	0	100	8176	8176
R2	20	80	4500	4917
R3	40	60	2477	2663
R4	60	40	1364	1646
R5	80	20	751	1178
R6	100	0	413	413

Footnote: [a] Viscosity value was measured by experimental procedure,
[b] Viscosity value was calculated by rule of mixture

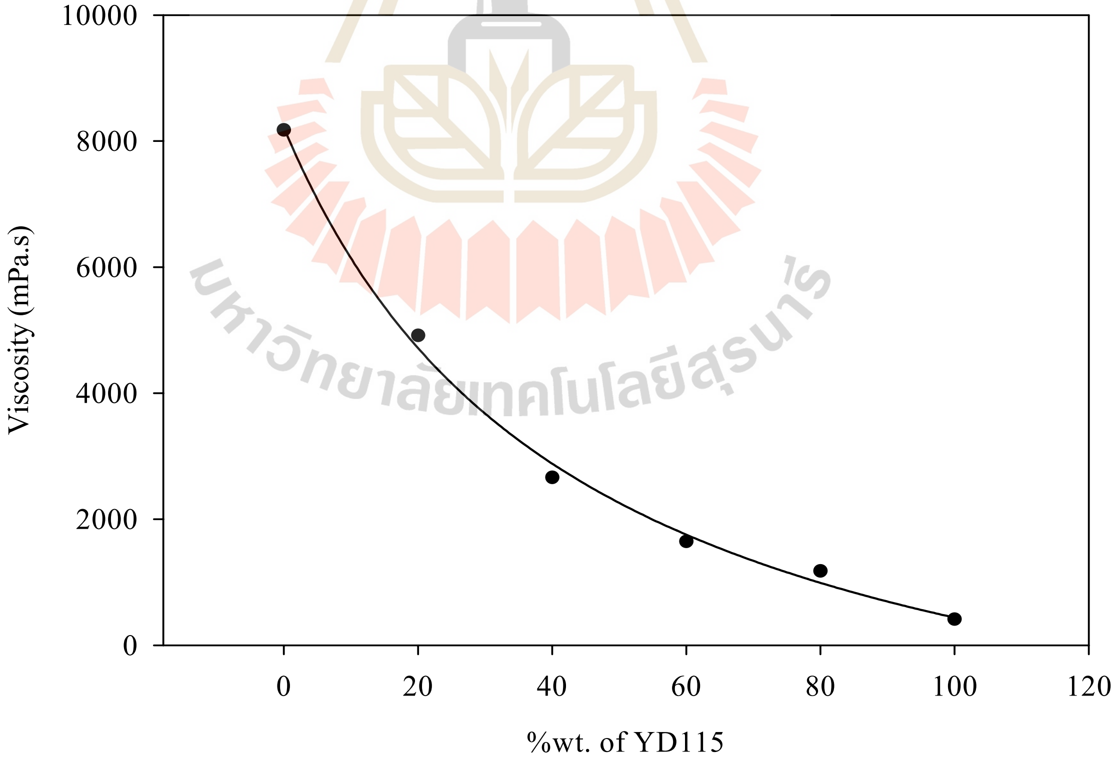


Figure 4.4 Relationship between the falling ball viscosity and % wt of YD115.

In the lamination process, the prepreg resin was prepared by mixing the resin and curing agent at the given phr ratio. The viscosity of the mixed resin is generally reduced due to the fact that the viscosity of curing agent is much lower than the resin. The actual viscosity figure can not be measured by a viscometer because the crosslink reaction will instantaneously occur while mixing. Therefore, the liquid/liquid rule of mixture (Robert, Don, and James, 1984) will be required to predict the viscosity this mixing phenomena. On this section, the validity of the rule of mixture, by using the experimental data obtained from the resin mixture viscosity, will be verified. The acceptance of the rule will be further used for approximating the viscosity of the mixed prepreg resin.

The rule of liquid/liquid mixture equation is the logarithm function of the viscosity (η_i) and weight fraction (w_i) of the mixed component as shown in equation 4.1.

$$\ln \eta_{mix} = w_1 \ln \eta_1 + w_2 \ln \eta_2 \qquad (4.1)$$

where η_{mix} = Viscosity of the liquid mixture

η_1 = Viscosity of liquid 1

η_2 = Viscosity of liquid 2

w_1 = Weight fraction of liquid 1

w_2 = Weight fraction of liquid 2

The viscosity of the mixed resin calculated according to rule of mixture, equation 4.1, is presented in Table 4.4. The result shows the similarity between the measured values and calculated ones. However, they are slightly lower than the values measured from the falling ball viscometer. By alternative presentation the product derived from the rule of mixture using linear relationship plot between ln(η_{mix}) with weight fraction of YD115 (w_1), the straight line is established as seen in Figure 4.5. The simulated line is almost identical, especially for the lower YD115 fraction, to one obtained from the experimental result.

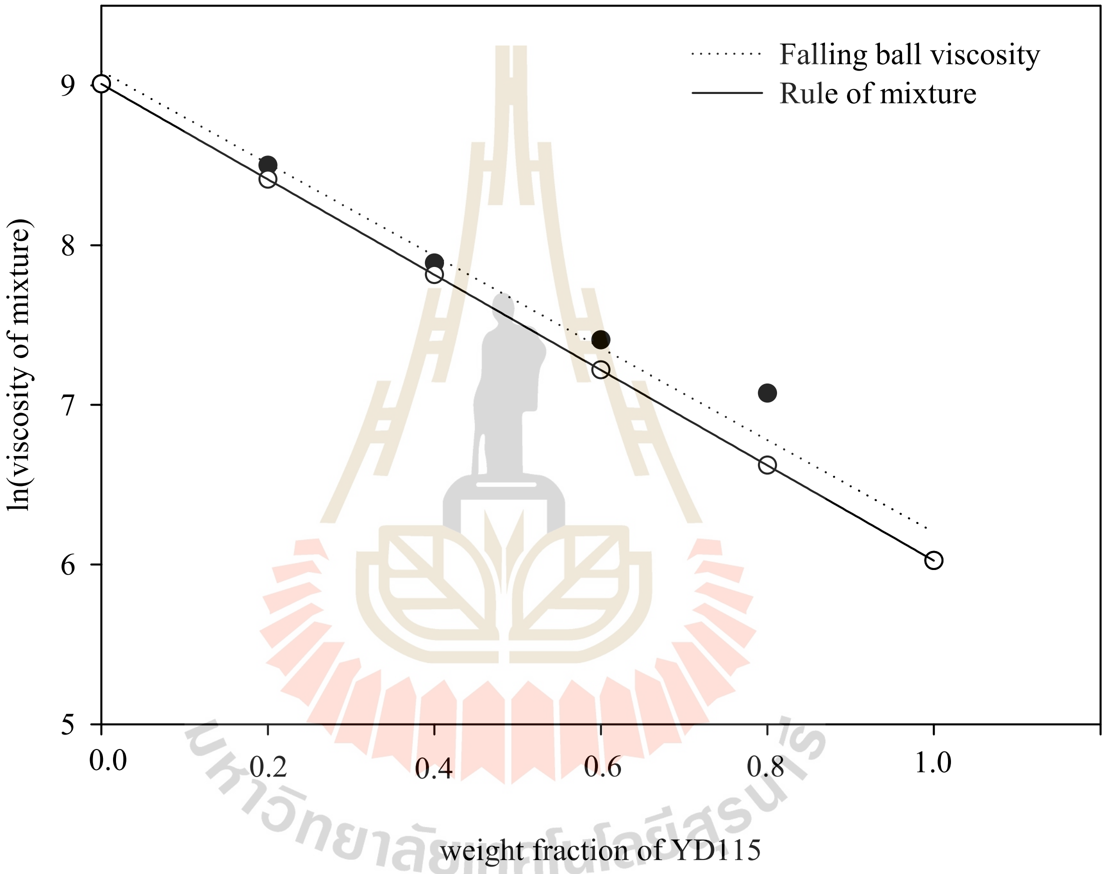


Figure 4.5 Linear relationship of ln(η_{mix}) with weight fraction of YD115 measured by falling ball viscometer and rule of mixture.

In order to verify the authenticity of the rule of mixture applied for the resins mixing, the statistical method is submitted. If the truth statement that the viscosities of resin mixture calculated from rule of mixture were identical to values obtained from falling ball viscometer, the mathematical mean sum of those values, $\overline{X}$ and $\overline{Y}$, would not be differentiated. To draw the conclusion of the statistical statement, the two tails *t*-test, as described in Appendix A, has to be applied. The null and alternative statistical hypothesizes are given as follow;

If $H_0 : \overline{X} - \overline{Y} = 0$, it means that the viscosities of mixed resins from equation 4.8 and falling ball viscometer are analogous

but if $H_1 : \overline{X} - \overline{Y} \neq 0$, it means that the viscosities of mixed resins from equation 4.8 and falling ball viscometer are differences

At the degree of confidence of 95 % therefore $\alpha/2 = 0.025$ for 2-tailed test and the degree of freedom equal to 10, $(n_X+n_Y) - 2$, the calculated t and α obtained from the computer programming are 0.129 and 0.900, respectively. According to the statistical table at the given α of 0.025, the critical t is ±2.228. The statistical calculation indicates that the calculated t is laid onto the hypothetical accepting region. Therefore H_0 is accepted. This lead to statistical conclusion that the rule of mixture can be applied for determining the viscosity of epoxy resins mixture at 95% degree of confidence.

As mentioned earlier that the viscosity of mixed prepreg formulation is resulted from both viscosities of epoxy resins mixture and the curing agent at the calculated phr ratio. At this research section, the curing agent is prepared from the Ancamine 1618, Ancamine 2165, Dyhard 100 and Dyhard UR200 at 25, 25, 40, and 10% by weight, respectively. The final viscosity of the curing agent measured by falling ball viscometer was 237 mPa.s. Based on this curing agent, the phr for R1, R2 and R3 are 20 but for R4, R5 and R6 are 19, consecutively. Using the validated rule of mixture shown above, the calculated viscosities of mixed epoxy resins are reported in

Table 4.5. The figures illustrate that the viscosity of mixed resin is approximately dropped into half when low viscosity curing agent is added. Nevertheless, the viscosity of R2 formulation is remained in the acceptable processability range for the manufacturing process.

Table 4.5 The viscosity of prepreg formulations by various YD115 and YD127 resin ratio.

Formula	**Resin (wt.%)**		**Viscosity[a] (mPa.s)**		**phr**	**Viscosity[b] (mPa.s)**
	YD115	YD127	Resin	Curing Agent		Formula
R1	0	100	8176	237	20	4530
R2	20	80	4917	237	20	2965
R3	40	60	2663	237	20	1779
R4	60	40	1646	237	19	1208
R5	80	20	1178	237	19	912
R6	100	0	413	237	19	378

Footnote: [a] Viscosity value was tested by falling ball viscometer,
[b] Viscosity value was observed by rule of mixture

Consideration both mechanical and rheological points of view, the R5 formulation has highest value in mechanical properties but too low HDT and viscosity for manufacturing application. However, R2 reviews the acceptable HDT and viscosity values but moderate in mechanical properties. This mechanical incompetence will be further improved by curing agent modification as the coming discussion throughout this research work. At this point forward, the R2 epoxy mixture comprised of 20% YD115 and 80% YD127 will be used as base resin for further experiments.

4.2 Curing Agents

As stated in section 4.1 that at the given base epoxy resin ratio, 20:80 for YD115 and YD127, the mechanical properties of the reinforced material was much lower than that for the 80:20 ratio. The figures were also far below the requirement from the industry. In contrast, the viscosity of the 20:80 resin mixture was prime important for the manufacturing process. In this section, enhancement the mechanical properties of the composite sample by focusing on the curing agent is the prime concerned.

4.2.1 Influence of Dicyandiamide Powder

Dicyandiamide, DICY, is the most widely used as one of component in curing agent in prepreg. Their advantages include low cost and good processablity. It is commercially available in solid powder from with different sizes. It will be normally dispersed in the curing ingredient. In this work, the influence of particle size of DICY on the properties of the cured composites was investigated. The identical chemical species, Dyhard 100 and Dyhard 100s, but having the average particle size of 40 μm and 10 μm, respectively reported by the supplier are employed. Two formula consisted of the alternated 40% of these two DICYs content, as shown in Table 4.6, were observed and notated as D1 and D2. It was incorporated into the curing agent, as employed in the previous section, which is comprised of Ancamine 1618, Ancamine 2165, and Dyhard UR 200 at the percentage ratio 25, 25 and 10, respectively. The mechanical and thermal properties results of the glass fiber reinforcement composites derived from those formulations are summarized in Table 4.6.

Table 4.6 Mechanical and thermal properties of fiber glass composite prepared by prepreg formulations using Dyhard 100s and Dyhard 100.

Formula	**DICY**		**Properties**					
	Dyhard 100	Dyhard 100s	σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
	(wt.%)	(wt.%)	(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(^oC)
D1	0	40	301±13	6.7±0.2	485±11	19.8±1.0	178±11	114±0.6
D2	40	0	281±17	6.6±0.1	484±14	18.6±0.9	176±14	113±0.6

The test results show that the overall figures obtained using Dyhard 100s is slightly higher than the hardener using Dyhard 100. With in the acceptable experimental standard deviation, it could declare that the particle size of the DICYs employed in this study, 40 μm and 10 μm, do not have the significantly contribution on the mechanical properties of the final reinforcement products derived from the prepreg formulations. It can be explained by rheological hypothesis that, at the given composition and also the particle size range, the viscosity of the hardener liquids were not considerably changed. Hence, the impregnation ability of the mixed resin during the applying process is not difference. Therefore, final outcome is almost indistinguishable. However, it had the report that the ultramicronized DICY shown the advantages in higher reactivity (Gilbert and Schneider, 1991). Moreover, according to the study done by Muroi, Ishimura and Outsuka (1986), they found that the curing reaction at ambient temperature was varied inversely with logarithmic of DICY particle size and directly with the total surface area of the DICY particles. At evaluated curing temperature, 150°C as performed in this study, the influence of the reactivity which perhaps leads to the incomplete crosslink reaction must be diminished.

From the above results, it could conclude that DICY powder particle, Dyhard 100 and 100s, having the difference in particle size do not have the significant influent on the mechanical and thermal properties of the composite product prepared from the prepreg lamination.

4.2.2 Effect of Amines

Amines are the most common chemical ingredient for manufacturing epoxy curing agent, especially for the room temperature curing agent. They are inexpensive comparing with other chemical ingredients. They are also having the great influence on chemical reactivity and mechanical and thermal properties of the cured epoxy. In this research work, TETA and DETA are represented as aliphatic amines. They are low cost and abundantly used in the industry. They provide the modulate mechanical and thermal properties. IPDA is a cycloaliphatic amine. It is slightly expensive but offers the better cured properties than the aliphatic ones. Ancamine 1618 is the mixture of IPDA in benzyl alcohol. It is the commercially available amine that gives the better control in curing time. Typically, benzyl alcohol is the catalyst used for accelerating the curing reaction. Ancamine 2165 is also the mixture of aromatic m-xylene diamine in benzyl alcohol. The mechanical and thermal properties of cure epoxy are greatly contributed from aromatic amines. For the sake of the safety concerned, pure m-xylene diamine can not be transported especially by air freight. The dilute solution form has to be modified to minimize the safety risk.

Study the effect of amines ingredient in the curing agent on the final properties of cured prepreg will be discussed in this section. According to the hardener formula shown in Table 3.4, B1 to B5, the Ancamine 1618, Ancamine 2165, TETA, DETA and IPDA were varied at 50% by weight with respect to 40% Dyhard 100 and 10% Dyhard UR200, respectively. Using those curing agents with 20:80 YD115 to YD127 resin mixture at the phr stiochiometric ratio and the fiber glass cloth as reinforcement, the test results of the laminated are presented in Table 4.7. The plots of the results against curing agents used are also shown in Figure 4.6 to 4.8, respectively. The lowest tensile strength (σ_u) and modulus (E) at 221±19 MPa and 5.9±02 GPa, respectively, are found when IPDA is employed. However, the maximum number at 295±15 MPa and 7.1±0.2 GPa are obtained when Ancamine 2165 is used. For the toughness by mean of flexural strength and impact strength, the brittle material is observed when TETA is incorporated into the curing ingredient. More tough reinforced composites are seen when Ancamine 1618 and Ancamine 2165 are used. Combining IPDA into curing formulation gives rise to the superior thermal characteristic at 125±0.6°C. Vice versa, Ancamine 1618 is obviously affected on the HDT reduction.

From the results found, it can be explained that aliphatic amines and pure cycloaliphatic amine having low AHEW, but higher in active hydrogen, when react with epoxide group on the epoxy resin would generate the high crosslink density. Therefore, the less fracture toughness but high HDT crosslinked polymers are established. Benzyl alcohol is not only act as solvent for the IPDA in Ancamine 1618, but it is also play the important role as the catalyst and chain terminator in the crosslink polymerisation. The later effect would reduce the number of crosslink bridges and hence crosslink density. As the result, tougher, but low HDT, plastics are obtained.

Table 4.7 Mechanical and thermal properties of fiber glass composite prepared by prepreg formulations using various type of amine curing agents.

Formula	**Amine curing agent**	**Properties**					
		σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
		(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(°C)
B1	Ancamine 1618	239±16	6.0±0.1	446±19	21.1±0.2	173±7	77±0.6
B2	Ancamine 2165	295±15	7.1±0.2	457±20	20.6±0.2	171±6	98±0.6
B3	TETA	249±19	6.1±0.3	385±16	17.6±0.3	160±9	119±1.0
B4	DETA	241±22	6.4±0.3	424±20	18.0±0.4	169±6	92±1.0
B5	IPDA	221±19	5.9±0.2	446±8	20.7±0.3	162±7	125±0.6

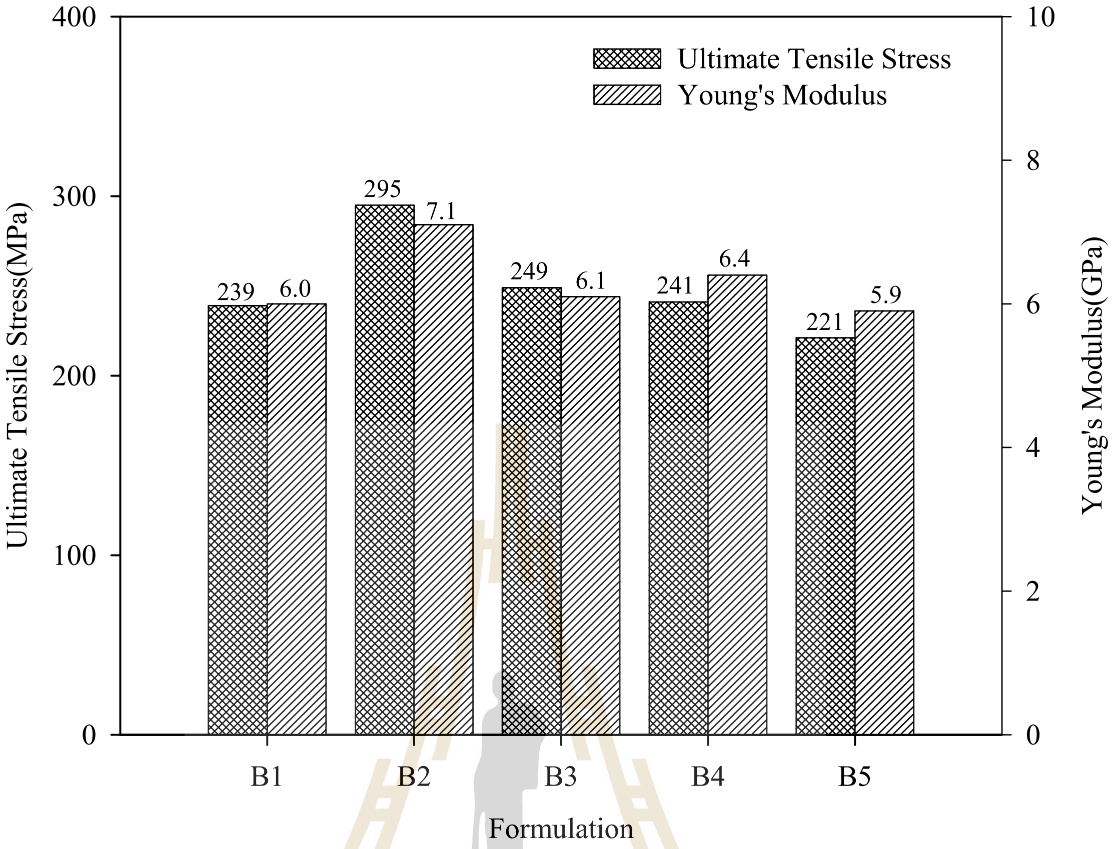


Figure 4.6 Ultimate tensile stress and Young’s modulus of fiber glass composite prepared by prepreg formulations using various type of amine curing agents.

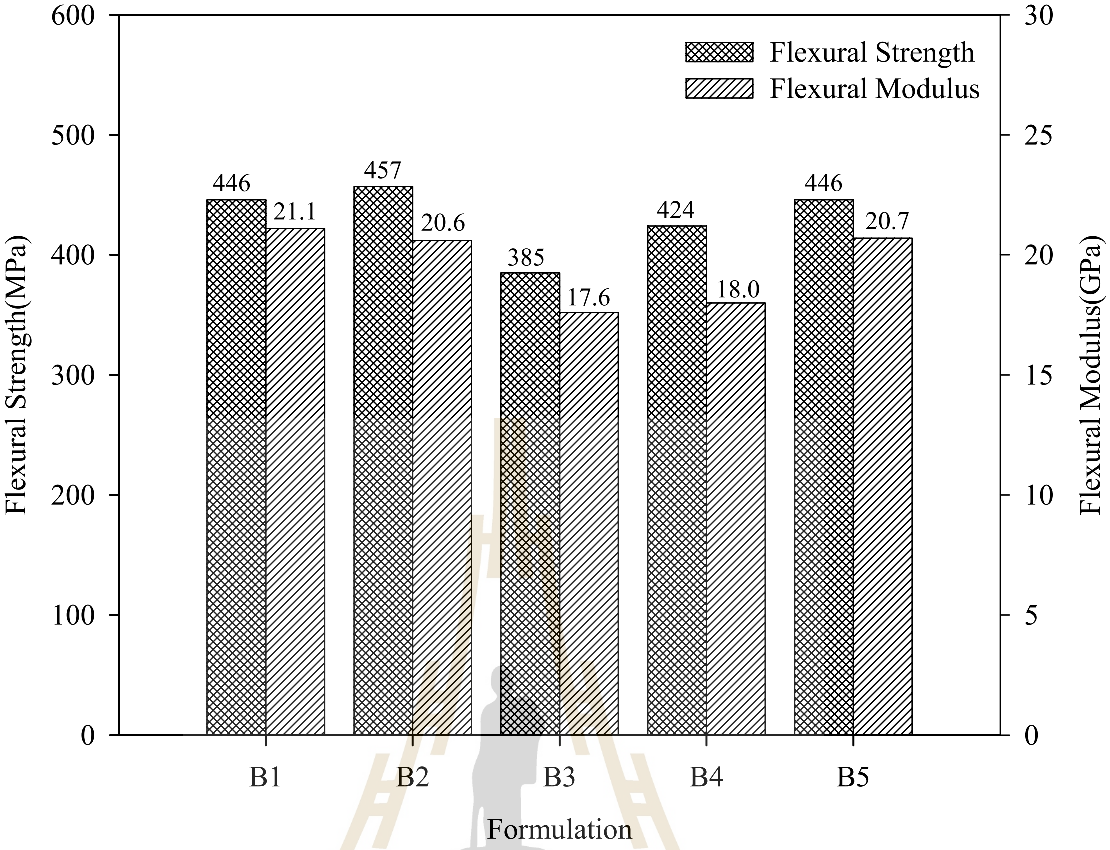


Figure 4.7 Flexural strength and flexural modulus of fiber glass composite prepared by prepreg formulations using various type of amine curing agents.

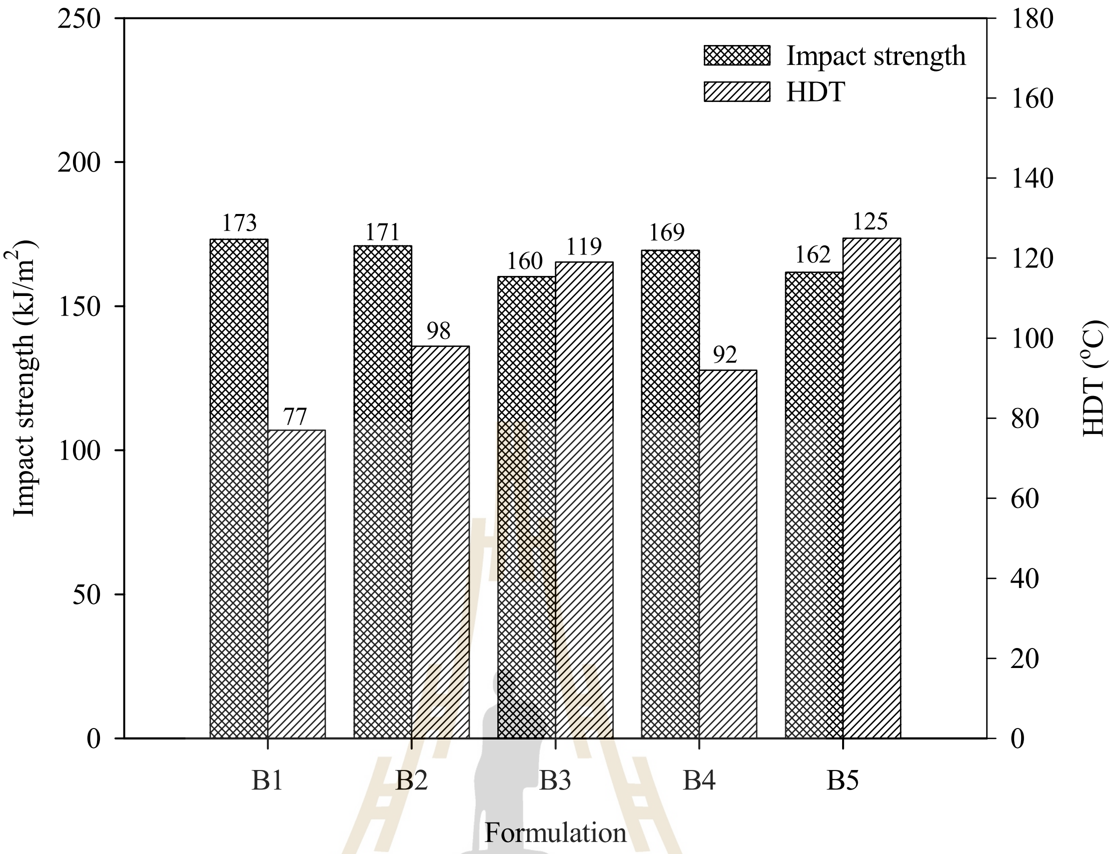


Figure 4.8 Impact strength and HDT of fiber glass composite prepared by prepreg formulations using various type of amine curing agents.

From results discovered, the general conclusion may be drawn that Ancamine 2165, mixture of m-xylene diamine and benzyl alcohol, was not only used to enhance the tensile property but also improved the toughness of cured prepreg composite. Inferior in service temperature is the hold back aspect of this chemical. However, to overcome this lack of ability but retaining the mechanical properties, small amount of pure IPDA and TETA could be added into the ingredient. These were successfully formulated in the actual industrial site.

4.2.3 Effect of Catalysts

It is commonly known that dicyandiamide (DICY) added in curing agent formulation for epoxy resins will prolong shelf lives of prepreg at room temperature. On the other hand, it will extend the cure reaction even at high temperature. The cured properties derived from the formulation are acceptable for many applications. To overcome the drawback characteristic of DICY, retarding the cure reaction, the high temperature catalyst must be incorporated. Common accelerators are BF_3 amine complexes, tertiary amines, Imidazoles, some proprietary compounds and substituted ureas. All of these accelerators offer some benefits but normally drawbacks to shelf life, cure profile and cured properties.

In this work, the catalysts comprised of imidazole and substituted urea, Dyhard UR200, Dyhard UR300, and Dyhard UR500 are used as DGEBA/DICY accelerators. The substituted urea, UR series, having the chemically different in substituted as show in Table 3.1, are employed. The outcome from this study will be use to decide which type of catalyst and its amount offer the superior properties that required by the windsurf industry. The effect of catalyst on mechanical and thermal properties will be observed and evaluated. The non-catalyzed curing formula, C1, consisted of Dyhard 100, Ancamine 1618 and Ancamine 2165 at weight ratio of 40:25:25 was a referee. The amount of each catalyst at 5, 10 and 15 weight ratio was added. The mechanical and thermal properties test results of fiber reinforced composites obtained from the prepreg using 5 part of those catalysts are summarised in Table 4.8 and also shown in Figure 4.9 to 4.11, respectively.

Table 4.8 Mechanical and thermal properties of fiber glass composite prepared by prepreg formulations using various type of catalysts.

Formula	**Catalyst Type**	**Properties**					
		σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
		(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(°C)
C1	No	247±11	6.2±0.1	363±14	18.0±0.6	143±8	97±0.6
C2	Imidazole	258±15	6.4±0.1	399±10	17.9±0.9	179±9	112±0.6
C3	Dyhard UR200	275±15	6.5±0.1	510±18	20.6±1.1	172±7	102±0.6
C4	Dyhard UR300	261±18	6.9±0.2	507±15	19.6±1.0	189±6	103±0.6
C5	Dyhard UR500	240±18	6.4±0.2	522±15	19.7±1.1	165±4	94±0.6

The results show that the overall properties obtained from catalyzed hardener are higher than the non-catalyzed. The test values also indicate that Dydard UR200 and Dyhard UR300 provide superior tensile and flexural properties but modulate in HDT. General speaking, Dyhard UR200 offers considerably better properties than using UR300. The maximum HDT found when Imidazole was used but it generates inferior mechanical properties. Highly steric hindrance substituted urea catalyst, Dyhard UR500, will lower the tensile and impact properties.

Within the experimental error, the results suggest that the Imidazole catalyst offer better HDT but not for the mechanical aspects. Dyhard UR200 and UR300 provide higher toughness tensile properties and modulate in HDT. Dyhard UR 500 give the outstanding flexural strength but inappreciative both tensile and HDT. At this stage of work and by the overall thoughtfulness, the Dyhard UR 200 catalyst would be the best interest because it has the lowest drawback.

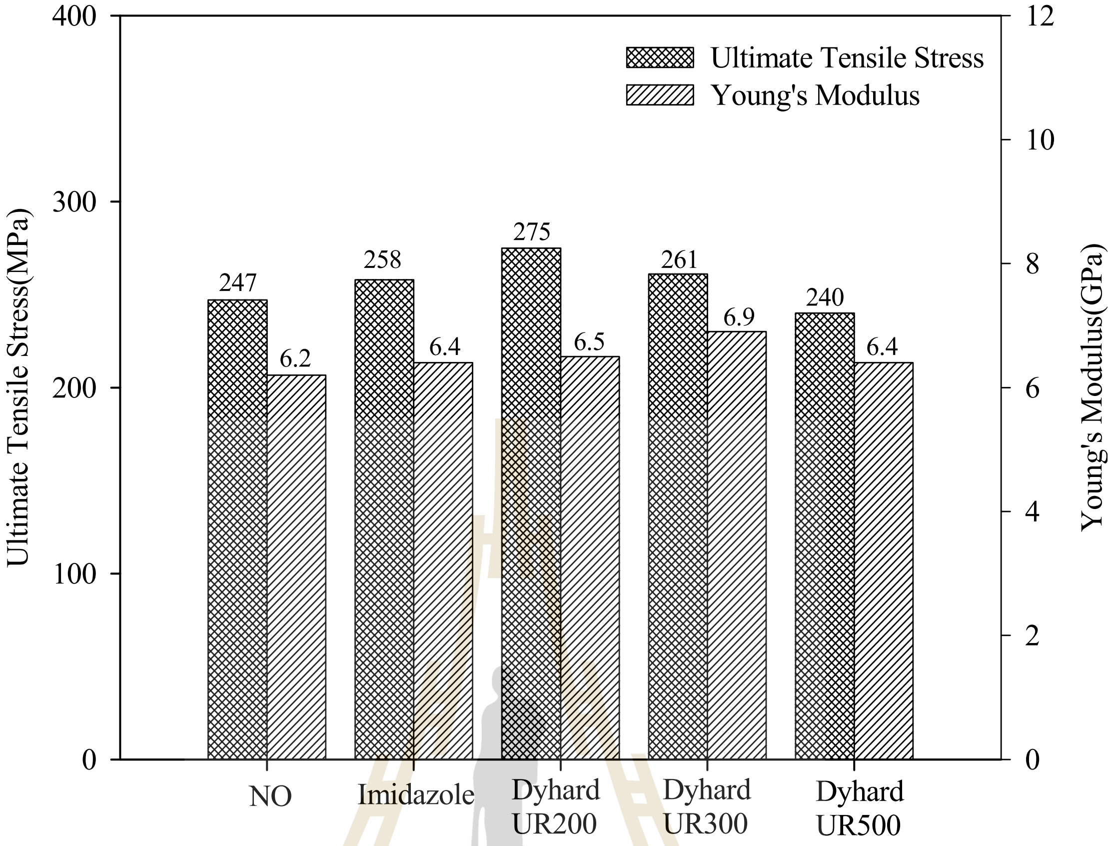


Figure 4.9 Ultimate tensile stress and Young’s modulus of fiber glass composite prepared by prepreg formulations using various type of catalysts.

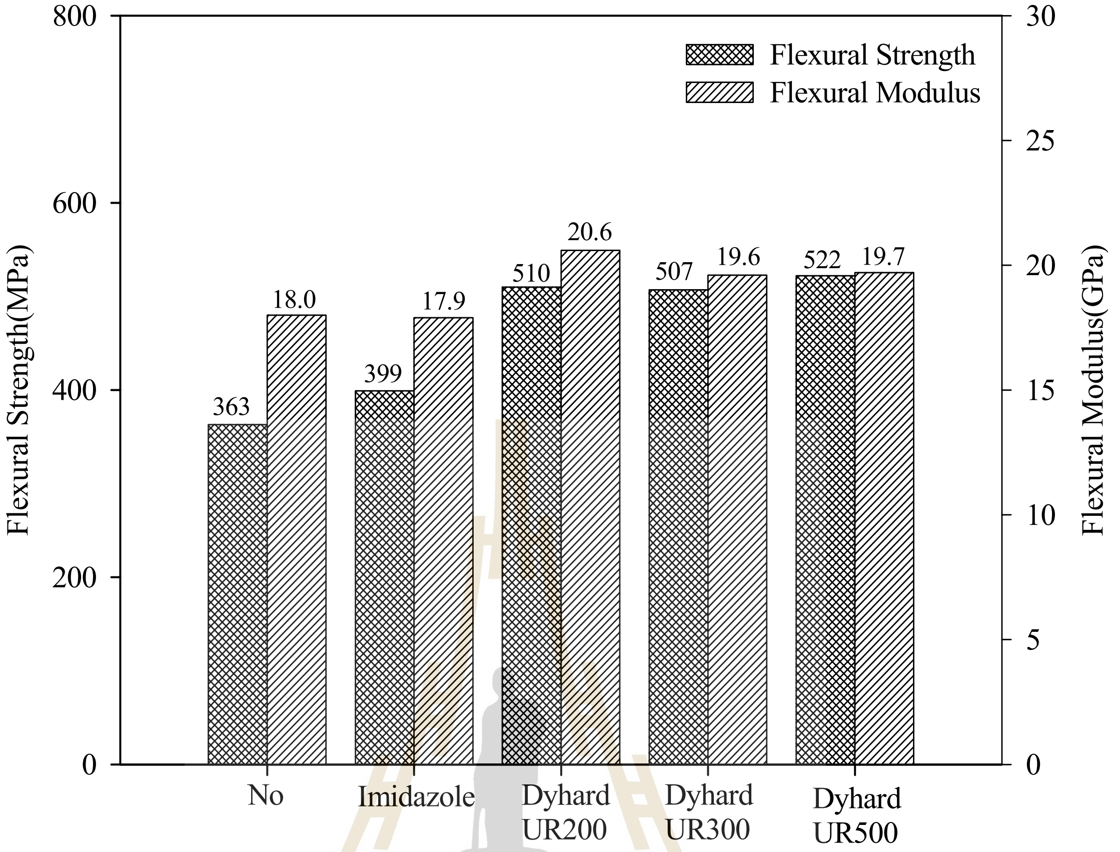


Figure 4.10 Flexural strength and flexural modulus of fiber glass composite prepared by prepreg formulations using various type of catalysts.

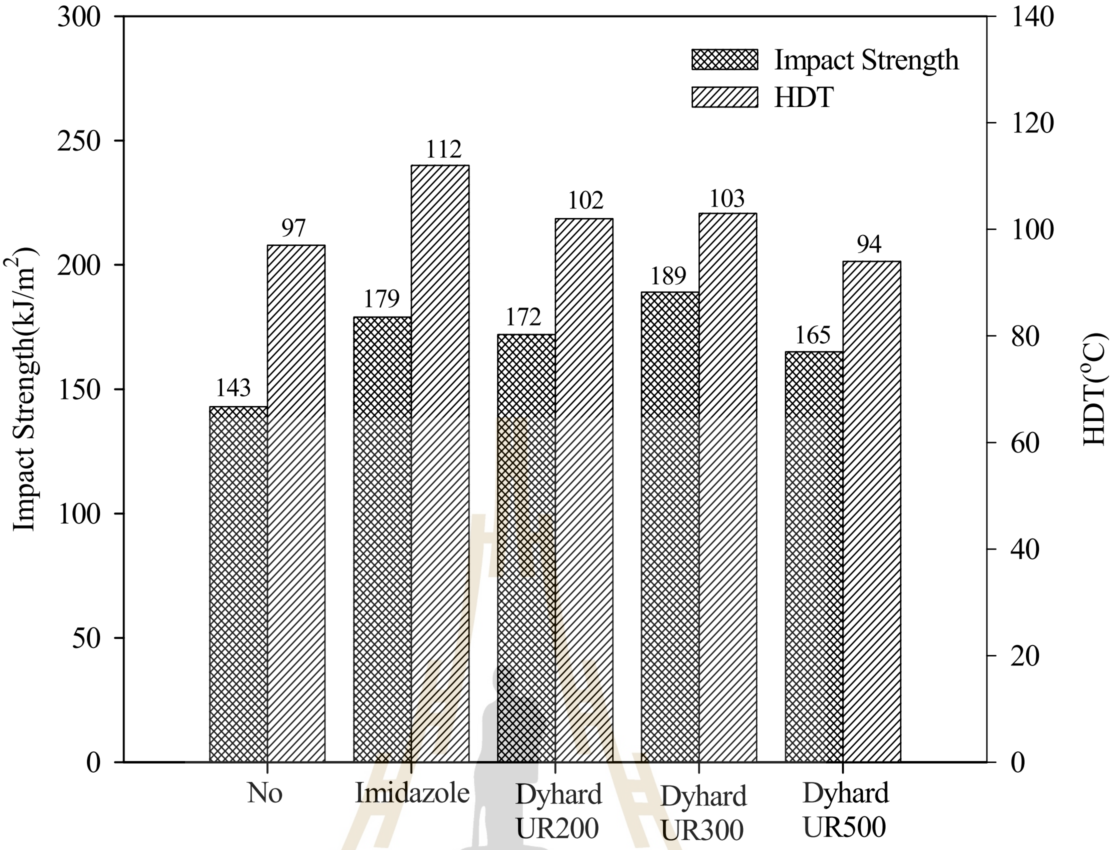


Figure 4.11 Impact strength and HDT of fiber glass composite prepared by prepreg formulations using various type of catalysts.

As Dyhard UR200 is the best candidate catalyst among those given choices. The optimal weight ratio of catalytic in curing ingredient is also prime interest of this research study. Most catalysts are relative expensive but essential for prepreg formulation especially when it is cured at elevated temperature. Over dose of this materials in the hardener not only the loss in capital cost but also perhaps damage in performance properties. Therefore, the lowest amount of Dyhard UR200 used but retaining in the properties is observed. The amount of Dyhard UR200 was increased from 5, 10 and 15 by weight ratio, respectively. The mechanical and thermal properties of the glass fiber laminated derived from those prepreg formulations are reviewed in Table 4.9 and graphically presented in Figure 4.12 to 4.14, respectively.

Table 4.9 Mechanical and thermal properties of fiber glass composite prepared by prepreg formulations using different amount of Dyhard UR200 catalyst.

Formula	**Dyhard UR200 (wt.%)**	**Properties**					
		σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
		(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(°C)
C1	0	247±11	6.2±0.1	363±14	18.0±0.6	143±8	97±0.6
C3	5	275±15	6.5±0.1	510±18	20.6±1.1	172±7	102±0.6
C7	10	276±6	6.9±0.2	469±11	19.0±0.6	161±10	114±1.0
C11	15	245±11	6.7±0.1	458±5	17.4±0.5	180±8	108±0.6

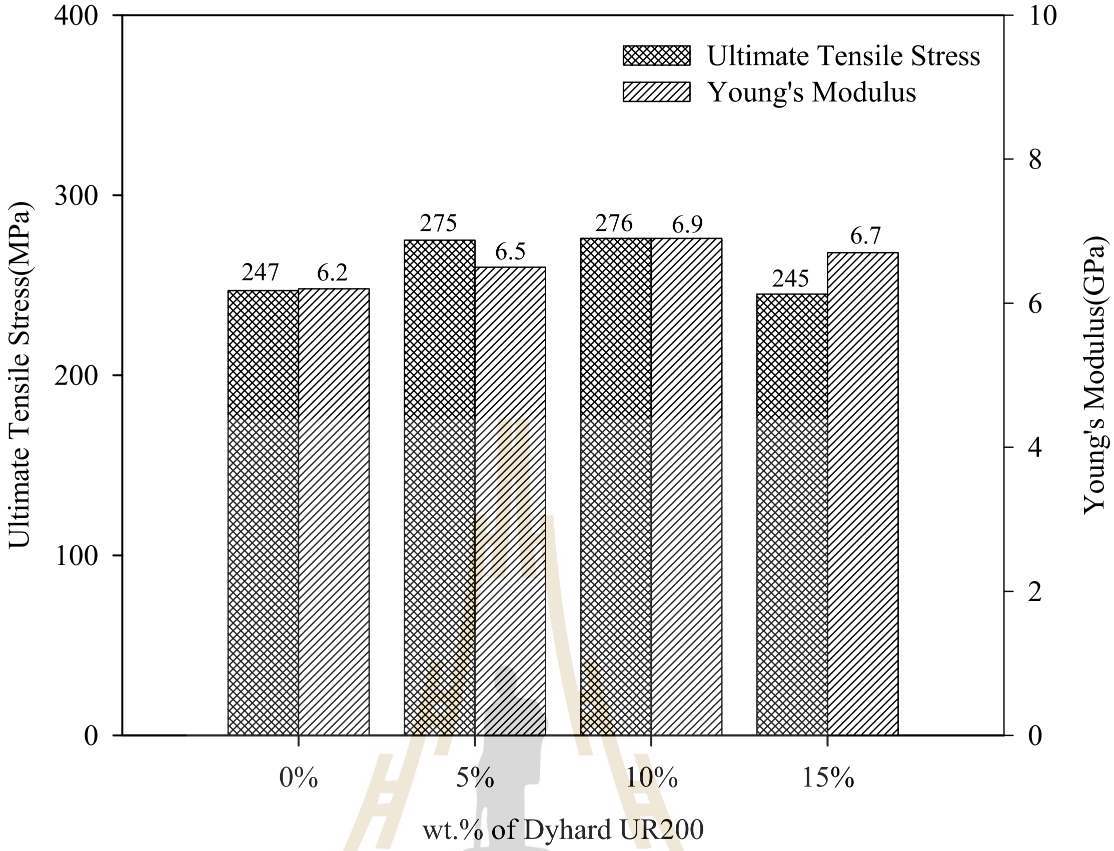


Figure 4.12 Ultimate tensile stress and Young’s modulus of fiber glass composite prepared by prepreg formulations using different amount of Dyhard UR200 catalyst.

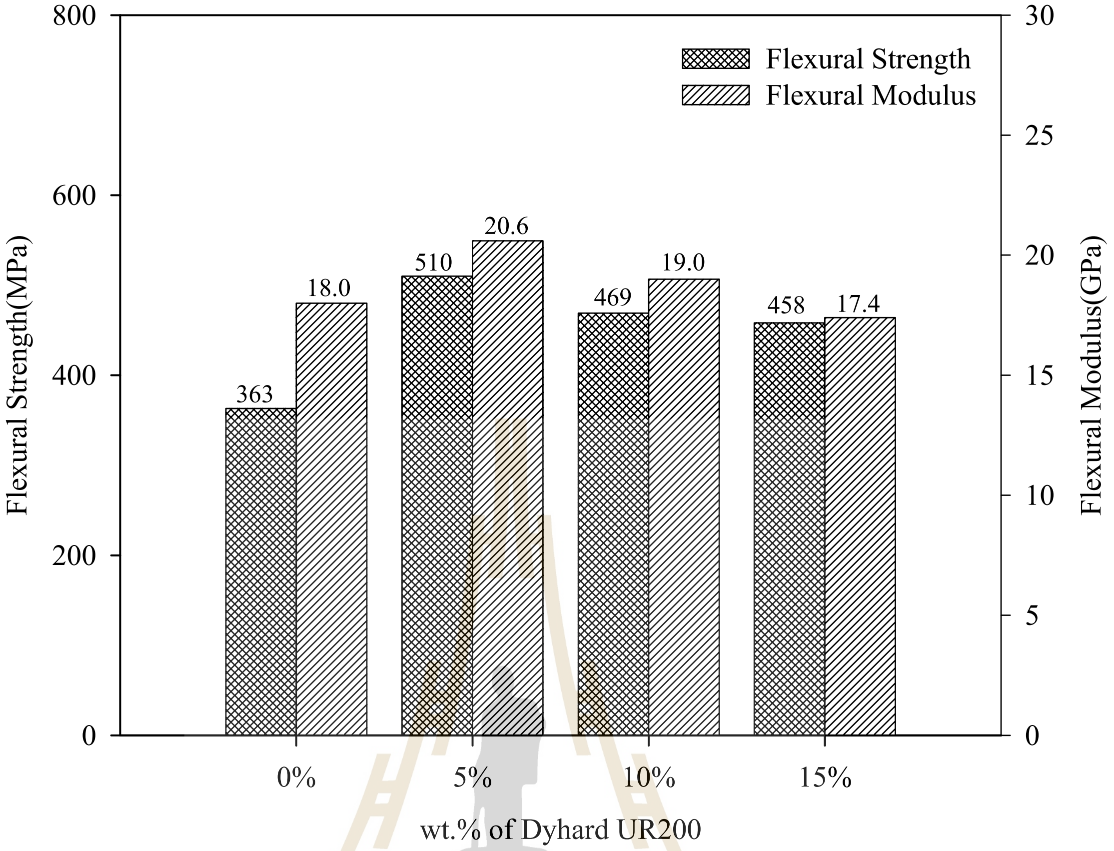


Figure 4.13 Flexural strength and flexural modulus of fiber glass composite prepared by prepreg formulations using different amount of Dyhard UR200 catalyst.

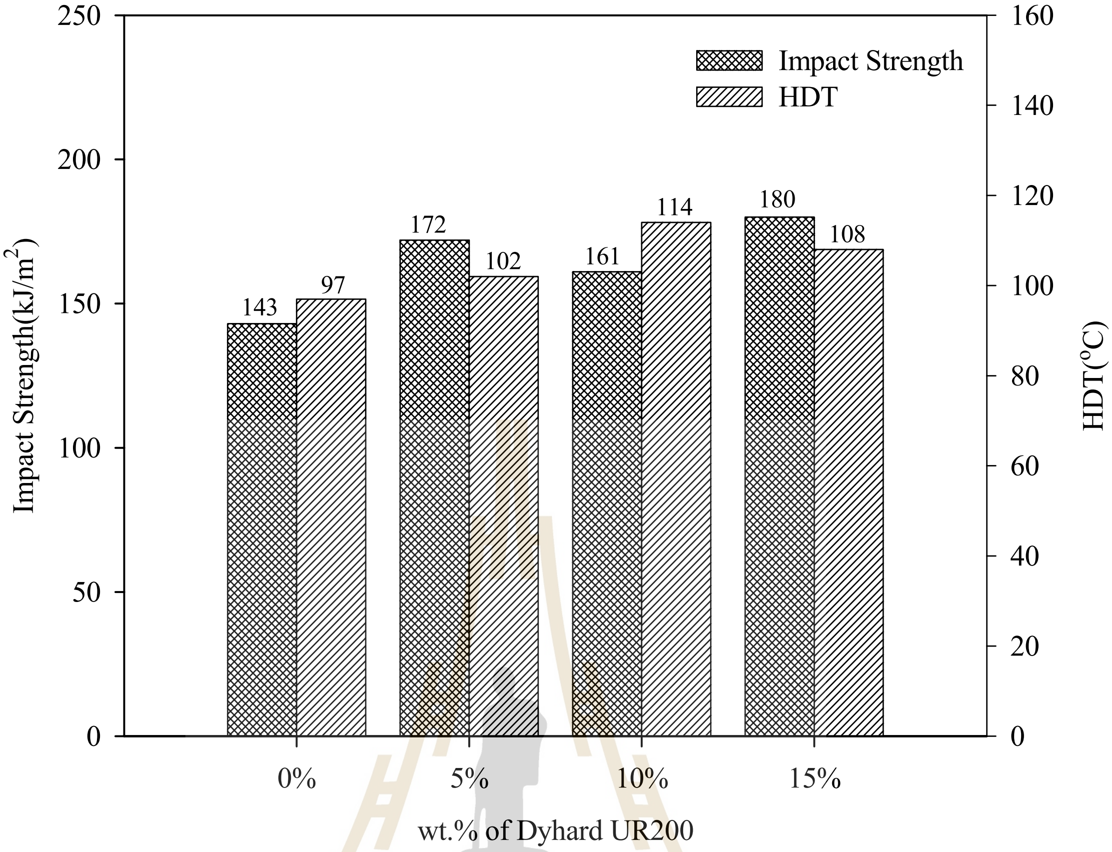


Figure 4.14 Impact strength and HDT of fiber glass composite prepared by prepreg formulations using different amount of Dyhard UR200 catalyst.

The results review that increasing amount of Dyhard UR200 from zero to 10 weight ratio in hardener ingredient both mechanical properties, by mean of tensile, flexural and impact strength, and thermal property are significantly increased. Further addition of the catalyst to 15 weight ratio, the properties are slightly decreased except for the impact strength. General speaking, it seems that the optimal amount of catalyst used in this system given rise to outstanding of all properties is 10 part of weight ratio. From the found out, it can be explained that at 5 part of catalyst the crosslink reaction had not yet been completed. For the content higher than 10 part of weight ratio, the unreacted catalyst would act as contaminant in the specimen and hence dilution effect will be contributed to the properties.

From the above results, it could conclude that urea substituted catalyst, Dyhard UR200, provide the distinguish performance properties against those given catalytic substances for the prepreg manufacturing. Using of 10 part of weight ratio of the UR200 has offered the best values of the both mechanical properties and HDT.

4.3 Cure Cycle

Cure cycle of fiber reinforced material is important for both manufacturing planning and processing time and also the final properties of the product. In prepreg processing, it is comprised of three steps cure cycle time, B-stage, pre and post cure. At the given system, those steps will largely depend on the temperature. The B-stage cure time is the period of the resin undergo partially cure and become sticky. After this stage, the resin drainage is prohibited. As a result, the prepreg is already to be laminated. Pre-cure and post-cure processes are prime important steps to properties of the finished product.

In this experiment, the B-stage cure was investigated under isothermal temperature at 80°C, 100°C and 120°C. It would take weeks to obtain the time at room temperature. Therefore, the B-stage time at 20°C, as typical storage temperature, is then further predicted using the kinetic reaction analysis. The pre cure conditions were isothermally cure at ranging temperatures from 120°C to 180°C and the cure time varying from 5 mins to 25 mins depend on the cure temperature. This length of time was sufficient to vitrify the epoxy system. The samples were then post cure at 150°C or 180°C for 8 hrs.

4.3.1 B-stage Cure

B-stage cure of the prepreg is important factor for preparing the pre-cured sheet. In this stage, it will enable prepreg to easily conform to different shapes and to allow stacks of plies to stick together in the molding process. At low temperature, both DICY and catalytic curing agents could not be reacted in the short time. Thus, amine curing agents will be used to control the B-stage of prepreg at ambient temperature. In this study, the B-stage time (t_B) of the prepreg was determined by hardness measurement with time under the isothermal conditions. The typical hardness-time curve is resulted and shown in Figure 3.1, in chapter III. The t_B is determined by interception of the linear line and exponential one.

The t_B measured at 80°C, 100°C and 120°C, respectively, of the B-series curing agent having difference in amines ingredient at 50% by weight is summarized in Table 4.10. As expected that the t_B are shorter with increasing the testing temperature. At all given temperatures, IPDA result the longest B-stage time while DETA give the shortest. General observation also indicate that the t_B is two fold decreased when the temperature is increased by 20°C for all formulations. In order to resolve the t_B at as lower temperature as 20°C, the mathematical prediction using reaction kinetic equation will be applied.

Table 4.10 Dependency of B-stage time on various amine curing agents used in the prepreg formulation at different testing temperatures.

Formula	**Amine Curing Agents**	**B-stage time (mins)**		
		80°C	100°C	120°C
B1	Ancamine 1618	48	20	11
B2	Ancamine 2165	38	16	9
B3	TETA	30	16	8
B4	DETA	26	14	7
B5	IPDA	52	22	12

According to Arrhenius equation, the rate of reaction kinetic depended on temperature can be derived as follow;

$$\text{Rate of Reaction} = \frac{d\alpha}{dt} = Af(\alpha)exp\left(\frac{-E_a}{RT}\right) \qquad (4.2)$$

where α = the conversation

$f(\alpha)$ = conversion function independent on temperature.

A = Arrhenius's constant

E_a = the apparent activation energy for overall function

R = the universal gas constant

and T = the absolute curing temperature

Assuming that the reaction conversion at the given t_B is identical for this studied systems. Rearrangement and then integration of equation 4.2 from $t = 0$ to $t = t_B$ where t_B is the time at which the B-stage prepreg occurred resulted that;

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A\,exp\left(\frac{-E_a}{RT}\right)\int_{t=0}^{t=t_B} dt = A\,exp\left(\frac{-E_a}{RT}\right)t_B \tag{4.3}$$

Taken the natural logarithm into equation 4.3 give rise to the linear equation form, $Y=aX+b$, as shown in equation 4.4 and 4.5.

$$ln\left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)}\right) = ln(A) - \frac{E_a}{RT} + ln(t_B) \tag{4.4}$$

and then;

$$ln(t_B) = \frac{E_a}{RT} + \left[ln\left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)}\right) - ln(A)\right] \tag{4.5}$$

Given that $Y = ln(t_B)$, $X = \frac{1}{T}$, $a = \frac{E_a}{R}$ and $b = ln\left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)}\right) - ln\,A$, the plot between $ln(t_B)$ with $1/T$ of the formulation B1 at the assigned three curing temperatures is illustrated in Figure 4.15. It is shown the straight line as expected by the equation 4.5. By using statistical linear regression analysis with assistant of SPSS programming, it is found that the slope and y-axis intercept of this data are 5.12 and -10.67, respectively. By using the statistical parameter, the correlation coefficient(r) which is calculated according to equation 4.6, it is equal to 0.997. From the correlation coefficient found, it is strengthen that the model equation is perfectly related to linear relationship. By substitution the B-stage cure at 20°C, 1/(273+20)K = X = $3.413\text{x}10^{-3}$ K^{-1}, into the linear equation obtained for the formulation B1, the t_B equal to 902 mins or 15 hrs is resolved.

$$r = \frac{\sum[(x_i - \overline{X})}{\sqrt{\sum(x_i - \overline{X})^2}} \frac{(y_i - \overline{Y})]}{\sqrt{\sum(y_i - \overline{Y})^2}} \tag{4.6}$$

where x_i = the t_B obtained by calculated using linear equation 4.5

y_i = the t_B obtained from the experiment

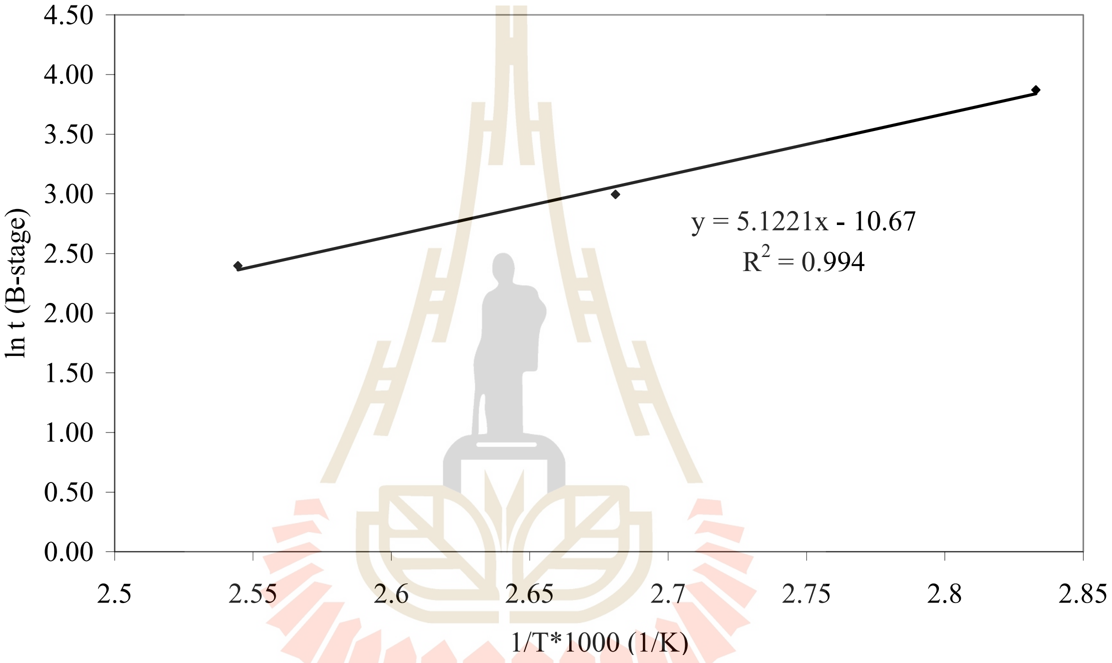


Figure 4.15 The plot between $ln(t_B)$ with $1/T$ of the Ancamine 1618 added curing agent, formulation B1.

Repeating the same manner as described above, the coefficient of determination (R^2), which it is the correlation coefficient factor (r) square, and also the linear equation form of the other formulations using Ancamine 2165, TETA, and IPDA, are summarized in Table 4.11. All the calculations are favorably agreement with the model equation purposed. Applying those linear relationships to predict the

t_B at 20°C, the calculated results are shown in Table 4.12. The curing agent using IPDA gives the maximum t_B at 18 hrs. Vice versa, the minimal time at 6 hrs is observed when DETA is used. These outcomes indicate that the t_B at storage temperature of the prepreg resolved from the hardener prepared from various amines largely controlled by the type of amines.

Table 4.11 Summary of the predicted linear relationship and correlation factors of the curing agent formulations.

Formula	**Amine Curing Agents**	**B-stage time (mins)**			**Linear Equation $Y = aX+b$**	**R^2**
		80°C	100°C	120°C		
B1	Ancamine 1618	48	20	11	Y=5.12X-10.67	0.994
B2	Ancamine 2165	38	16	9	Y=5.07X-10.64	0.994
B3	TETA	30	16	8	Y=5.00X-10.59	0.993
B4	DETA	26	14	7	Y=4.52X-9.59	0.996
B5	IPDA	52	22	12	Y=5.23X-10.86	0.994

Table 4.12 Summary of the calculated B-stage time of curing agent formulations at 20°C.

Formula	**Amine Curing Agents**	**B-stage time (mins.)**	**Approximate B-stage time (hrs.)**
B1	Ancamine1618	902	15
B2	Ancamine2165	639	11
B3	TETA	442	7
B4	DETA	343	6
B5	IPDA	1086	18

In accordance with the industry requirement as previous mentioned, the t_B of prepreg ranging from 10 to 16 hrs at 20°C is acceptable. From the above t_B reported, the Ancamine 1618 and Ancamine 2165 will be the most suitable for the industrial application. However, as discussed in section 4.2.2 that Ancamine 2165 give rise to superior tensile strength and HDT but inferior in impact strength when compare with Ancamine 1618. Accordingly using the mixture of the Ancamine 1618 and Ancamine 2165 is the prime interests for both industry and academic point of view. The mixing weight ratios were varied from 40:10, 30:20, 20:30 and 10:40 for Ancamine 1618 and Ancamine 2165, and they are assigned as B6 to B9, respectively. The B-stage time at 80°C, 100°C and 120°C and also the model linear equations and correlation factors derived from the statistical method of those formula are presented Table 4.13. The extrapolated t_B at 20°C are also reported in Table 4.14.

As expect, the results illustrate that the t_B is decreased with increasing the amount of Ancamine 2165. The tendency of decreasing in t_B with increasing temperature is also similar to those the single component formula, 2 fold decrease with 20°C increase. The linear correlation factor (R^2) for all mixtures are well closely to 1.0 which indicated that the tested data are strongly related to linear relationship. The equations were then accepted to calculate the t_B at 20°C. The results show that the predicted t_B is decreased from 15 hrs for B6 to 11 hrs for B9, respectively. When comparing the t_B of the formula to the one use at the windsurf manufacturer, Cobra International Co. Ltd., the B8, 20:30 weight ratio and having the t_B equal to 12 hrs at 20°C, is acceptable in term of B-stage aspect. As mention that not only cure parameters are important for manufacturing but the performance properties of the product are also concerned. The mechanical and thermal properties of the laminated samples obtained from the given prepreg formulations were tested and is reported in Table 4.15. The plots of the results are also presented in Figure 4.16 to 4.18, respectively. Within the experimental errors, the tested properties of those formulations are not significantly difference. There are on the bench marks for the actual industrial applications. In overall balancing and taken both B-stage cure parameter and performance properties, the B8 is the suitable for transferring into the manufacturing.

According to both the B-stage and also the properties had been reported throughout this section, it can be concluded that the hardener for prepreg formulation derived from the mixture of Ancamine 1618 and Ancamine 2165 at 20:30 weight ratio together with 40:10 by weight of Dyhard 100 and Dyhard UR200 is superlative acceptable. It is shown the calculated t_B of 12 hours at 20°C when it is used with the R2 epoxy resin, 20:80 by weight of YD115 and YD127, respectively. Whereas, the mechanical and thermal properties of this formulae are retained.

Table 4.13 Summarizing of B-stage times at 80°C, 100°C and 120°C and the linear equation of the prepreg formulations obtained from using Ancamine 1618 and Ancamine 2165 mixtures.

Formula	**Ratio (wt.%)**	**B-stage time (mins)**			**Linear Equation $Y = aX+b$**	**R^2**
		80°C	100°C	120°C		
B6	40 : 10	48	19	11	Y=5.13X-10.74	0.990
B7	30 : 20	43	18	10	Y=5.07X-10.64	0.994
B8	20 : 30	39	17	9	Y=5.09X-10.78	0.998
B9	10 : 40	38	16	9	Y=5.00X-10.59	0.993

Footnote: Ratio by percent ratio of Ancamine1618 and Ancamine 2165 of totalcuring agents.

Table 4.14 Summarizing of the predicted B-stage time at 20°C of the prepreg formulations obtained from using Ancamine 1618 and Ancamine 2165 mixtures.

Formula	**Ratio** (wt.%)	**B-stage time (mins)**	**Approximate B-stage time (hrs)**
B6	40 :10	886	15
B7	30 : 20	771	13
B8	20 : 30	718	12
B9	10 : 40	639	11

Table 4.15 Mechanical and thermal properties of fiber glass composite prepared by prepreg formulations using various ratios of Ancamine 1618 and Ancamine 2165 in curing agent.

Formula	**Ratio** (wt.%)	**Properties**					
		σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
		(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(°C)
B6	40 :1 0	247±11	6.2±0.1	502±14	18.9±0.6	180±18	109±0.6
B7	30 : 20	275±15	6.5±0.1	482±18	18.9±1.1	172±14	111±0.6
B8	20 : 30	278±12	6.6±0.2	479±11	18.4±0.6	171±12	114±1.0
B9	10 : 40	281±11	6.5±0.1	458±5	17.4±0.5	168±10	115±0.6

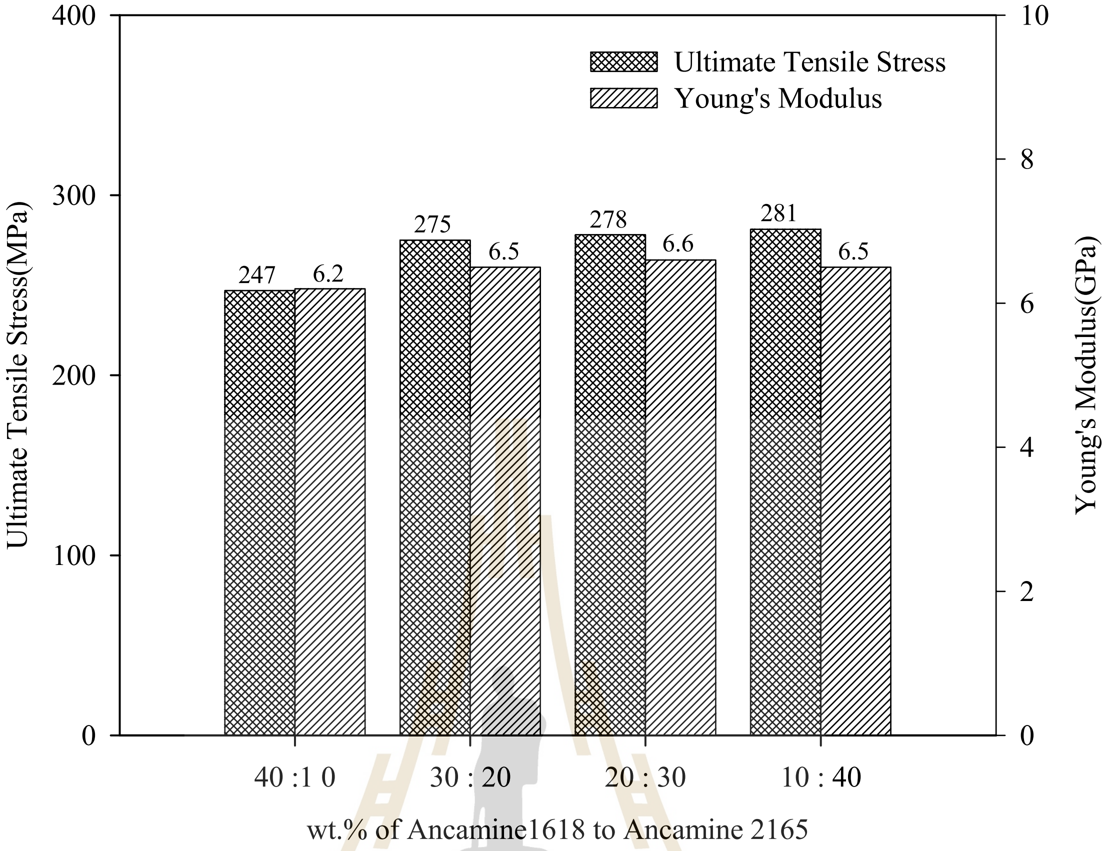


Figure 4.16 Ultimate tensile stress and Young’s modulus of fiber glass composite prepared by prepreg formulations using various weight ratio of Ancamine 1618 to Ancamine 2165.

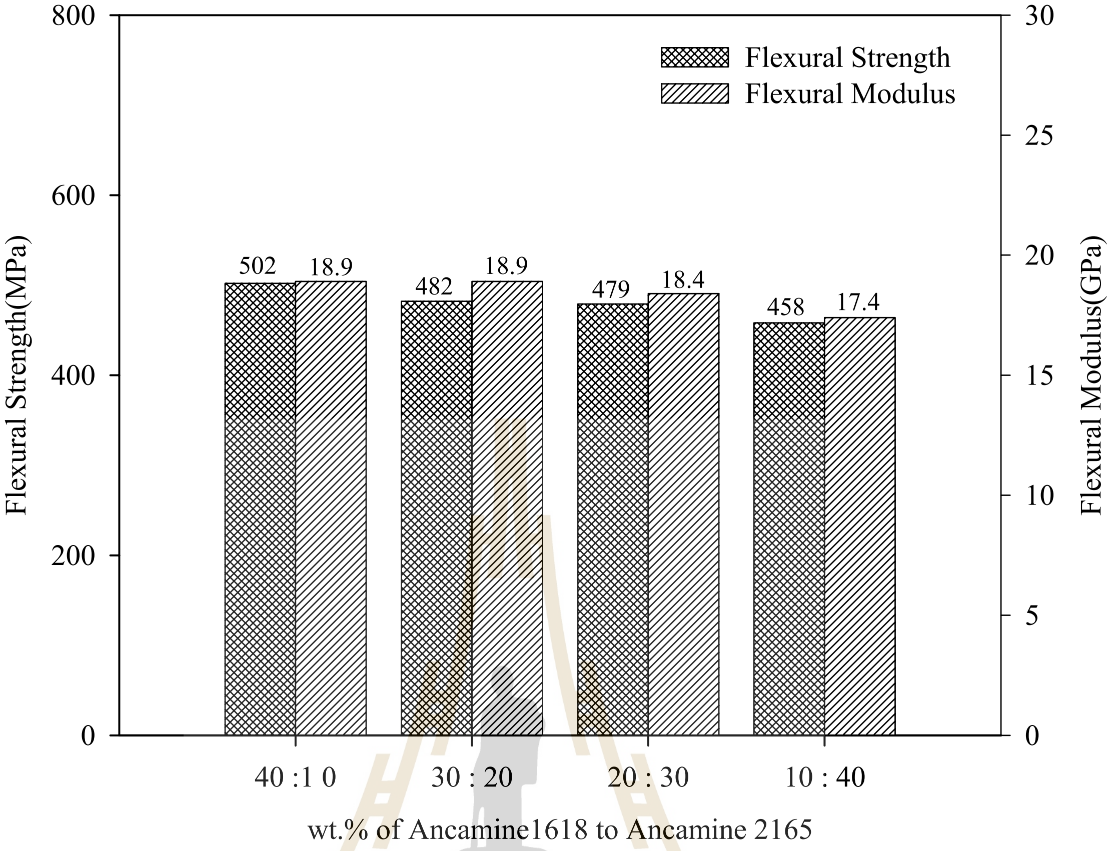


Figure 4.17 Flexural strength and flexural modulus of fiber glass composite prepared by prepreg formulations using various weight ratio of Ancamine 1618 to Ancamine 2165.

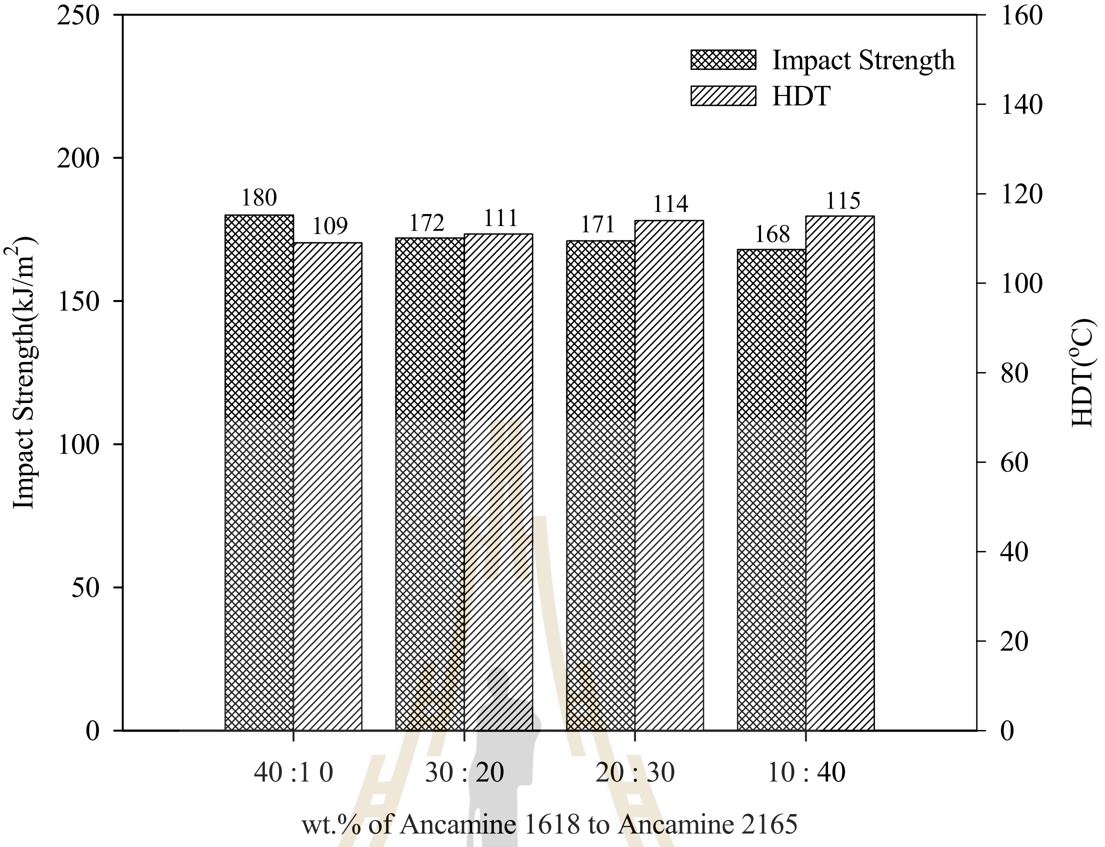


Figure 4.18 Impact strength and HDT of fiber glass composite prepared by prepreg formulations using various weight ratio of Ancamine 1618 to Ancamine 2165.

In the actual industrial application, the epoxy resin will be mixed with curing agent at the given calculated stiochiometric ratio or phr as shown in equation 3.1. Base on this calculation, the phr of B7, R2 and B8 are 20.50, 20.04 and 19.59, respectively, and summarised in Table 4.16. The round number, for example phr equal to 20, would make the production process in term of weighing much more easier compare with the other odd or even ones. General comparison between those three formulations, it is reviewed in Table 4.16 that the mechanical properties and thermal properties are not significantly difference. Moreover, applying the ANOVA test on the properties; as described in section 4.1, also confirms that those three formula are indistinguishable. Even though, the t_B of the R2 had not been examined. By using the Ancamine 1618 and Ancamine 2165 ratio in R2 at 25:25 which is in the middle between the ratio in B7 and B8, it is strongly believed that the calculated t_B at 20°C would fall in between 13 and 12 hrs. It will be accepted for the manufacturing application. In fact, when the R2 was transferred into the workable industrial site, it was fully satisfied.

Table 4.16 Summary of the process parameters, mechanical and thermal properties of the B7, R2 and B8 formulations.

Properties	**B7**	**R2**	**B8**	**F-test**
phr	20.50	20.04	19.59	-
B-stage time	13	-	12	-
σ_u(MPa)	275±15	281±17	278±12	H_0 Accepted
E(GPa)	6.5±0.1	6.6±0.1	6.6±0.2	H_0 Accepted
σ_{fM}(MPa)	482±18	484±14	479±11	H_0 Accepted
E_f(GPa)	18.9±1.1	18.6±0.9	18.4±0.6	H_0 Accepted
a_{iN}(kJ/m^2)	172±14	176±14	171±12	H_0 Accepted
HDT(°C)	111±0.6	113±0.6	114±1.0	-

Taken all justification discussed above, the R2 rather than B7 or B8 comprised of the epoxy resin obtained from mixture of YD115 and YD127 at 80:20 weight ratio and curing agent derived from Ancamine 1618, Ancamine 2165, Dyhard

100 and Dyhard UR200 at the 25:25:40:10 ratio is satisfied. The stiochiometric mixing ratio between epoxy resin and hardener of the prepreg formulation is the phr equal to 20. This formulae will be used as matrix for further study as will be discussed in the following section.

4.3.2 Effect of Cure Conditions

There are two important steps in curing of composite laminated, pre-cure and post-cure. The former stage is needed for resin solidification. The completion cure reaction and removing internal residual stress are effectively done the later. The final performance properties are affected by both two processes. The post-cure temperature is normally operated at above the T_g or HDT of the cured resin. The post-cure time will be shortened with higher post cure temperature.

In this research work, the processing parameters; temperature and time, for both curing conditions are studied. Regarding to the previous outcome, the formulation R2 is the most privilege by all mean and then it is chosen in this study. The temperature and time of pre-cure performed in the compression molding were at 120°C for 20, 25 and 30 mins, at 150°C for 10, 15 and 20 mins, and at 180°C for 5, 10 and 15 mins, respectively.

The mechanical and thermal properties of the glass woven laminated composites at different cure temperature and time are summarised in Table 4.17. At curing temperature of 120°C, the results illustrate that the mechanical properties are almost in depended on cure time. Except for the HDT, it is increased with increasing the curing time. This tendency review that the curing reaction had not yet been completed at 120°C for a period of shorter than 30 mins. However, when consider the overall performance of the samples at all curing times, they suggest that the curing time at 30 mins will be the most suitable candidate for further post curing investigation. At the pre-cure temperatures of 150°C and 180°C, the similar trends are sighted. Nevertheless, closer observation the test results demonstrate the depletion of the properties with curing temperature. Especially when the temperature was increased to 180°C and curing time of 15 mins, the inferior properties are obviously seen. It might be explained from the speculation that raising the temperature over the boiling point limit of the ingredient in prepreg formulation would create the void in the matrix phase. The void fraction will have the negative contribution to the properties of the composite. Another assumption might be included in the discussion is the matrix degradation. Curing the composite at high temperature for longer period of time, the polymer chain degradation might possibly be occurred. If it does in the process, the slightly brown laminated and then lower in mechanical properties will be recovered. However from the visual observation, the physical appearance of the sample cured at 180°C for 15 mins was look normal. It indicates that at this curing condition the chain deterioration is not significantly occurred. The contribution of properties declining may come only from the void generation.

Taking the number figures from all testing categories, the candidate of pre-cure times at 150°C and 180°C are 20 mins and 5 mins, respectively. These conditions having outstanding in the overall properties. However at 150°C and 10 mins cure condition is exceptional chosen because it is the parameter that has been adopted by the concerned composite manufacturer. For further post-curing discussion, the samples were the pre-cure at 120°C, 150°C and 180°C for 30, 10 and 20, and 5 mins, respectively.

Table 4.17 Effect of pre-cure temperature and time on the properties of fiber glass composite.

Cure Temperature (°C)	**Cure Time (mins)**	**Properties**					
		σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
		(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(°C)
120	**20**	329±20	7.3±0.4	402±22	16.7±1.2	159±5	71±0.6
	25	353±20	7.7±0.3	372±15	17.7±1.7	151±7	76±0.6
	30	335±7	6.7±0.2	385±26	17.9±2.00	179±10	81±1.0
150	**10**	282±16	6.7±0.2	408±22	18.6±0.5	175±7	85±1.0
	15	311±18	7.4±0.3	373±9	17.6±0.7	189±6	104±0.6
	20	325±17	7.2±0.3	413±13	18.3±1.0	196±14	103±0.6
180	**5**	326±22	7.2±0.1	375±28	19.2±0.6	160±6	112±0.6
	10	297±8	7.0±0.1	353±12	17.2±0.4	131±9	93±0.6
	15	287±14	6.8±0.2	454±11	20.6±0.9	158±5	88±0.6

Table 4.18 shows the effect of post-cure temperature on the final properties of the laminated sample obtained from R2 prepreg formulation. The standard pre-cure condition employed was pre-cure at 150°C for 10 mins and post-cure for 8 hrs as routine practically performed in the windsurf manufacturer. The result show that the properties are improved when the sample is post-cured. Further increase the post-cure temperature to 180°C, the properties are slightly decreased. The sample become more brittle as seen from the flexural and impact testing. According to the values obtained, the numbers at 150°C post-cure temperature for 8 hrs will be used as bench mark for further discussion.

The dependency of the properties of the laminated composites on the cure conditions are reported in Table 4.20. The four pre cure conditions at 120°C for 30 min, 150°C for 10 mins and 20 mins, and at 180°C for 5 mins were performed. The samples were post-cure at 150°C for 8 hrs in the incubating oven. Considering the testing results of the samples prepared at 120°C and 150°C pre-cure temperatures with and without post cures, they are shown that the properties are significantly enhanced by post-cure process. Especially at low temperature and short pre-cure time, the post-cure process is essentially needed. For the 150°C and 20 mins pre-cure, the requirement for the sample post-cure seems less important. These are accomplished by the common fact that the completion of cure reaction is driven by higher reaction temperature and time. Therefore, post-cure step might not be needed in order to achieve the completed reaction. However, care have to be taken for removing the internal residual stress. It is typically done by post-curing method.

Based on the results summarised in Table 4.19, they are also reviewed that performing the pre-cure at extreme conditions, for example at to high temperature, would ruin the final properties of the composite product. In accordance with this research work, it illustrates that elevating the pre-cure temperature to 180°C. The performance of the laminated composite was not further improved by post-cure condition. Contradictory, some properties, such as HDT, are inferior. As explained in previous section that pre-curing at temperature close to boiling point of the formulation ingredients, the voids and, perhaps, chain degradation would occur. These sample defects can not be diminished while performing the post-curing condition. They would be retained in the final product.

Table 4.18 Effect of post cure condition on the properties of fiber glass composite.

Post Cure Temperature (°C)	**Properties**					
	σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
	(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(°C)
No	272±16	6.7±0.2	408±22	18.6±0.5	175±7	85±1.0
150	281±17	6.6±0.1	484±14	18.6±0.9	176±14	113±0.6
180	317±8	7.3±0.1	452±14	18.5±0.3	168±3	114±0.6

Footnote: Post cure time at standard time 8 hrs.

Table 4.19 Effect of post-cure condition at 150°C for 8 hrs on the properties of fiber glass composite.

Pre Cure Condition (°C, min)	**Post Cure**	**Properties**					
		σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
		(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(°C)
120,30	O	335±7	6.7±0.2	385±26	17.9±2.0	179±10	81±1.0
120,30	X	298±13	6.7±0.2	463±23	17.6±0.4	173±7	86±0.6
150,10	O	272±16	6.7±0.2	408±22	18.6±0.5	175±7	85±1.0
150,10	X	281±17	6.6±0.1	484±14	18.6±0.9	176±14	113±0.6
150,20	O	325±17	7.2±0.3	413±13	18.3±1.0	196±14	103±0.6
150,20	X	312±8	7.7±0.1	429±10	18.7±1.0	195±8	94±1.0
180,5	O	326±22	7.2±0.1	375±28	19.2±0.6	160±6	112±0.6
180,5	X	295±16	7.4±0.2	386±18	20.1±1.3	161±8	108±0.6

Footnote: O is not post cure and X is post cure at 150°C for 8 hrs.

From the above results, it could be conclude that the both pre-cure and post-cure condition have the significant effect on the thermal and mechanical properties of the composites derived from prepreg formulation. The optimal candidate condition by mean of the overall properties is pre-cure at 150°C for 10 mins and post cure at 150°C for 8 hrs. This condition give rise to the highest in flexural strength and HDT, and moderate of tensile properties and impact strength.

4.4 Solvents and Reinforcements

The solvent is commonly incorporated into the epoxy resin of prepreg formulation. It improves the resin flow and hence resin impregnation and also wettability phenomenon in the fiber lamination process. One of the criterion for best solvent is low boiling point. Because it will finally and easily removed by evaporation. One of the common draw back points of applying the solvent into the prepreg formulation, especially high boiling point one, is the solvent residual in the matrix. This will create more void defect and pin holes on the final product. The poorer properties will be experienced by the former one.

The strength of the laminated composites is combined by the strength of matrix and fiber reinforcement. The excellence combination is mainly contributed from the matrix/fiber adhesion. Not all kind of thermosetting resins are best for all type of fiber reinforcement. For example, unsaturated polyester resin is better suitable matrix for fiber glass than carbon or Kevlar fibers. In the prepreg industry, all kind of fibers have been used. It would be commercially appropriate to investigate which type of fiber is the best combination for the prepreg formulation prepared in this study.

In this section, the effects of solvents and fiber reinforcements on the mechanical and thermal properties the completed cured laminated composite derived from the R2 prepreg formulae will be discussed. The solvents used in this study were ethyl acetate (EA) and methyl ethyl ketone (MEK) which has the boiling temperature, according manufacturer data sheet, of 77°C and 80°C, respectively. These solvents are commonly and commercially used in prepreg industry. It was added into prepreg formulation at 1 and 5% by weight.

Table 4.20 shows the properties of the glass woven laminated samples obtained from R2 formulation using those solvents at 1 and 5% weight compositions. The samples were pre-cured in the compression molding at 150°C for 10 mins and then cut and post-cured in the oven at 150°C for 8 hrs.

Table 4.20 Mechanical and thermal properties of glass reinforced composite obtained from the prepreg formulation with and without solvents.

Solvent	**Properties**					
	σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
	(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(^{o}C)
No Solvent	281±17	6.6±0.1	484±14	18.6±0.9	176±14	113±0.6
1% EA	274±14	7.1±0.2	490±16	19.3±0.2	181±3	84±0.6
5% EA	279±6	7.4±0.2	511±11	20.1±0.6	191±7	76±0.6
1% MEK	241±11	6.7±0.2	430±20	17.0±0.6	183±8	108±0.6
5% MEK	226±15	7.4±0.3	462±19	19.6±1.1	201±8	80±0.6

Footnote: R2 Formulation using as the base value for non solvent.

According to the results shown in Table 4.20, the tensile strength and HDT of the non-solvent prepreg are higher than the ones diluted with solvents. The fracture toughness by mean of flexural and impact properties of non-solvent formula are lower than the others, except for the flexural strength of the prepreg using MEK as solvent. At the given solvent, the properties, except HDT, were superior with higher the content. The results also indicate that the solvent having lower boiling point, EA, give rise to the better overall properties than the higher boiling point one, MEK.

The improvement of mechanical properties by incorporating EA as diluent may be explained by the impregnation efficiency of the lower viscosity matrix onto the reinforcement. On the other hand, the improvement might be inhibited by high boiling solvent used. Because, the voids would be generated by the solvent residual. The HDT of the finished product is lowered by using the solvent. The affect might come from the crosslink inhabitation by the foreign molecule in B-stage reaction. Consequently, the lower crosslink density will be obtained and hence lower in HDT but higher in fracture toughness. Based on these research outcomes, carefully consideration must be taken into account for either the presence of the solvent in the epoxy formulation or type of solvent used. The solvent could improve the processability and mechanical properties but the thermal property is hassled.

In addition, by comparing the influence of solvents in the system using carbon and glass woven reinforcement at the same fiber to matrix weight fraction. The properties of the carbon reinforced composite are presented in Table 4.21. The results show that the tensile and flexural properties of the samples prepared from prepreg without solvent are higher than the formula with solvent at both concentrations. The HDT of the carbon reinforced composite are higher than 200°C that out of the range of testing machine capability. Therefore the real test values of the HDT can not be reported. The test figures also review that the properties are slightly dropped with increasing the solvent content.

From the above discussion based on the experimental results, it is difficult to draw the solid conclusion whether solvent type and its content used has real effect on the final properties of the laminated using glass and carbon fibers as reinforcement. Thus, the statistical analysis, two tails *t*-test, as previously described and summarized in Appendix A is submitted. The level of significant (α) used in the test is 0.05.

The statistical hypothesizes for testing the effect of solvent type on the properties of the composite as followed;

If $H_0 : \overline{X} - \overline{Y} = 0$, it means that solvent types, EA and MEK at given concentration, does not have an effect on the properties of cured composite

But if , $H_1 : \overline{X} - \overline{Y} \neq 0$, it means that solvent types, EA and MEK at given concentration, does have an effect on the properties of cured composite

The similar hypothesis is erected for testing the effect of the content at the given solvent. The Null hypothesis, H_0, will be accepted if the α value calculated from the SPSS is greater than the given level of significant. Vice versa, the H_0 will be rejected. The statistical test result and the conclusions derived from the *t*-test are summarized in Table 4.22.

Table 4.21 Mechanical and thermal properties of carbon reinforced composite obtained from the prepreg formulation with and without solvents.

Solvent	**Properties**					
	σ_u	E	σ_{fM}	E_f	a_{iN}	HDT
	(MPa)	(GPa)	(MPa)	(GPa)	(kJ/m^2)	(°C)
No Solvent	408±24	12.3±0.4	730±49	51.1±3.1	50±3	> 200
1% EA	404±29	13.3±0.9	702±35	45.1±2.6	56±9	> 200
5% EA	387±14	13.4±0.7	702±43	50.5±2.5	57±3	> 200
1% MEK	392±17	12.3±0.6	708±45	48.6±1.5	55±3	> 200
5% MEK	372±13	13.1±0.2	623±36	50.5±1.2	52±2	> 200

From the *t*-test results as summarized, it is found that, for the glass reinforcement, by using the mechanical and thermal properties as testing parameter most of H_1 are accepted either by type or amount of solvent added. However, for the carbon woven, the results are ambiguous. Both H_0 and H_1 are accepted independence of type and amount of the solvents used. Rely on the statistical testing, it is confirmed that the mechanical and thermal properties of the laminated composite prepared from the R2 prepreg formulation and using glass woven as reinforcement are depended on type and amount of solvent used as diluent. In contradictory, the firm conclusion can not be made for the carbon woven reinforcement. General observation, the results seem to indicate that there are not significant dependency of solvent and its amount used on the final properties of the composite.

Table 4.22 Summary of statistical T-test

Property	Solvent	Glass Fiber		Carbon Fiber	
		Sig.	**Conclusion**	**Sig.**	**Conclusion**
Tensile Strength	Type	0.00	H_1 Accepted	0.00	H_1 Accepted
	Amount	0.413	H_0 Accepted	0.066	H_0 Accepted
Tensile Modulus	Type	0.000	H_1 Accepted	0.044	H_1 Accepted
	Amount	0.800	H_0 Accepted	0.108	H_0 Accepted
Flexural Strength	Type	0.000	H_1 Accepted	0.091	H_0 Accepted
	Amount	0.003	H_1 Accepted	0.049	H_1 Accepted
Flexural Modulus	Type	0.002	H_1 Accepted	0.096	H_0 Accepted
	Amount	0.000	H_1 Accepted	0.002	H_1 Accepted
Impact Strength	Type	0.076	H_0 Accepted	0.273	H_0 Accepted
	Amount	0.000	H_1 Accepted	0.536	H_0 Accepted
HDT	Type	0.000	H_1 Accepted	-	-
	Amount	0.000	H_1 Accepted	-	-

CHAPTER V

CONCLUSIONS

The aim of this research work was to investigate the prepreg formulation for windsurf and surfboard manufacturing. Based on the thermal and mechanical properties justification and also confirmation by the statistical testing using the ANOVA, the results showed that increasing in the YD115 composition the properties were slightly increased. Vice versa, the thermal property by mean of HDT was decreased. The optimal ratio between YD115 and YD127, which gave rise to the superior mechanical properties, was 80:20 by weight, R5. However, this ratio caused low HDT and viscosity for the manufacturing process. It was explained by the influence of active diluent presented in the liquid epoxy. On the other hand from the rheological points of view, the ratio at 20:80, R2, provided the acceptable HDT and viscosity values but moderate in mechanical properties when compared with formulation prepared by the ratio of 80:20. According to the well verified rule of mixture and also the manufacturing constrain, the R2 formula, the ratio of 20:80, was accepted as the base epoxy resin for the prepreg formulation.

The influence of the particle size of Dicyandiamide, the results indicated that the size did not have the significant influent on the mechanical and thermal properties of the composite product prepared from the prepreg based on R2 formulation. On the effect of amines study, it was concluded that Ancamine 2165, mixture of m-xylene diamine in benzyl alcohol, was not only used to enhance the tensile property but also improved the toughness of cured prepreg composite. But inferior in service temperature was experienced. Catalysts used to trigger the reaction at high temperature for the prepreg curing agent was also investigated. It was found that urea substituted catalyst, Dyhard UR200, provided the distinguish performance properties against those given catalytic substances for the prepreg manufacturing. At 10 part of weight ratio of the UR200 offered the best values of the both mechanical properties and HDT.

The Arrhenius approach was applied for determination of B-stage time at 20^{o}C. The calculation reviewed that t_B of the prepreg derived from the mixture of Ancamine 1618 and Ancamine 2165 at 20:30 weight ratio was successfully accepted for windsurf and surfboard manufacturing. The approximated t_B of 12 hours at 20^{o}C was obtained whereas the mechanical and thermal properties were retained. However, carefully consider on both the experimental results found and actual manufacturing in practices, the optimal prepreg formulation for windsurf and surfboard production was the combination of the R2 epoxy resin mixture, 20:80 of YD115 and YD127, and the hardener derived from 25:25:40:10 of Ancamine 1618, Ancamine 2165, Dyhard 100 and Dyhard UR200, respectively.

Studying of pre-cure and post-cure of the optimal prepreg formulation on the properties of glass woven reinforced composite, it was found that the both cure conditions had the significant effect on both the thermal and mechanical properties. The best candidate condition by mean of the overall properties was pre-cure at 150°C for 10 mins and post cure at 150°C for 8 hrs.

Observation of the diluent solvents added in the prepreg formulation, the results was found the ambiguous agreement for the given chemicals and reinforcements. The strong recommendation on the solvent used for the assigned reinforcement systems could not be reached either by experiment or statistical evaluation.

Recommendation for the Further Works

The main interesting research focus for the further studies could be:

(i) To study the effect the other types of the epoxy matrix, such as multi-functional epoxide groups, on the properties of the composites made from prepreg process.

(ii) To study the fillers such as nano-particle to improve the performance properties of the composites.

and (iii) To investigate the high performance epoxy prepreg for the other advanced applications

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APPENDIX A

STATISTICAL TESTING

A1. One Way ANOVA testing

The analysis of variance (ANOVA) sometimes called an F test, is closely related to the *t* test. The major difference is that, where the *t* test measures the difference between the means of two groups, an ANOVA tests the difference between the means of two or more groups.

One-way ANOVA, or single factor ANOVA, tests differences between groups that are only classified on one independent variable.

The basic principle of the analysis is to divide the variance of total data (SS_T) into two component parts namely variance between groups or treated variance (SS_{Tr}) and variance within groups or variance of error (SS_E), as shown in equation A1;

$$SS_T = SS_{Tr} + SS_E \tag{A1}$$

where SS_T = The variance of total data

SS_{Tr} = The summation of variance between groups or treated variance

SS_E = The summation of variance within groups or variance of error

The SS_{Tr} and SS_E are calculated by using the following equations;

$$SS_{Tr} = J\left[\sum_{i=1}^{I}\left(\bar{X}_i - \bar{X}_T\right)^2\right] \tag{A2}$$

$$SS_E = \sum_{i=1}^{I} S_i^2 \tag{A3}$$

$$\overline{X}_i = \frac{\sum_{j=1}^{J} x_{ij}}{J} \tag{A4}$$

$$\overline{X}_T = \frac{\sum_{i=1}^{I} \overline{X}_i}{I} \tag{A5}$$

$$S_i^2 = \frac{\sum_{i=1}^{J} \left(x_{ij} - \overline{X}_i\right)^2}{J-1} \tag{A6}$$

where J = A number of data obtained in each groups of experiment

I = A number of experimental groups designed in this test

x_{ij} = The data obtained from the experimental ith group and the jth observation count

$\overline{X}_i$ = Mean value of the data obtained from the experimental ith group

$\overline{X}_T$ = Mean value of the overall data

The test hypothesis are;

H_0 : $\overline{X}_1 = \overline{X}_2 = \overline{X}_3 = \overline{X}_i$

and H_1 : $\overline{X}_i \neq \overline{X}_j$ for any i and j

The statistical ***f***-test could also be used for verifying the level of confidence regarding to the H_0 acceptation. The value of the ***f*** can be calculated by using equation A7. The calculated one would be compared with the critical value ($\boldsymbol{f}_{1-\alpha,\ v1,\ v2}$ or $\boldsymbol{f}_{\text{critical}}$) If the calculated $\boldsymbol{f} < \boldsymbol{f}_{\text{critical}}$, then the H_0 is accepted. Vice versa, the would be rejected.

$$f = \frac{MS_{Tr}}{MS_E} \tag{A7}$$

$$\text{Mean square}\,(MS_{Tr}) = \frac{SS_{Tr}}{\nu_1} \tag{A8}$$

$$\text{Mean square}\,(MS_E) = \frac{SS_E}{\nu_1} \tag{A9}$$

where ν_1 = degree of freedom of $SS_{Tr} = I - 1$

and ν_2 = degree of freedom of $SS_E = IJ - I$

The calculated ***f*** value of the data obtained by using the equation A2 to A9 are presented in Table A1

Table A1. One way ANOVA

Source of Variation	Sum of Square	df	Mean Square	Calculated f	Critical f
Between Groups	SS_{Tr}	I-1	MS_{Tr}	$f = \frac{MS_{Tr}}{MS_E}$	
Within Groups	SS_E	IJ-I	MS_E		
Total	SS_T	IJ-1			

A2. Two tails *t* test

The *t* test statistical method, the difference in the average mean value, ($\bar{X} - \bar{Y}$), for the experimental data, will be tested.

The statistical hypothesizes, null (H_0) and alternative (H_1) will be identified as shown below;

If $H_0 : \overline{X} - \overline{Y} = 0$, it means that $\boldsymbol{x}$ and $\boldsymbol{y}$ is analogous,

and if $H_1 : \overline{X} - \overline{Y} \neq 0$, it means that $\boldsymbol{x}$ and $\boldsymbol{y}$ is, somehow, difference.

By using the 2-tailed, the value can be calculated. It is known that if $\boldsymbol{t}$ value falls into the range of $-\boldsymbol{t}_{1-\alpha/2} < \boldsymbol{t} < \boldsymbol{t}_{1-\alpha/2}$ the $\boldsymbol{H_0}$ is accepted. However, the H_0 would be rejected when $-\boldsymbol{t}_{1-\alpha/2} > \boldsymbol{t} > \boldsymbol{t}_{1-\alpha/2}$. The calculated $\boldsymbol{t}$ can be determined by using equation A10 as show following;

$$t = \frac{\left(\overline{X} - \overline{Y}\right)}{S_p \sqrt{\frac{1}{n_x} + \frac{1}{n_y}}} \qquad \text{(A10)}$$

$$S_p = \sqrt{\frac{(n_x - 1)S_x^2 + (n_y - 1)S_y^2}{\nu}} \qquad \text{(A11)}$$

$$S_i = \frac{\sum \left(x_i - \overline{X}\right)^2}{n_i - 1} \qquad \text{(A12)}$$

$$\nu = n_x - n_y - 2 \qquad \text{(A13)}$$

where S_i = the variant of **i**-data

and ν = the degree of freedom

APPENDIX B

STATISTICAL ANALYSIS RESULTS

Statistical Analysis by Using SPSS Program

Table B1. One way ANOVA table of the ultimate tensile stress of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

Source of Variation	**Sum of Square**	**df**	**Mean Square**	**Calculated *f***	**Critical *f***	**Sig.**
Between Groups	13318.60	5	2663.72	11.78	2.62	0.00
Within Groups	5426.49	24	226.10			
Total	18745.09	29				

Table B2. One way ANOVA table of the Young's modulus of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

Source of Variation	**Sum of Square**	**df**	**Mean Square**	**Calculated *f***	**Critical *f***	**Sig.**
Between Groups	1150826	5	230165.2	6.916	2.62	0.00
Within Groups	798677	24	33278.2			
Total	1949503	29				

Table B3. One way ANOVA table of the flexural strength of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

Source of Variation	**Sum of Square**	**df**	**Mean Square**	**Calculated *f***	**Critical *f***	**Sig.**
Between Groups	5810.718	5	1162.144	5.854	2.62	0.001
Within Groups	4764.597	24	198.525			
Total	10575.315	29				

Table B4. One way ANOVA table of the flexural modulus of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

Source of Variation	**Sum of Square**	**df**	**Mean Square**	**Calculated *f***	**Critical *f***	**Sig.**
Between Groups	10432120	5	2086424	4.342	2.62	0.006
Within Groups	11533202	24	480550			
Total	21965322	29				

Table B5. One way ANOVA table of the impact strength of fiber glass composite prepared by prepreg formulations using difference epoxy resin, YD115 and YD127, ratio.

Source of Variation	**Sum of Square**	**df**	**Mean Square**	**Calculated *f***	**Critical *f***	**Sig.**
Between Groups	2069.249	5	413.850	5.202	2.62	0.002
Within Groups	1909.410	24	79.559			
Total	3978.660	29				

APPENDIX C

RESEARCH PUBLICATIONS

Research Publications

Parts of this work were published in the following conferences,

Nasai, W., and Meekum, U. (2002). Thermal and Mechanical Properties improvement of Epoxy Formulation Mold Manufacturing for Surfboard and Windsurf Production. In **The 3rd national symposium on graduate research.** Nakhon Ratchasima, Thailand.

Nasai, W., and Meekum, U. (2004). Effect of Fibrous Reinforcement and Solvents on the Mechanical Properties in Epoxy Prepreg Composite Materials. In **The 4th national symposium on graduate research.** Chiang Mai, Thailand.

Nasai, W., and Meekum, U. (2005). Experimental Design for Preprg Formulation : Part I Hardener. In **The 31st Congress on science and technology of Thailand.** Nakhon Ratchasima, Thailand.

BIOGRAPHY

Wannaporn Nasai was born in Nakhonphanom, Thailand. She obtained her undergraduate degree in Polymer Engineering at the state university at Nakhon Ratchasima, Suranaree University of Technology, before continued her graduate degree in Polymer Engineering at the same university. Her expertise includes the field of polymer composites. During graduate study she presented three paper entitled of "Thermal and Mechanical Properties improvement of Epoxy Formulation Mold Manufacturing for Surfboard and Windsurf Production" in the 3rd National Symposium on Graduate Research on July 18-19, 2002 in Nakhon Ratchasima, Thailand, "Effect of Fibrous Reinforcement and Solvents on the Mechanical Properties in Epoxy Prepreg Composite Materials" in the 4th Grad Research Conference on August 10-11, 2004 in Chiang Mai, Thailand, and "Experimental Design for Prepreg Formulation: Part I Hardener" in 31st Congress on Science and Technology of Thailand on October 18-21, 2005 in Nakhon Ratchasima Thailand.