

วัสดุเชิงประกอบแบบแซนวิชพอลิยูรีเทนน้ำมันละหุ่งและเส้นใยธรรมชาติ



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NATURAL FIBER/CASTOR OIL POLYURETHANE SANDWICH COMPOSITES



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การเตรียมวัสดุเชิงประกอบแบบแกนวิซพอลิยูรีเทนน้ำมันละหุ่งและเส้นใยธรรมชาติ ได้มุ่งเน้นเพื่อทดแทนผ้าใยสังเคราะห์ ผ้าใยธรรมชาติเป็นตัวช่วยเสริมแรงในวัสดุเชิงประกอบแบบแกนวิซซึ่งใช้พอลิยูรีเทนจากน้ำมันละหุ่งเป็นสารยึดติด ในงานวิจัยนี้วัสดุเชิงประกอบแบบแกนวิซพอลิยูรีเทนน้ำมันละหุ่งและเส้นใยธรรมชาติ ถูกเตรียมโดยเทคนิคแบบมือทา โดยมีผ้ากันขงเซลลูโลสและผ้าใยสังเคราะห์ที่จัดวางชั้นผ้าแตกต่างกัน โดยมีการวิเคราะห์สมบัติเชิงกลของวัสดุเชิงประกอบแบบชีวภาพ ภายใต้ผลกระทบของน้ำทะเล ด้วยแรงดัดโค้งและการวิเคราะห์สมบัติทางกลแบบไดนามิก จากการนำวัสดุเชิงประกอบแบบแกนวิซและแผ่นลามิเนตแซในน้ำทะเล พบว่าวัสดุเชิงประกอบแบบชีวภาพที่เสริมแรงด้วยผ้าเซลลูโลสร้อยละ 100 โดยน้ำหนัก มีการดูดซึมน้ำทะเลมากที่สุด ในขณะที่การเสริมแรงด้วยผ้าใยธรรมชาติและผ้าใยสังเคราะห์ที่ร้อยละ 50/50 โดยน้ำหนักมีการดูดซึมน้ำต่ำสุด เมื่อเปรียบเทียบกับวัสดุเชิงประกอบที่ไม่ถูกบำบัด วัสดุเชิงประกอบที่เสริมแรงด้วยผ้าใยแก้วซึ่งผ่านการบำบัดด้วยไฮโดรอกไซด์ร้อยละ 5 โดยน้ำหนักแสดงค่าร้อยละการดูดซึมน้ำทะเลลดลงในขณะที่สมบัติเชิงกลเพิ่มขึ้น จากการวิเคราะห์สมบัติเชิงกลแบบไดนามิก ค่ามอดุลัสสะสมและมอดุลัสสูญเสียของวัสดุเชิงประกอบแบบแผ่นลามิเนตที่ใช้ผ้าใยแก้วซึ่งผ่านการบำบัดมีค่าเพิ่มขึ้น คุณทงมิสภาพแก้วจะเพิ่มขึ้นจาก 49.7 องศาเซลเซียส เป็น 57.2 องศาเซลเซียส

ศูนย์วิทยทรัพยากร  
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## 5073429023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE  
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The preparation of natural fabric/castor oil polyurethane sandwich composites and laminated sheet was investigated aiming for synthetic fabric replacement. The natural fabric gave the reinforcement of sandwich composites which the castor oil polyurethane was required as an adhesive. In this work, the natural fiber/castor oil polyurethane sandwich composites were prepared by hand-lay up technique of various combination of hemp and cellulose layers. Mechanical properties, flexural strength of biocomposites under sea-water effect and the dynamic mechanical analysis were investigated. From the immersion of sandwich composites and laminate sheets in sea-water, it was found that the biocomposites reinforced with 100 wt% cellulose fabric had maximum absorption while the natural fabric and the synthetic fabric at 50/50 wt% reinforced composite had minimum absorption. Comparison with the non-treatment biocomposites, the treated hemp by 5 %wt NaOH reinforced composite showed the decreasing percentage absorption while the mechanical properties increased. From the dynamic mechanical analysis, the storage modulus and loss modulus of the treated hemp fabric composite laminate sheet increased. Glass transition temperature was also increased from 49.7 °C to 57.2 °C.

Field of Study :Petrochemistry and Polymer Science

Student's Signature

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ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

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# CHAPTER I

## INTRODUCTION

### 1.1 The Purpose of the Investigation

A composite is a material that combines more than two different properties of materials to make a new structural material that is used for general products and other structural engineering purposes. Composites materials have better properties than traditional materials like metal, such as its stiffness and strength but with low density. This means the light weight material with high stiffness and strength. The cost will be reduced if the inexpensive materials are used. These materials have their advantages on the durability of chemical and environmental corrosion. Owing to their advantages, the composites was used in making several products with increasing efficiency as water sport products such as water-ski, ski board, windsurf board, surf board, kite board prepared by sandwich construction. Disposal problem can be occurred when the based raw-materials from thermoset product is broken down or immersed for a long time in sea water. Some chemicals may be decomposed and affect the sea animals. Global environmental issues have led to a renewed interest in bio-based materials with the focus on renewable raw materials [1].

Polyurethane resins are attractive due to their structural versatility (as elastomer, thermoplastic, thermosetting, rigid and flexible foams), for the fact that they can be derived from either petroleum or vegetable oils. They still present the particularity to be more compatible to vegetable fibers compared to other resins, due to possible reaction of hydroxyl groups of the fibers and the isocyanate groups of the polyurethane [2]. The traditional polyurethane can cause environmental problem, therefore this led to renewable resource for replacement of polyol part by the plant seed oil.

## 1.2 Objectives

1. To prepare natural fiber reinforced castor oil based polyurethane sandwich composites and laminate sheet by hand-lay up technique of various combination of hemp, cellulose and fiber glass reinforcement hybrid layers.
2. To investigate the mechanical properties and morphology of biocomposites.
3. To investigate the effect of sea water on absorption and desorption properties of composites.

## 1.2 Scope of the Investigation

Natural fiber/castor oil polyurethane sandwich composites and composites laminate sheet were prepared by hand-lay up technique of various combination of hemp, cellulose and fiber glass layers. Hemp fabric were improved for composite laminate sheet by the chemical treatment, mercerization. The effect of chemical treatment and fiber content on mechanical properties and morphology of composites under sea-water effect were investigated.

The experimental procedures were carried out as follows:

1. Literature survey and study the research work.
2. Prepare foam core from polyurethane by compression molding
3. Hemp fabric were improved by the chemical treatment as mercerization (5 wt% NaOH) for laminate sheet.
4. Prepare composites sandwich panel and composite laminate sheet by hand-layup technique.
5. Study the sea water effect on composites by sea water immersion for 30 days at room temperature.
6. Investigate the mechanical properties of composite sandwich panel by three points bending flexural test.
7. Study mechanical properties of laminate sheet by dynamic mechanical analysis.
8. Study morphology of treated hemp fabric and laminate sheet after sea water immersion by Scanning Electron Microscope (SEM).
9. Summarize the result.

## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Natural Fiber as Reinforcement in Composite [3]

Natural fibers are typically grouped into four different types: leaf, bast, fruit and seed, depending on their source. The leaf and bast fibers are generally used in composite processing. Examples of leaf fiber include sisal, henequen and pineapple leaf fiber (PALF). Bast fiber examples are flax, hemp, ramie, cellulose and jute. One of the major difficulties of natural fibers is that their properties are intrinsically dependent on where they are grown (locality), what part of the plant they are harvested from (leaf or stem), the maturity of the plant (age) and how the fibers are harvested and preconditioned in a form of mats or chopped fibers, woven or unwoven. These factors result in significant variation in properties compared to their synthetic fiber counterparts (glass, aramid and carbon). Natural fiber is very important in biocomposite product because it is used as reinforcement of the resin in biocomposite material that can increase material strength and stiffness. Natural fibers use lower energy for production when compared with other fiber as presented in Table 2.1

**Table 2.1** Some data on energy utilization for fiber production [4].

Fiber Type	Energy consumption (MJ/kg)
Lignocellulosic fibers	4-15
Natural fiber mat	9.7
Glass fiber	30-50
Glass fiber mat	55
Carbon fiber	130
Hemp*	10

\* Hemp can store about 0.75 kg of CO<sub>2</sub> per kg of fibers during growth

\* Hemp release 10 MJ/kg upon incineration (with energy recovery)

The main components of natural fiber are cellulose ( $\alpha$ -cellulose), hemicelluloses, lignin, pectins, and waxes. Cellulose is a natural polymer consisting of D-anhydroglucose ( $C_6H_{11}O_5$ ) repeating units joined by 1, 4- $\beta$ -D-glycosidic linkages at C1 and C4 position. The degree of polymerization (DP) is around 10,000. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. The most interesting aspect about natural fibers is their positive environmental impact. Biofibers are renewable resource with production requiring little energy. They are carbon dioxide neutral i.e. they do not return excess carbon dioxide into the atmosphere when they are composted or combusted. The processing atmosphere is friendly with better working conditions and therefore there will be reduced dermal and respiratory irritation. Biofibers possess high electrical resistance. Thermal recycling is also possible. The hollow cellular structure provides good acoustic insulating properties. The world wide availability is an additional factor [5].

## 2.2 Glass Fiber [6]

Glass fibers are the most common of all the reinforcing fiber for polymer matrix composites. The principle advantages of glass fibers are the low cost and high strength. However, glass fibers have poor abrasion resistance, which reduces their usable strength. They also exhibit poor adhesion to some polymer matrix resins, particularly in the presence of moisture. To improve adhesion, the glass fiber surface often is treated with chemicals called coupling agents (mostly silane). The comparison between natural and glass fibers is presented in Table 2.2.



**Table 2.2** Comparison between natural fiber and glass fibers [7].

<b>Properties</b>	<b>Natural fibers</b>	<b>Glass fibers</b>
Density	Low	Twice of natural fibers
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO <sub>2</sub> neutral	Yes	No
Abrasion to machines	No	Yes
Health and risk when inhaled	No	Yes
Disposal	Biodegradable	Not Biodegradable

### 2.2.1 Production of Glass Fibers [8]

The American Standard Society for testing and materials (ASTM), in standard C167-71, defines glass as “an inorganic product of fusion, which has cooled to a rigid condition without crystallizing.” Because glass is amorphous, it is isotropic, and like other amorphous polymer has a glass transition point rather than a melting point or first-order transition characteristic of crystalline products. Glass fiber is made from molten glass marbles forced at 1266 °C through orifices in the base of bushing to produce continuous or staple (discontinuous) fibers. The glass is not a definite compound, but is primarily silica produced by heating sand (SiO<sub>2</sub>), limestone (CaCO<sub>3</sub>), and boric acid (H<sub>3</sub>BO<sub>3</sub>) in a high-temperature refractory furnace. As presented in Figure 2.1, diagram of glass fiber manufacturing process, the glass marbles are used to produce various type of glass product such as glass roving, continuous roving, chopped strand, chopped strand mat and knitting fabric.

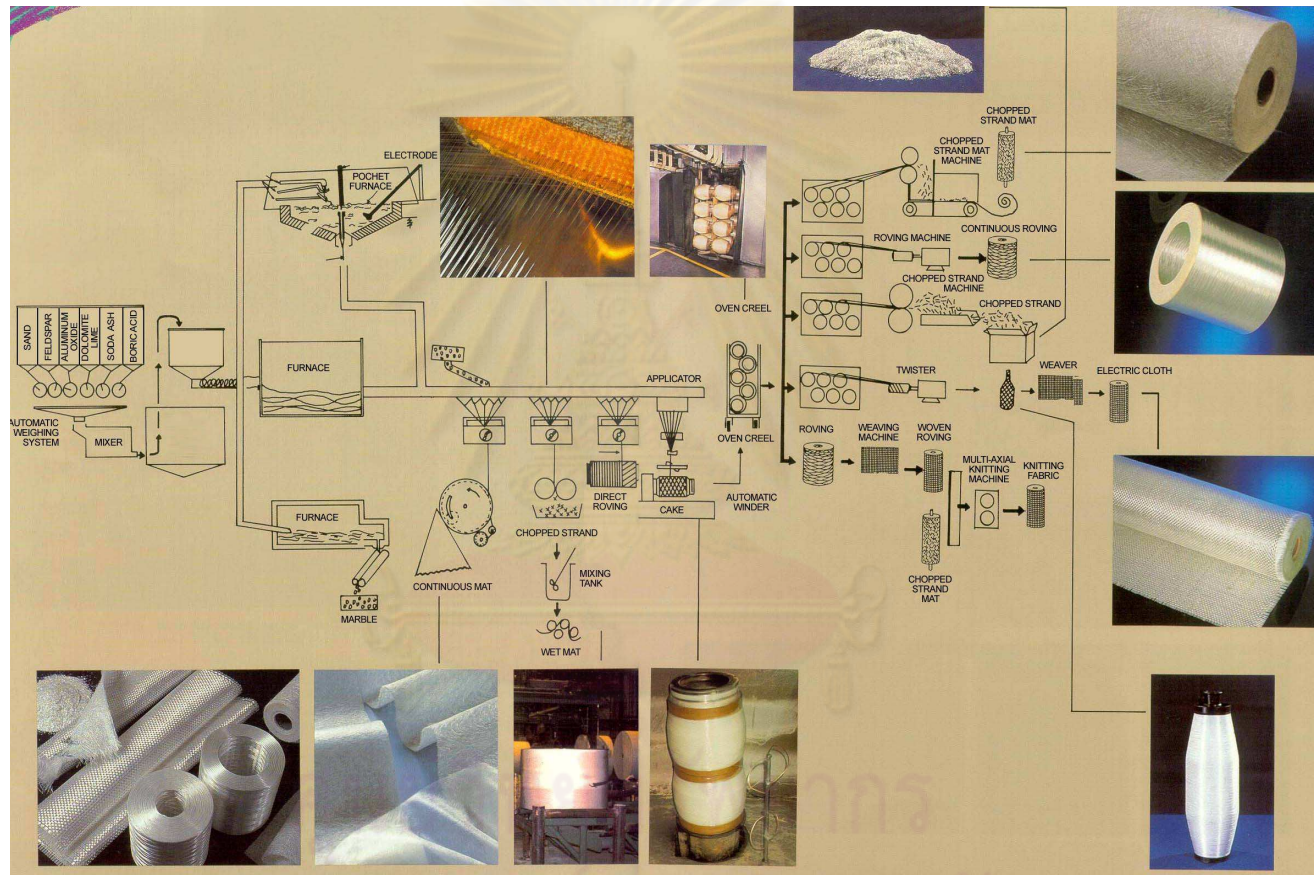
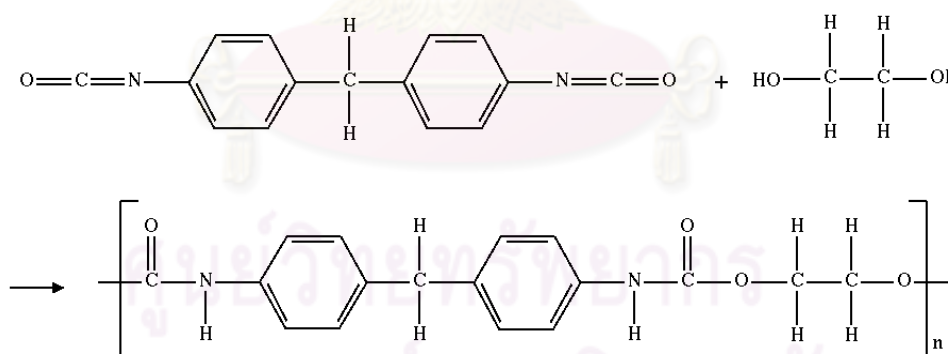


Figure 2.1 Diagrams of glass fiber manufacturing process [9].

### 2.3 Polyurethane [10]

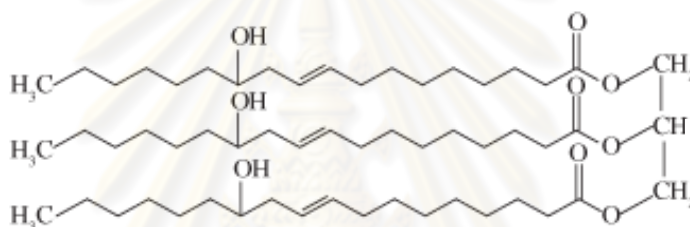
Polyurethane (IUPAC abbreviation PUR, but commonly abbreviated PU) is any polymer consisting of a chain of organic units joined by urethane (carbamate) links. Polyurethane polymers are formed through step-growth polymerization by reacting a monomer containing at least two isocyanate functional groups with another monomer containing at least two hydroxyl (alcohol) groups in the presence of a catalyst. Polyurethanes are widely used in high resiliency flexible foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and sealants, Spandex fibers, seals, gaskets, carpet underlay, and hard plastic parts (such as for electronic instruments). Polyurethane products are often called "urethanes". They should not be confused with the specific substance urethane, also known as ethyl carbamate. Polyurethanes are neither produced from ethyl carbamate, nor do they contain it. The example of synthesis of a polyurethane, the urethane group  $\text{-NH-(C=O)-O-}$  linking the units of the product is shown in Figure 2.2.



**Figure 2.2** Example of synthesis of polyurethane [10].

### 2.3.1 Biobased Polyurethane from Castor Seed Oil [11]

The polyurethane was synthesized from polyol and diisocyanate. Both raw materials come from petroleum and scientists have investigated the replacement with materials from renewable energy such as polyol part with several vegetable seed oil. Vegetable seed oil contains triglyceride with different fatty acid chain in molecule. Diisocyanate part is diphenylmethane diisocyanate or MDI used for this research. Polyol part from castor seed oil has ricinoleic acid triglyceride structure (89.55 %) as shown in Figure 2.3. Ricinoleic acid triglycerides have three hydroxyl functional groups which are highly reactive at C12 position, double bond at C9 position and carbonyl group at C1 position.

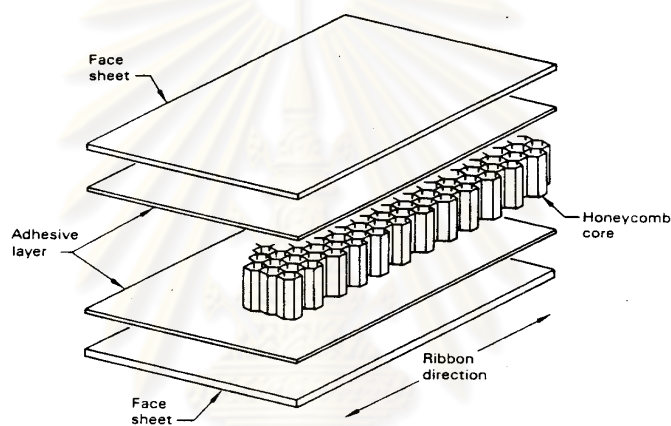


**Figure 2.3** Ricinoleic acid triglyceride [11].

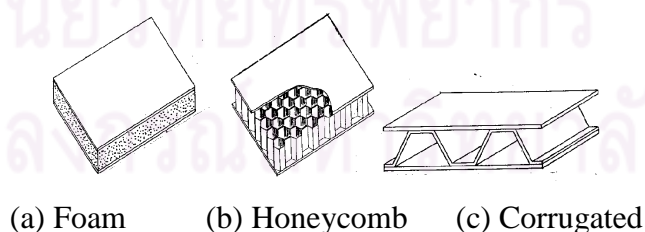
### 2.4 Sandwich Structured Composite [12]

Sandwich structured composite is a special class of composite materials that is fabricated by attaching two thin but stiff skins to a lightweight but thick core. The core material is normally low strength material, but its higher thickness provides the sandwich composite with high bending stiffness with overall low density. Open and closed cell structured foams like polyvinylchloride, polyurethane, polyethylene or polystyrene foams, balsa wood, syntactic foams and honeycombs are commonly used core materials. Laminates of glass or carbon fiber reinforced thermoplastics or mainly thermoset polymers (unsaturated polyesters, epoxies) are widely used as skin materials. Sheet metal is also used as skin materials in some cases. The core is bonded to the skins with an adhesive. Composite sandwich panels are incredibly useful materials to form strong lightweight structures used in everyday life.

Sandwich panels using honeycomb, balsa, or foam are constantly helping to reduce weight and increase strength [13]. Sandwich construction has found extensive application in aircraft, missile and spacecraft structures due to high strength to weight ratio. This type of construction consists of thin, stiff and strong sheets of metallic or fiber composite material separated by a thick layer of low density material as shown in Figure 2.4. The thick layer of low density material commonly known as core material may be light foam type e.g. Nomex core or Rohacell as shown in Figure 2.5a or metallic honeycomb as shown in Figure 2.5 b or corrugated core as shown in Figure 2.5c. The core material is generally adhesively bonded to the face sheets [14]. Figure 2.6 shows the sandwich construction of surfboard.



**Figure 2.4** Honeycomb construction [14].



(a) Foam (b) Honeycomb (c) Corrugated

**Figure 2.5** Types of cores [14].

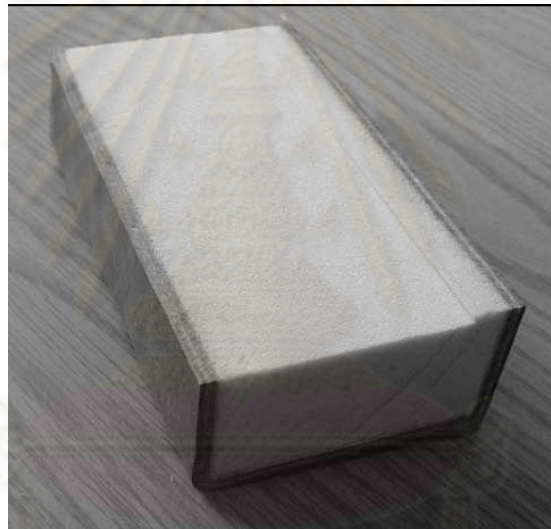


Figure 2.6 Surf board sandwich construction [15]

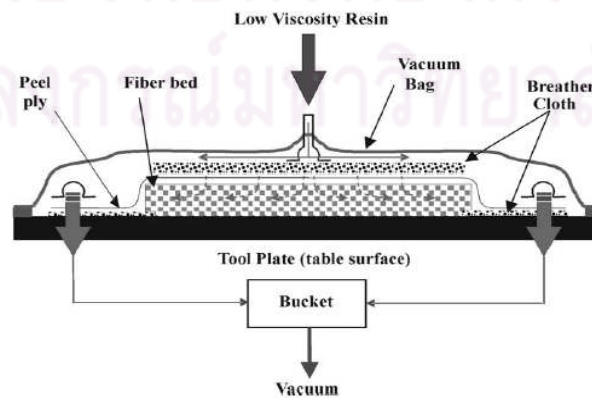
## 2.5 Literature Reviews

Donnell *et al.* [16] studied the natural fiber composites with plant oil-based resin. Figure 2.7 shows the composite sandwich structure. VARTM -vacuum assisted resin transfer molding or resin vacuum infusion process (Figure 2.8) was used to make composite panels out of plant oil-based resin named acrylated epoxidized soybean oil (AESO) and natural fiber mats made of flax, cellulose, pulp and hemp with rigid foam core. Characterization of the resin and various composite materials was made using both mechanical and dynamic mechanical analysis. The permeability of the natural fiber mats was also studied. Dynamic mechanical analysis testing showed that with natural fiber reinforcement, the storage modulus of the soybean oil resin was improved to more than five times with recycled paper. Recycled paper is a cheap source of cellulose fiber and was successfully impregnated with AESO. These natural composites were found to have mechanical strength suitable for applications such as housing and automotive. The void content was found to be within an acceptable range for composites made using vacuum infusion.

The composites formed by room temperature cure with natural fiber reinforcement of about 10–50 wt% increased the flexural modulus to a range between 1.5 and 6 GPa depending on the nature of the fiber mat. The AESO resin reinforced with woven E-glass fiber was tested as a reference and gave a flexural modulus of 17 GPa, while a room temperature curing of the neat resin gave a flexural modulus of about 1.1 GPa. Recycled paper was used as a cheap resource of cellulose fiber and found to work well with AESO resin in terms of flow, impregnation, and surface bonding, giving a modulus of over five times that of the neat resin (high Tan delta). These low-cost natural composites were found to have mechanical strength and properties suitable for applications in housing construction materials, furniture and automotive parts.



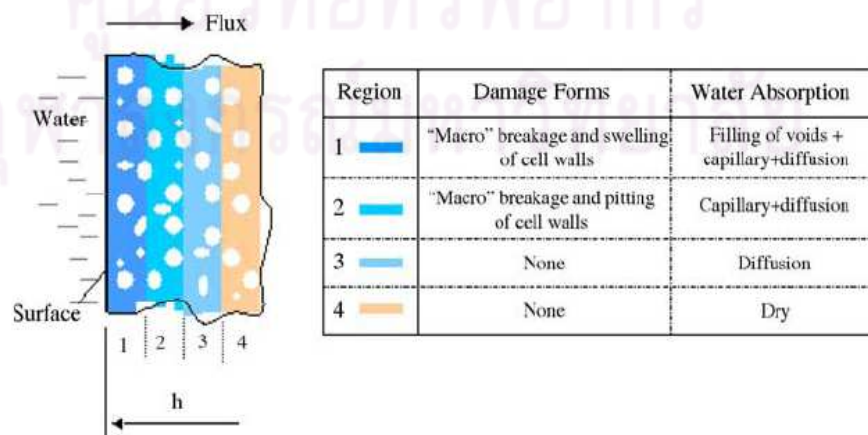
**Figure 2.7** Sample of composites structure [16].



**Figure 2.8** Schematic showing vacuum-assisted resin transfer molding process and resin flow into the fiber bed [16].

Xiaoming *et al.* [17] studied the effects of sea-water on foam cored composite sandwich structures under long-term exposure. Special attention is focused on sea-water induced damage in foam materials, weight gains and expansional strains, as well as on possible degradation in the properties of foam materials due to such extended exposure. In addition, sea-water effects on the fracture behavior of foam materials and on face/core interfacial debonding fracture were investigated experimentally and interpreted by means of computational fracture mechanics.

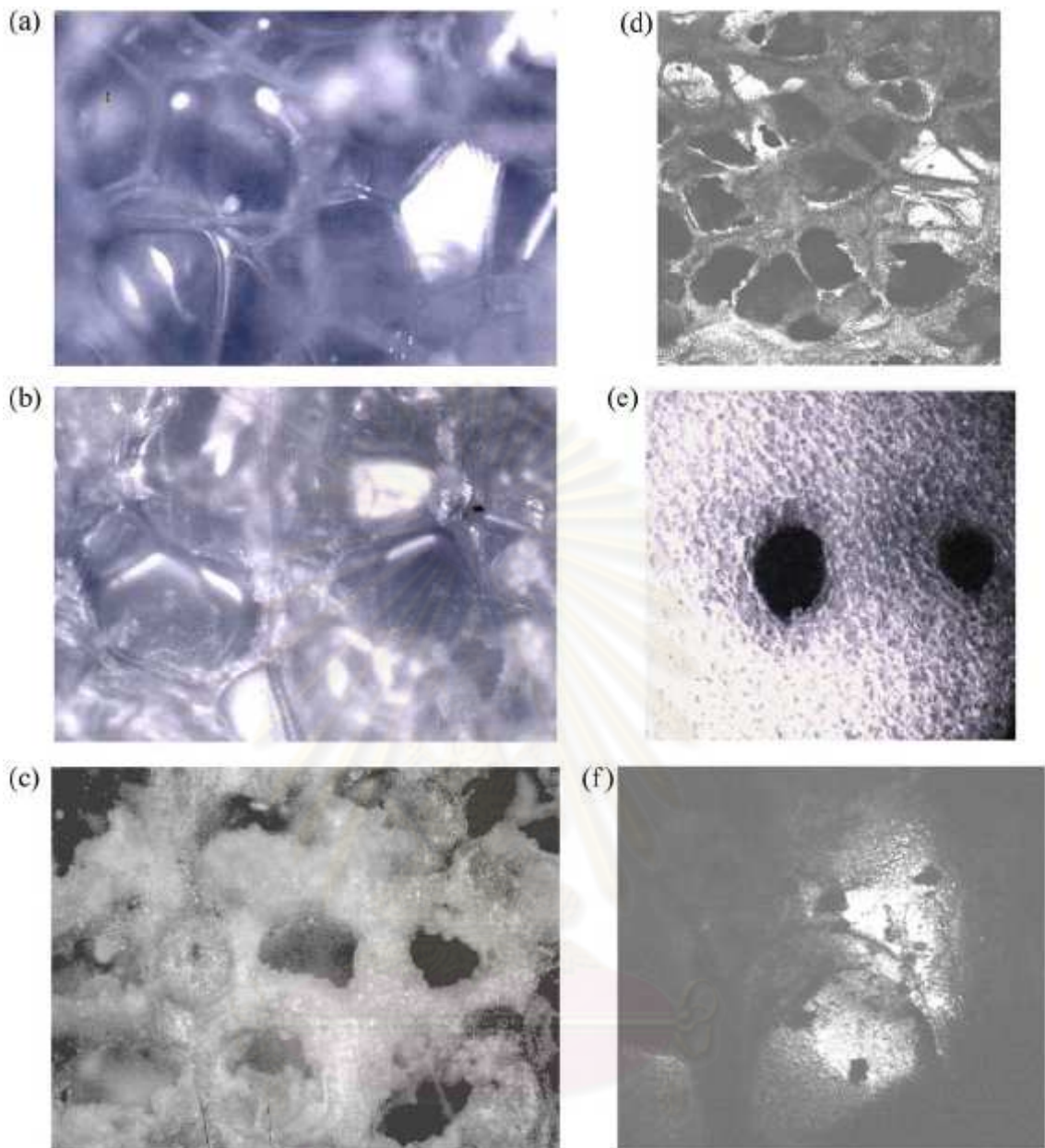
Two closed-cell polymeric foam materials (H100 PVC and H200 PVC), and their polymeric composite facing sandwich specimens, were immersed in simulated sea-water for up to two years. It was noted that the largest amount of sea-water that entered the foams was confined to the exterior regions of those materials by penetrating and filling the outer cells. This process, which was completed within 1–2 months, caused several forms of irreversible damage to the foam on the micro-structural level and induced swelling strains within the above mentioned exterior zones. The effect of sea-water on the toughness of foam materials was studied experimentally. It was found that absorption of sea-water in the crack tip regions increased the toughness value of the foam materials by 31 and 8% for the H100 PVC and H200 PVC, respectively. The debonding fracture toughness at the core/facing interfaces was investigated experimentally under both dry and wet conditions, showing degradations of about 36% for the H100 PVC and 17% for the H200 PVC sandwiches, respectively, attributable to the presence of sea-water. The schematic map of the water absorption and damage in a PVC foam was presented in Figure 2.9.



**Figure 2.9** A schematic map of the water absorption and damage in PVC foam [17].



Kolat *et al.* [18] studied the effect of sea water exposure on the interfacial fracture of some sandwich systems in marine use. The fracture toughness of the sandwich systems which contain the various core materials (wood, plywood, polyurethane, coremat) have been experimentally studied by Mode-I Cracked Sandwich Beam tests. Cores of these systems, which were used widely in the boat building sector, were chosen by considering their advantages such as availability in the local market and low cost. The effect of the environmental degradation on the fracture toughness was investigated by means of pre-conditioning with sea water. Fracture toughnesses of the systems with wood, plywood and polyurethane core materials are low. It has been found that the fracture toughness of the system with coremat was higher compared with its counterparts. The effect of environmental degradation on fracture toughness was investigated by means of the pre-conditioning with seawater. While fracture toughness of sandwich systems with wood and plywood cores were found to decrease more than the others. The others were found to increase under the environmental effect of sea water. Effects of sea-water induced damage in the foam are presented in Figure 2.10.



**Fig 2.10** Undamaged PVC foams and sea-water induced damage in the same foam materials. (a) and (b) Undamaged dry PVC foams. (c) Sea-water causes swelling of foam cell walls. (d) Confocal microscope photograph shows damage (pits and breakage of cell walls) inside the core, 1.78 mm below the surface. (e) Cavities were observed to form on the surfaces of the foam materials after extended immersion in sea-water. (f) A confocal microscope photograph shows pits forming at the bottom of a cavity (2.8 mm below the surface).

Silva *et al.* [19] studied the fracture toughness of natural fibers/castor oil polyurethane composites. The main interest in studying these biomass composites arised from the fact that both fibers and matrix were derived from renewable resources and the formed composite constitute an attempt towards environmental preservation. Sisal and coconut short fibers and woven sisal fabric were used 'in natura' and sodium hydroxide treated. The best fracture toughness performance was displayed by the sisal fabric composite. The alkaline treatment showed to be harmful for fracture toughness of the sisal fiber composites since the improved interfacial adhesion impaired the main energy absorption mechanisms. On the other hand, an enhancement on the fracture toughness of coconut fiber composites was observed, which was credited to the fibrillation process occurring under the severest condition of the alkaline treatment, which created additional fracture mechanisms.

The results show that performance of coconut fiber composites was inferior to the sisal fiber ones and even to the neat polyurethane matrix, whereas the best performance was displayed by the sisal fabric composite. In general, the fracture toughness was not affected by the applied strain-rate. The alkaline treatment was harmful to fracture toughness of the sisal fiber composites because in improving the interfacial adhesion, it reduced the main energy absorption mechanisms namely, debonding and fiber pull-out. For the coconut fiber composites the fracture toughness increased with the alkaline treatment. This behavior was credited mainly to the fibrillation process, which seems to result from the severe conditions imposed during the treatment and was facilitated by the slow loading rate of the test.

Kostic *et al.* [20] studied the quality of chemical modified hemp fibers. Hemp fibers were modified with sodium hydroxide solutions (5% and 18% w/v), at room and boiling temperature, for different periods of time, and both under tension and slack, in order to partially extract noncellulosic substances, and separate the fiber bundles. The quality of hemp fibers was characterized by determining their chemical composition, fineness, mechanical and sorption properties. The modified hemp fibers were finer, with lower content of lignin, increased flexibility, and in some cases tensile properties were improved. An original method for evaluation of tensile properties of hemp fibers was developed. Hemp fibers were modified with sodium hydroxide solutions with the aim to remove noncellulosic substances and improve quality of hemp fibers (fineness, flexibility, etc.). Analyses of obtained results showed

that as a result of the modification the fibers acquired a high level of divisibility, with good levels of the physical and mechanical properties. This method covered the determination of the tensile strength or tenacity of hemp fibers as a flat bundle using extrapolated values to zero distance between grips (zero test length). Values obtained for flat bundle tenacity extrapolated to the zero test length showed a high correlation with values measured on single fibers and required much less time and skill.

This method could be useful in research studies for determining the influence of environment, and processing on fiber strength, as well as in studies of the relationships between these fiber properties, processing conditions, and quality of end-product. Also, this method could be used for testing of commercial shipments. In general, the alkali treatment yielded higher flexibility of modified fibers, except for the fibers modified with 18% NaOH, under tension. Changes in flexibility with certain treatments reflected changes in chemical composition (part removing of lignin and other noncellulosic substances) and structure (fibrils rearranging). The water retention values of alkali modified hemp were lower than value of untreated hemp, as a consequence of removing the easily accessible noncellulosic water-absorbing and holding materials, as well as changing in the fiber structure. The modification temperature had a significant effect on water holding capacity, the water retention value decreased by 65% after modification with 5% NaOH, at boiling temperature, and 30 min treatment time.

Huang *et al.* [21] studied the glass fiber reinforced unsaturated polyester laminated by using VARI (vacuum assisted resin infusion) technique. Laminates were immersed in the artificial seawater for various periods. Moisture absorption would increase the weight of the specimen; soluble elements extraction decreased the weight of the material. The tensile and bending strength of the seawater treated samples showed a decreased trend with prolonged treating time implying the degradation of the composites. The SEM photograph of the broken section after the treatment illustrated serious corrosion of the interface. The weight gain change of the glass fiber reinforced unsaturated polyester composites after immersing in the seawater was the consequence of two effects: water absorption and soluble material extraction.

In the first period of the seawater immersion, water absorption was predominant; in the later part, the soluble material extraction would play a major role. The gradually reduced bending and tensile strength with prolonged seawater immersion time indicated that the material had experienced some forms of physical damage and/or irreversible chemical degradation. The soaked moisture would cause the matrix to swell and break, react with the function groups in the matrix and filament. All these would cause the material to deteriorate. The SEM image of the broken section of the specimen after seawater immersion showed that the fiber/matrix interface had been seriously damaged.

James *et al.* [22] studied the three different formulations of polyurethane pultruded samples immersed in 150°F water over a 30-33 day period. Three-point flexural tests, short-beam tests, and compression tests were conducted over the 30 days of water immersion. These data were compared with a large database of properties for common pultruded composites using other resins exposed to similar environmental conditions. These comparisons show that the polyurethane composites offer better mechanical performance compared with pultruded composites produced from more commonly used resin systems. It is apparent that all three of the polyurethane pultruded composites perform better under conditions of 150°F water immersion exposure than do the selected polyester and vinlyester composites for which direct comparison data was available. However, it is also apparent that not all polyurethane composites are equal in their mechanical property response.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Raw Materials

**Table 3.1** Resin, fiber and chemicals used in this study

Chemicals	Function	Commercial Name	Supplier
Polyol	Laminate resin	Rescon 503 garicin	Proquinator
MDI	Laminate resin	Rescon 503 proquicin	Proquinator
Polyol	Foam core	Respan D40	Proquinator
MDI	Foam core	Respan D40	Proquinator
NaOH	Treatment	NaOH (Sodium Hydroxide)	Suksapan
Hemp Fabric	Reinforcement	Hemp CTL-5	Hemp Trader
Cellulose fabric	Reinforcement	Cellulose fabric 200g/m <sup>2</sup>	Porcher
Glass fabric	Reinforcement	Glass fabric 6Oz/m <sup>3</sup>	Asia Kungnum

#### 3.2 Instruments

- 1) Hydrometer (Salinity) : Suksapan
- 2) Universal Tensile Machine (UTM) : Instron model H5K
- 3) Dynamic mechanical analyzer (DMA) : NETZCH model DMA242
- 4) Scanning Electron Microscopy (SEM) : JEOL model JSM-5410LV
- 5) Hot air oven : Memmert model 400
- 6) Pressing machine : WINNER (30Tons)
- 7) Digital weight balance : TS scale model QTW-30

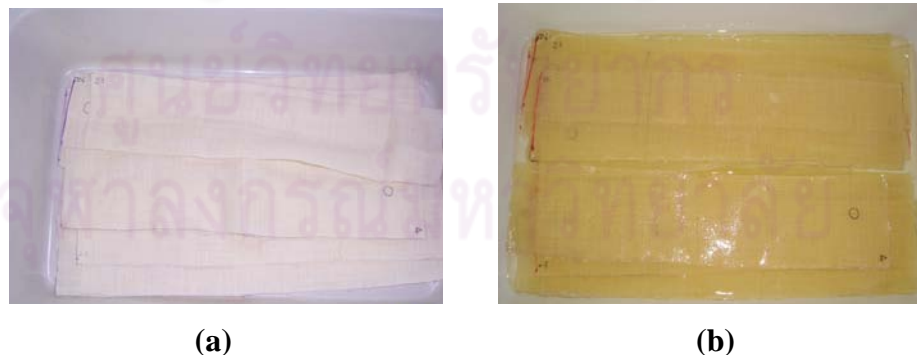
### 3.3 Procedures

#### 3.3.1 Preparation of Composite Panel (Core)

For polyurethane foam preparation Rescon 503 as polyol at 57% by wt was mixed with MDI at 43% by wt (total 229 grams) for each panel and poured into rectangular shape metal mold for specimen dimension 13X2.75x2.125 inch<sup>3</sup>. The specimen was pressed with pressed machine at pressure of 8-10 tons at room temperature until the foam was cured about 40 min. After demolding, the panel was kept at room temperature for 2 weeks until constant weight.

#### 3.3.2 Alkaline Treatment of Hemp Fabric

Hemp fabric was immersed in sodium hydroxide solution (NaOH) as shown in Figure 3.1. The amorphous part as hemicelluloses, lignin, pectin, other impurities and wax could be removed from the surface of fiber [23-25]. Therefore, the interfacial bonding between skin and matrix could be improved. Dried hemp fabric was also treated with 5% NaOH for 30 min at room temperature. To remove hemicelluloses, lignin and wax associated on fibers, alkaline treated fiber was washed with running tap water followed by distilled water until no alkaline was present in the wash water.



**Figure 3.1** Treatment of hemp fabric by mercerization with 5% NaOH  
(a) before treatment (b) during treatment

### **3.3.3 Sandwich Composite Preparation**

Sandwich composite was prepared by hand lay-up for 6 pieces per formula by the same person to prevent any error about human experience. The sandwich composite was reinforced with fiber and bio-resin was foam core. The formulations of sandwich composites are shown in Table 3.2.

### **3.3.4 Composite Laminate Sheet Preparation**

The composite laminate sheet was prepared by hand lay-up technique on the metal plate at 1 ton pressure and room temperature for cure time of 2 hours. The bio-resin was reinforced with 6 layers of fabric (13 x 2.75 inch<sup>2</sup>) and thickness of 2-3 mm. The formulation of composites laminate sheet is shown in Table 3.3.

### **3.3.5 Sea Water Immersion**

For water sport product used in the sea, the sea water could affect the composite strength and weight. In this study, biocomposite was immersed in sea water (from Bangsaen, Chonburi, Thailand) with salinity of 35 ppt. The composites were immersed in sea water tank at room temperature for 30 days and hold at room temperature after immersion for 30 days.

The biocomposite properties were determined to compare the properties before and after immersion at various time. The overall schematic procedure for composite preparation was shown in Figure 3.2



**Table 3.2** Sandwich composite formulation

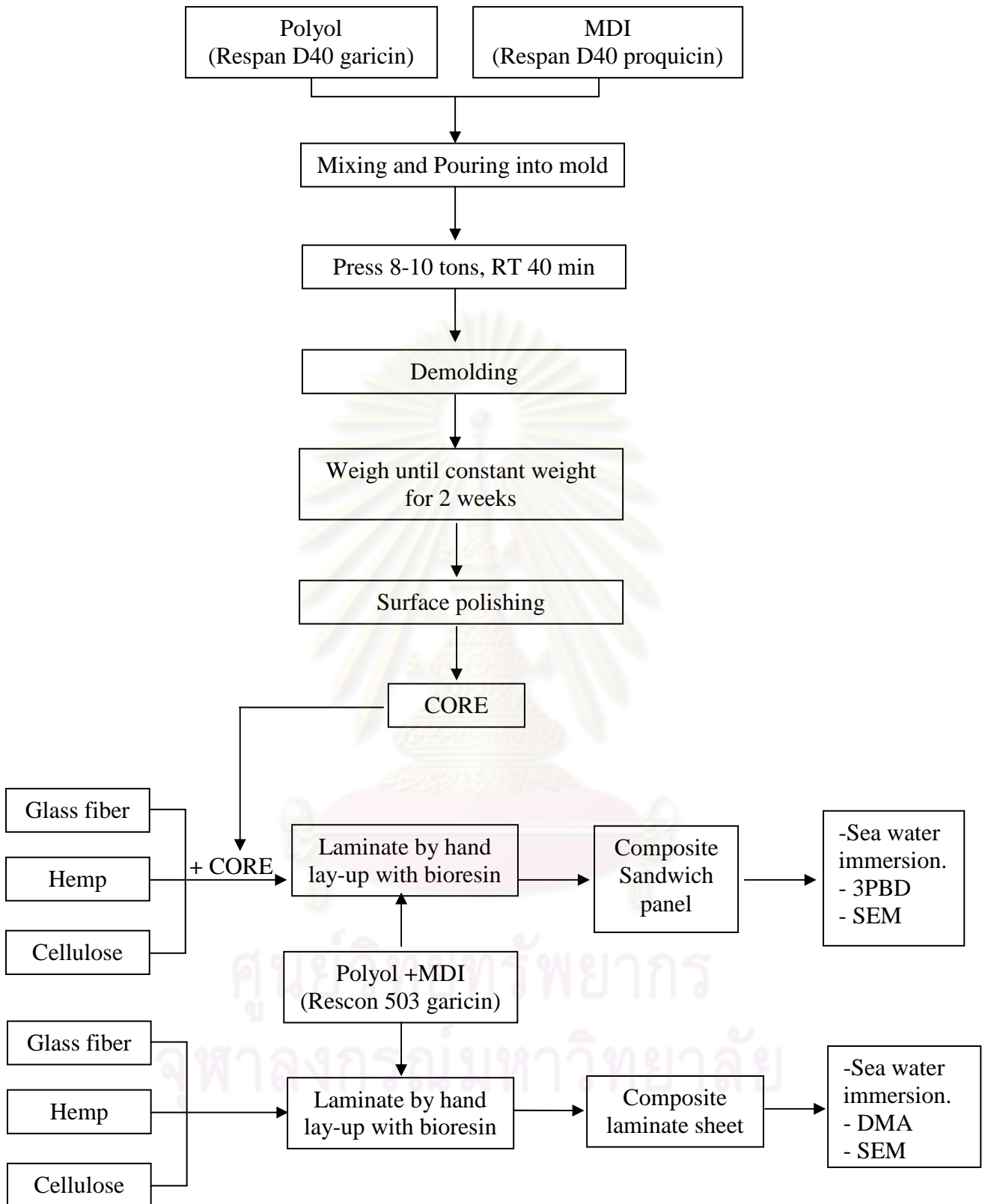
No.	Code	Core	Layer1 X 2 ply	Layer2 X 2 ply	Resin
1	FFBFF	Bio	FG	FG	Bio
2	FHBHF	Bio	Hemp	FG	Bio
3	HFBFH	Bio	FG	Hemp	Bio
4	FCBCF	Bio	Cellulose	FG	Bio
5	CFBFC	Bio	FG	Cellulose	Bio
6	HHBHH	Bio	Hemp	Hemp	Bio
7	CCBCC	Bio	Cellulose	Cellulose	Bio
8	B	Bio	no	no	no

\*FG = fiber glass, PU= polyurethane, B = biofoam panel

**Table 3.3** Laminate sheet formulation

No.	Code	Resin	Layer 1 X 3 ply	Layer 2 X 3 ply
1	FH	Bio	FG	Hemp
2	FC	Bio	FG	Cellulose
3	HH	Bio	Hemp	Hemp
4	CC	Bio	Cellulose	Cellulose
5	FF	Bio	FG	FG
6	TH/TH	Bio	T-Hemp*	T-Hemp

\*T-Hemp=Treat hemp



**Figure 3.2** The overall schematic procedure of composite preparation.

### 3.4 Properties Measurement

#### 3.4.1 % Absorption and % Desorption

For % Absorption determination, the sample was brought out of water and rubbed with towel then the weight was measured. For % desorption determination, the samples were kept at room temperature for 30 days after long period of immersion. % Absorption and % desorption were calculated as follows.

$$\% \text{ Absorption} = \frac{(W_1) - (W_0)}{(W_0)} \times 100 \quad (3.1)$$

$$\% \text{ Desorption} = \frac{(W_2) - (W_0)}{(W_0)} \times 100 \quad (3.2)$$

Where:

$W_0$  = initial weight before immersion

$W_1$  = weight after immersion

$W_2$  = weight after keep in room temperature

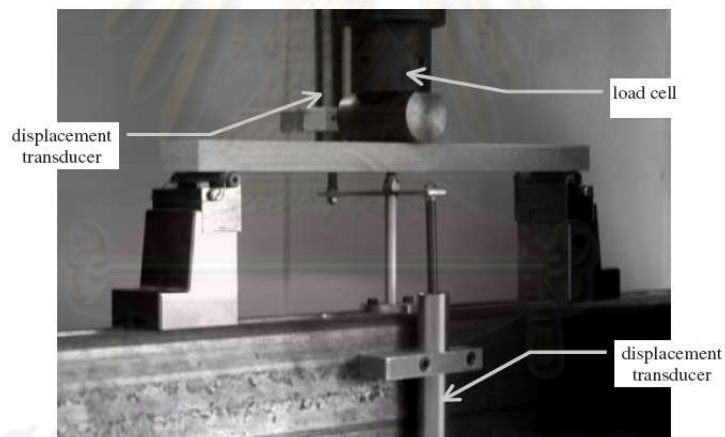
#### 3.4.2 Flexural Properties by Three Point Bending Test [26]

Flexural strength, or cross breaking strength, is the maximum stress developed when a bar-shaped test piece, acting as a simple beam, is subjected to a bending force perpendicular to the bar. An acceptable test specimen is one that is at least 3.2 mm in depth, 12.7 mm in width, and long enough to overhang the supports (however, the overhang should be less than 6.4 mm at each end). Figure 3.3 shows three point bending test.

The load was applied at a specified cross-head rate, and the test was terminated when the specimen bended or was deflected by 0.05 mm/min. The flexural strength (S) is calculated from Eq.3.3 in which P is the load at a given point on the deflection curve, L is the support span, b is the width of the bar, and d is the depth of the beam:

$$S = \frac{PL}{bd^2} \quad (3.3)$$

The flexural strength and flexural modulus of all composite sandwich panel samples were determined following ASTM D790. A Universal Testing Machine (Shimadzu model DSS-10T) was used at the cross-head speed of 50 mm/min. The average of two specimens was considered as the representative value.



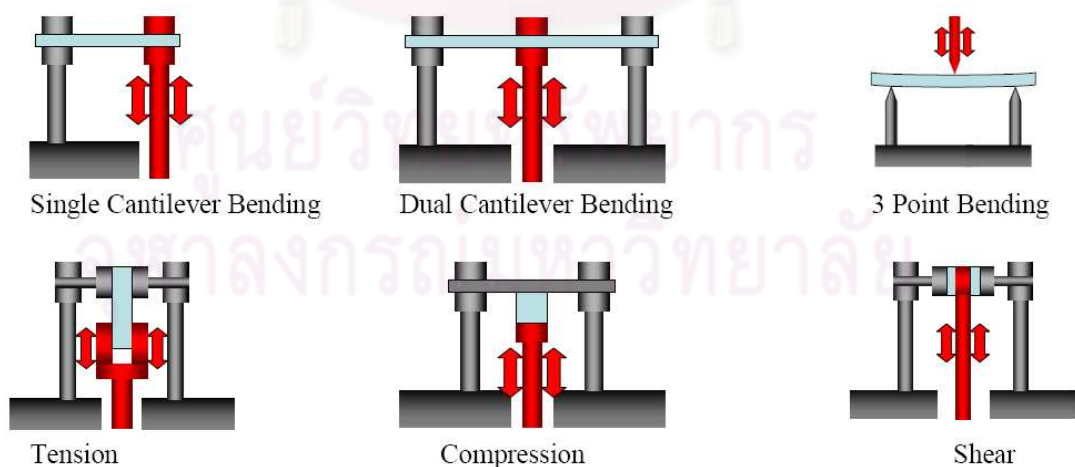
**Figure 3.3** Three point bending test [26].

### 3.4.3 Dynamic Mechanical Analysis [27]

The dynamic mechanical properties of biocomposites was studied by using dynamic mechanical analyzer (NETZSCH DMA 242) at a heating rate of 3.0K/min in the range of -30°C to 120°C. The glass transition temperature was obtained from the maximum point of the  $\tan \delta$  curve.  $\tan \delta$  is the ratio of the loss modulus to storage modulus or the ratio of the energy loss to the energy retained during loading cycle. The storage modulus and loss modulus of the composite laminate sheet specimens was measured according to ASTM D5023.

A dynamic mechanical analyzer, commonly referred to as just DMA, measures the stiffness and damping properties of a material. The stiffness depends on the mechanical properties of the material and its dimensions. It is frequently converted to a modulus to enable sample inter-comparisons. Damping was expressed in terms of  $\tan \delta$  and was related to the amount of energy that material can store. DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behavior is observed. The instrument operation is relatively simple to understand.

The sample can be mounted in the DMA in a number of ways depending on the characteristics of the sample. The 6 common geometries are shown in Figure 3.4. Dual cantilever bending mode was used for this research work.



**Figure 3.4** The 6 common geometries for DMA testing [27].

#### 3.4.4 Morphology Study

The morphology of the treated hemp fiber surface and sea water immersion sheet surface was also analyzed using scanning electron microscopy (SEM). The surface of laminate sheet and fabric were cut and stitched on a SEM stub using double-sided tape. The samples were then sputter-coated with gold and examined using an electron microscope, JEOL model JSM-5401LV operated at 15 kV.



## CHAPTER IV

### RESULTS AND DISCUSSIONS

The properties of composites after sea water immersion were determined in term of % absorption and % desorption by weight measurement. The mechanical properties in term of flexural strength, flexural modulus, storage modulus and loss modulus of composites were evaluated. The flexural strength and flexural modulus of all composite sandwich panel samples were determined. The morphology of the treated hemp fabric surface and sea water immersion sheet surface was also analyzed.

#### 4.1 Mercerization of Natural Fabric

The hemp fabric surface was improved by mercerization with 5%NaOH for 30 minutes. The scanning electron microscope (SEM) was used to examine the hemp fabric surface after pretreatment. From Figure 4.1, the comparison of the SEM micrograph between untreated hemp and treated hemp fabric showed the surface of treated hemp fabric was slightly smooth. The adhesion between fiber and matrix could be improved. The alkali-soluble polysaccharides and partly lignin were removed [20].

Later studies about the alkali treatment of jute-fibers, for instance, reports about the removal of lignin and hemicelluloses which affects the tensile characteristics of the fibers. When the hemicelluloses are removed, the interfibrillar region is likely to be less dense and less rigid and thereby makes the fibrils more capable of rearranging themselves along the direction of tensile deformation. When natural fibers are stretched, such rearrangements amongst the fibrils would result in better load sharing by them and hence result in higher stress development in the fiber [1].



**Figure 4.1** SEM micrographs of hemp fabric (a) untreated, (b) treated with 5% NaOH

## 4.2 Biocomposite Sandwich Panel at Room Temperature

### 4.2.1 Appearance

The biocomposites sandwich panel was rigid at room temperature. Appearance of composites kept at room temperature is shown in Figure 4.2. Density of composites sandwich panel was shown in Table C-1



**Figure 4.2** Appearance of biocomposite sandwich panel at room temperature.

### 4.2.2 Mechanical Properties by Three Point Bending

From Table 4.1, Figure 4.3 and 4.4, the 100% fabric reinforcement composites (FFBFF, HHBHH, and CCBCC) exhibited decreased flexural strength and flexural modulus in the following order:

Flexural Strength (MPa):

FFBFF (3.9) ~ CCBCC (3.9) > HHBHH (2.6)

Flexural Modulus (MPa):

CCBCC (59.1) > FFBFF (51.7) > HHBHH (51.1)



The CCBCC composite exhibited similar result nearly to FFBBF composite due to the cellulose fabric is produce from pure cellulose fiber that had improved the surface by removal of lignin and hemicelluloses which affects the tensile characteristics of the fibers that give highly crystalline, good fiber rearrangement, high strength that related to improved fiber–matrix adhesion [1]. But HHBHH composite is not pure cellulosic material that not improved the surface of fabric. HHBHH composite contained hemp fabric reinforcement that the surface had lignin and hemicelluloses that decreased the modulus of composite when comparing with 100% cellulose reinforcement.

The 50% hybrid cellulose fabric reinforced composites (CFBFC, FCBCF) was compared with 100% cellulose and glass fabric reinforced composite (CCBCC, FFBBF) that can be concluded in the following order:

Flexural Strength (MPa):

FFBBF (3.9) ~ CCBCC (3.9) > FCBCF (3.3) ~ CFBFC (3.4)

Flexural Modulus (MPa):

CCBCC (59.1) > FCBCF (57.4) > FFBBF (51.7) > CFBFC (46.3)

From the result, the 50% hybrid cellulose on external layer exhibited decrease in flexural strength and flexural modulus. Because the hydrophilic nature of cellulose that can absorb humidity from air during process and decrease the adhesion between fiber and matrix.

The 50% hybrid hemp fabric reinforced composites (HFBFH, FHBHF) was compared with 100% hemp and glass fabric reinforced composite (HHBHH, FFBBF) that can be concluded in the following order:

Flexural Strength (MPa):

FFBBF (3.9) > FHBHF (3.2) > HFBFH (3.1) > HHBHH (2.6)

Flexural Modulus (MPa):

FFBBF (51.7) > FHBHF (47.9) > HFBFH (42.0) > HHBHH (31.5)

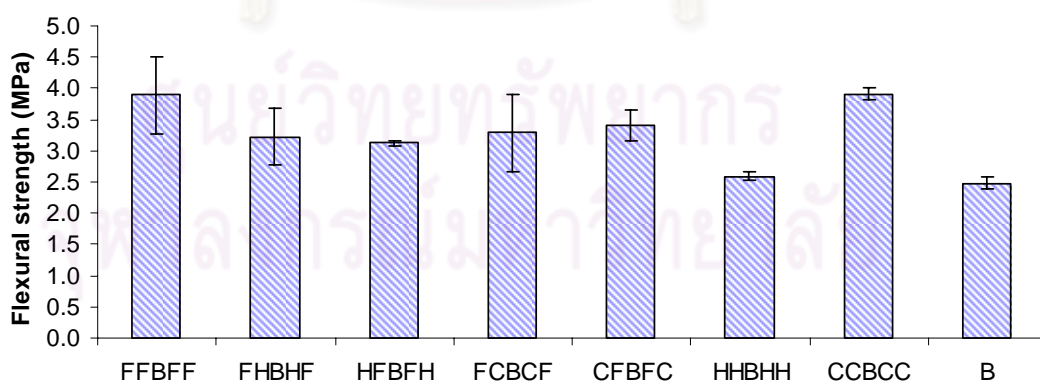
From the result, the 50% hybrid hemp fabric on external layer (HFBFH) exhibited decrease in flexural strength and flexural modulus. Because the hydrophilic nature of cellulose part in the hemp fabric that can absorb humidity from air during process and decrease the adhesion between fiber and matrix. Therefore, the 50% hybrid hemp and glass fabric reinforced composite (FHBHF, HFBFH) can

improve the mechanical properties that show the flexural strength and flexural modulus was higher than 100% hemp fabric reinforced composite (HHBHH).

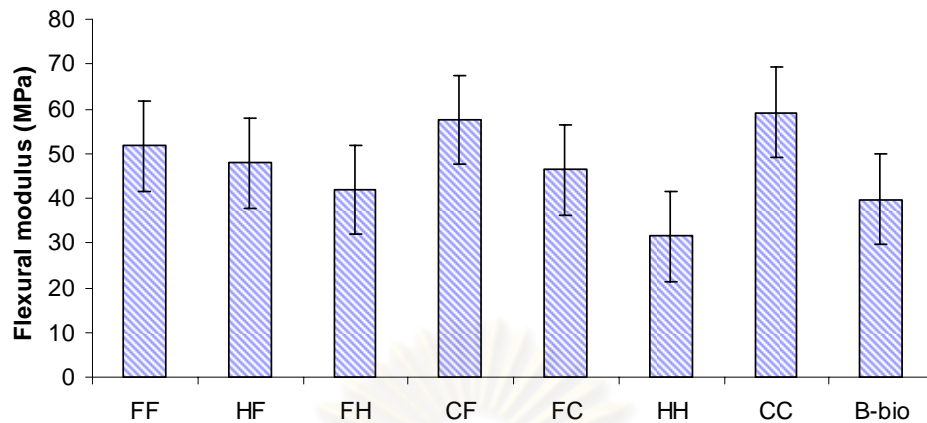
From Table 4.1 the biofoam panel with reinforcement exhibited the increased flexural strength and flexural modulus compared with the biofoam without reinforcement (B). It can be conclude that the reinforcement with fabric on panel can improved the mechanical properties of biofoam panel at room temperature. The fabric helps to reinforce the strength of panel by used of biorein as matrix.

**Table 4.1** Flexural strength and flexural modulus of sandwich panel at room temperature.

<b>Formula</b>	<b>Flexural strength MPa, (SD)</b>	<b>Flexural modulus MPa, (SD)</b>
<b>FFBFF</b>	3.9 (0.62)	51.7 (16.2)
<b>FHBHF</b>	3.2 (0.45)	47.9 (2.32)
<b>HFBFH</b>	3.1 (0.04)	42.0 (9.47)
<b>FCBCF</b>	3.3 (0.61)	57.4 (16.1)
<b>CFBFC</b>	3.4 (0.25)	46.3 (11.2)
<b>HHBHH</b>	2.6 (0.06)	31.5 (0.06)
<b>CCBCC</b>	3.9 (0.10)	59.1 (15.2)
<b>B</b>	2.5 (0.10)	39.7 (2.84)



**Figure 4.3** Flexural strength of sandwich panel at room temperature.

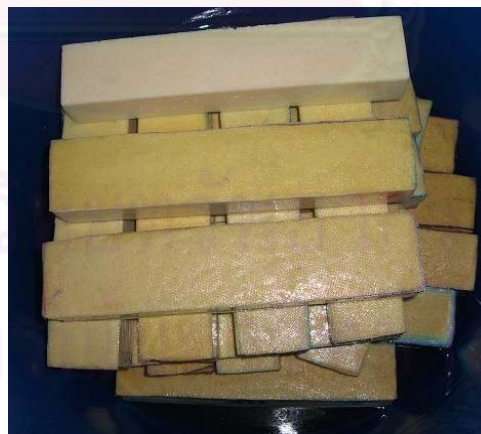


**Figure 4.4** Flexural modulus of sandwich panel at room temperature.

### 4.3 Sea-water Immersion of Biocomposite Sandwich Panel

#### 4.3.1 Appearance

All the specimens had less density than water; therefore, they floated over sea water (Figure 4.5). A concrete block was used to press the specimens beneath the water surface.



**Figure 4.5** Sandwich panel during immersion in sea water tank for 30 days.

### 4.3.2 Density

The fabric reinforced composite sandwich panel after immersion in sea water exhibited a slightly increase in density (Table 4.2) and some composite sandwich panel (HFBFH, FHBHF, CFBFC, CCBCC) exhibited decrease in density due to the foam core failure during immersion and mass loss in sea water.

**Table 4.2** Density of biocomposite sandwich panel.

Sample	Density (g/cm <sup>3</sup> )	
	Before immersion	After immersion
FFBFF	0.184	0.184
HFBFH	0.174	0.170
FHBHF	0.183	0.175
CFBFC	0.174	0.173
FCBCF	0.185	0.188
HHBHH	0.176	0.177
CCBCC	0.183	0.179
B	0.151	0.155

### 4.3.3 Mechanical Properties by Three Point Bending (Sea-water Effect)

From Table 4.3, Figure 4.6 and 4.7, the 100% fabric reinforcement composites (FFBFF, HHBHH, and CCBCC) exhibited decreased flexural strength and flexural modulus in the following order:

Flexural Strength (MPa):

FFBFF (3.4) > CCBCC (3.3) > HHBHH (2.9)

Flexural Modulus (MPa):

CCBCC (44.1) > FFBFF (41.6) > HHBHH (37.0)

The result of flexural strength and flexural modulus have similar trend to composite at room temperature in 4.2.2 and could be explained that the result is the same as the hydrophilic nature of natural fabric as explained above.

From the result of composite after sea water immersion that exhibited decreased in flexural strength and flexural modulus compared to composite at room temperature because sea water has reduced the adhesion between fiber and polymer matrix. The decrease in mechanical properties after water immersion can be related to the weak fiber–matrix interface due to water absorption. Due to the presence of a

high –OH group on natural fibers tend to show low moisture resistance. This leads to the dimensional variation of composites products and poor

Interfacial bonding between the fiber and matrix, causing a decrease in the mechanical properties [30, 31]. When the composite is exposed to moisture, the hydrophilic hemp or cellulose fibers as well. As a result of fiber swelling, micro cracking in the matrix occurs. As the composite cracks and gets damaged, capillarity and transport via micro cracks become active. The capillarity mechanism involves the flow of water molecules along fiber–matrix interfaces and a process of diffusion through the bulk matrix. The water molecules are actively attack the interface, resulting in debonding of the fiber and matrix. [32]

The 50% hybrid cellulose fabric reinforced composites (CFBFC, FCBCF) was compared with 100% cellulose and glass fabric reinforced composite (CCBCC, FFBFF) that can be concluded in the following order:

Flexural Strength (MPa):

CFBFC (3.5) > FFBFF (3.4) ~ CCBCC (3.3) > FCBCF (3.3)

Flexural Modulus (MPa):

CFBFC (48.4) > CCBCC (44.1) > FFBFF (41.6) > FCBCF (40.3)

From the result, the 50% hybrid cellulose on external layer exhibited an increase in flexural strength and flexural modulus after immersion in sea water for 30 days. Because of the hydrophilic nature of cellulose fabric that will decrease the fiber and matrix adhesion when combined with glass fabric it can help to improve the strength of composite.

The 50% hybrid hemp fabric reinforced composites (HFBFH, FHBHF) was compared with 100% hemp and glass fabric reinforced composite (HHBHH, FFBFF) that can be concluded in the following order:

Flexural Strength (MPa):

FFBFF (3.4) > FHBHF (3.1) ~ HFBFH (3.1) > HHBHH (2.9)

Flexural Modulus (MPa):

FFBFF (41.6) > HFBFH (40.3) ~ FHBHF (39.2) > HHBHH (37.0)

From the result, the 50% hybrid hemp fabric on external layer (HFBFH) and internal layer (FHBHF) was not different in flexural strength and flexural modulus. The results are also similar to the composite at room temperature

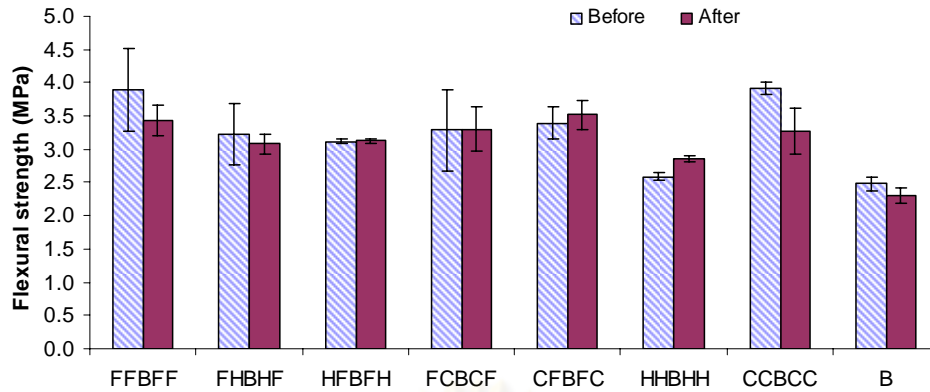
in 4.2.2 and could be explained that the result is the same as the hydrophilic nature of natural fabric as explained above.

From Table 4.3 the biofoam panel with reinforcement exhibited a slightly decreased in flexural strength and flexural modulus compared with the biofoam without reinforcement (B).

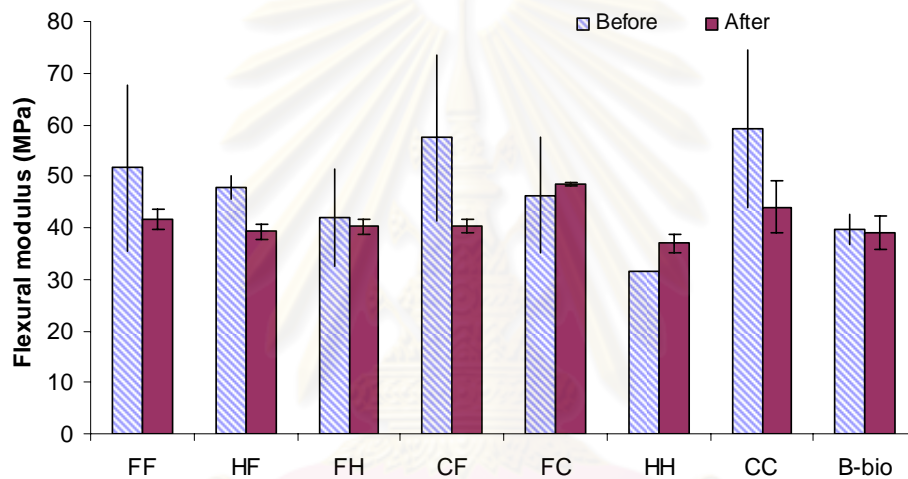
It can be concluded that the sea-water was highly effected on to the reinforcement and matrix, but a little effect to foam core. The resulting composite after immersion in sea water exhibited decreased in flexural strength and flexural modulus because of the hydrolysis reaction promotes the extraction of low molecular weight of matrix species from the composite into the water, these would deteriorate the construction. Cations from sea water will penetrate along with the water molecules into the composite, causing damage to the matrix and the fiber. Since the matrix and the natural fiber have different moisture expansion coefficients, the absorbed moisture may induce different expansion of the resulting in debonding in the interface. These would damage the material, resulting in a decreased tensile strength [32].

**Table 4.3** Flexural strength and flexural modulus of sandwich panel after immersion in sea water and exposure in air for 30 days.

Formula	Flexural strength (MPa)	Flexural modulus (MPa)	Reduction (%)	
			Flexural strength	Flexural modulus
<b>FFBFF</b>	3.4 (0.23)	41.6 (1.90)	11.8	19.4
<b>FHBHF</b>	3.1 (0.15)	39.2 (1.37)	4.3	18.1
<b>HFBFH</b>	3.1 (0.03)	40.3 (1.53)	0.0	4.1
<b>FCBCF</b>	3.3 (0.33)	40.3 (1.30)	-0.4	29.9
<b>CFBFC</b>	3.5 (0.22)	48.4 (0.26)	-3.5	-4.6
<b>HHBHH</b>	2.9 (0.05)	37.0 (1.65)	-10.6	-17.1
<b>CCBCC</b>	3.3 (0.35)	44.1 (4.92)	16.3	25.5
<b>B</b>	2.4 (0.12)	39.0 (3.27)	7.3	2.0



**Figure 4.6** Flexural strength of sandwich panel after sea-water immersion for 30 days.



**Figure 4.7** Flexural modulus of sandwich panel after sea-water immersion for 30 days.

#### 4.3.4 Absorption-Desorption Properties

From the absorption properties of sandwich panel with 50% natural fabric reinforcement during immersion in sea water 30 days, as shown in Figure 4.8, composite with 50% cellulose reinforcement had higher water absorption than composite with 50% hemp reinforcement.

From the absorption properties of sandwich panel with 100% reinforcement during immersion in sea water 30 days, as shown in Figure 4.9, composite with 100% cellulose had higher water absorption than composite with 100% hemp and 100% glass fabric.

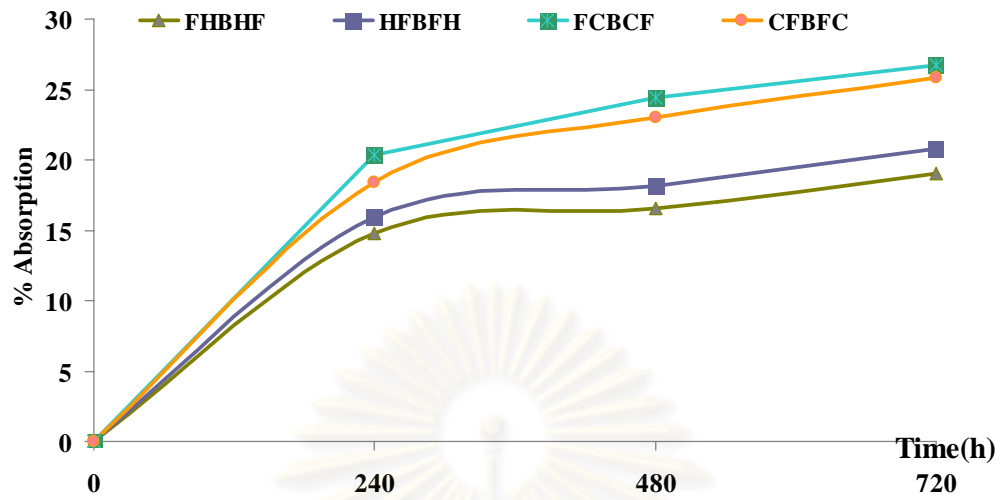
From the desorption properties of sandwich panel with 50% natural fabric reinforcement, after immersion and exposure in air for 30 days (Figure 4.10), the 50% cellulose reinforced composite desorbed slower than composites reinforced with 50% hemp but at 480 hours, the desorption rate was faster and at 720 hours % desorption did not change.

From the desorption properties of sandwich panel with 100% natural fabric reinforcement and 0% natural fabric reinforcement, after immersion and exposure in air for 30 days (Figure 4.11), the composite with 100% natural fabric reinforcement desorbed slower than composite with 100% glass fabric but at 480 hours, the desorption rate of composite with 100% natural fabric was faster than composite with 100% glass fabric and at 720 hours % desorption did not change.

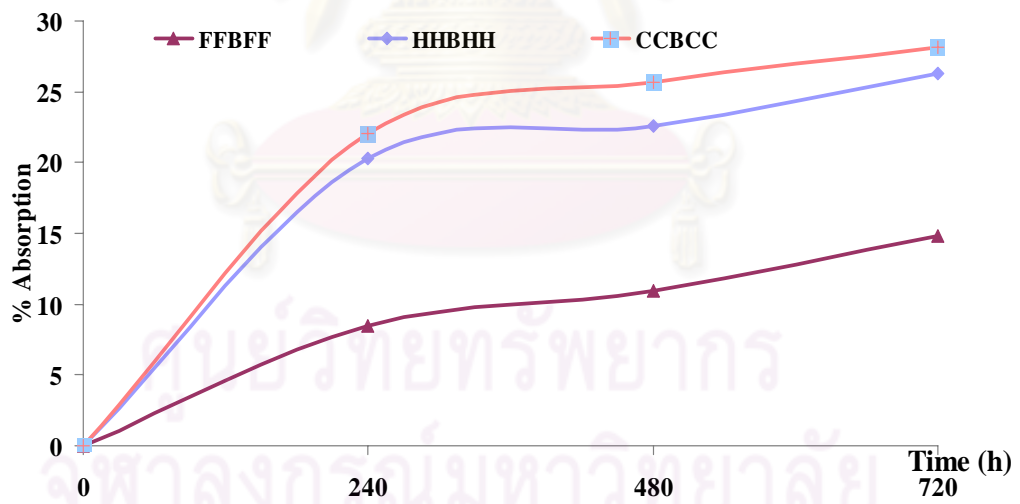
It can be concluded that cellulose absorbed water fast with high absorption and desorbed slowly. Hemp is an interesting fabric because of lower absorption and rapid desorption same as glass fabric. Because cellulose fabric exhibited the hydrophilic than hemp fabric. The higher moisture absorption rates can be attributed to the hydrophilic property of natural fiber due to the hydroxyl group (-OH) on the cellulose molecules. Hydrogen bond may form between the hydroxyl group and water molecules [32].

The sea-water absorption correlated to the damage of the sandwich panel. The primary mechanisms of water absorption include filling of the near-surface voids by the ambient water, followed by flow of water into neighboring cells with fluid-induced broken cell walls, and subsequent diffusion into the interior. These mechanisms are associated with a damaged surface layer where 'macro-breakage' and cell wall swelling dominate, followed by a lesser degree of wall breakage within the next foam cells and diffusion in the walls of an undisturbed, inner, cell structure. In view of the excessively slow diffusion process, it is most likely that the central part of the foam remains dry [17].

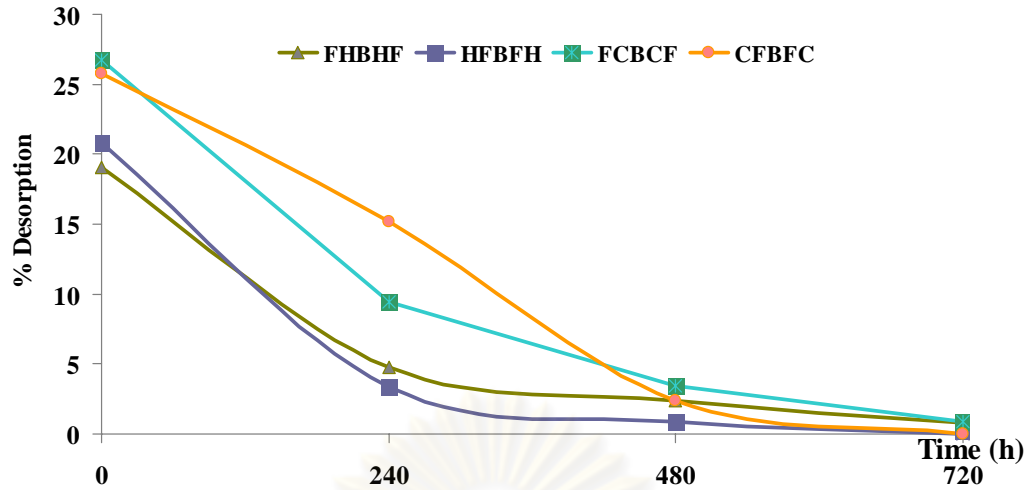




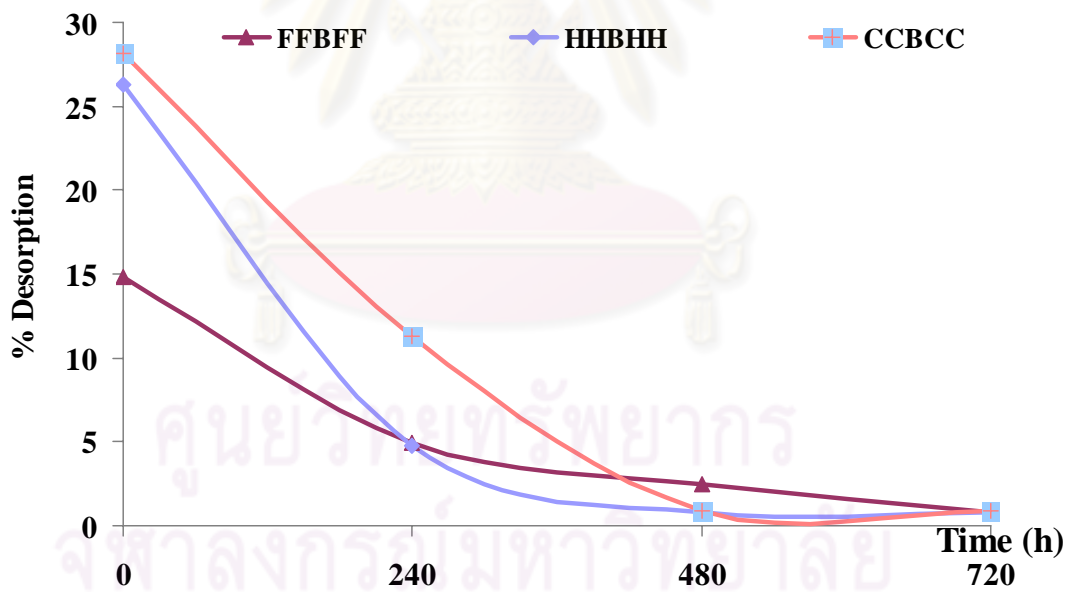
**Figure 4.8** Absorption properties of sandwich panel with 50% natural fabric reinforcement during immersion in sea water for 30 days.



**Figure 4.9** Absorption properties of sandwich panel with 100% natural fabric reinforcement during immersion in sea water for 30 days.



**Figure 4.10** Desorption properties of sandwich panel with 50% natural fabric reinforcement after immersion water for 30 days.



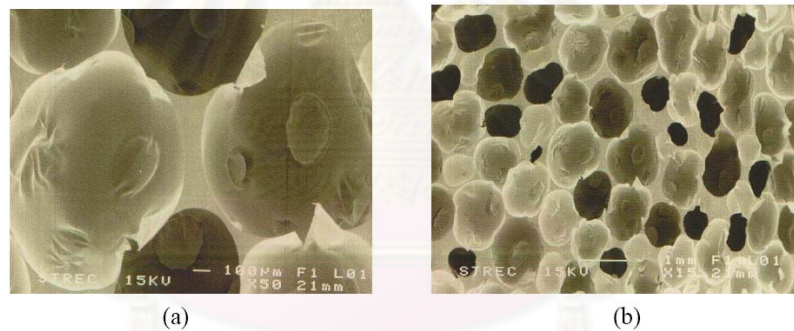
**Figure 4.11** Desorption properties of sandwich panel with 100% natural fabric reinforcement after immersion in seawater for 30 days.

### 4.3.5 Morphology of Biofoam for Sandwich Panel

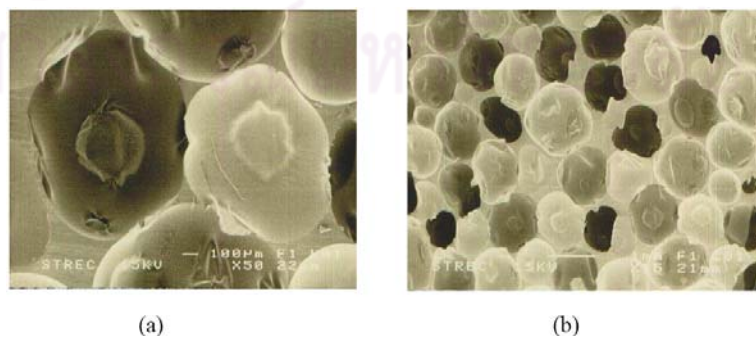
Figure 4.12 shows the surface of biofoam after polishing. Figure 4.13 and Figure 4.14 show the SEM micrograph of biofoam before immersion and after immersion. The foam deformation was not observed but small defect appeared near the cell border (Figure 4.14). Therefore, foam could be degraded for 1-2 years. For this research work the immersion time was only 2 months, the slightly defect was observed.



**Figure 4.12** Surface of polyurethane foam after polishing on surface before laminate by hand lay up.



**Figure 4.13** SEM micrographs of polyurethane foam at room temperature  
(a) X50 magnification (b) X15 magnification.

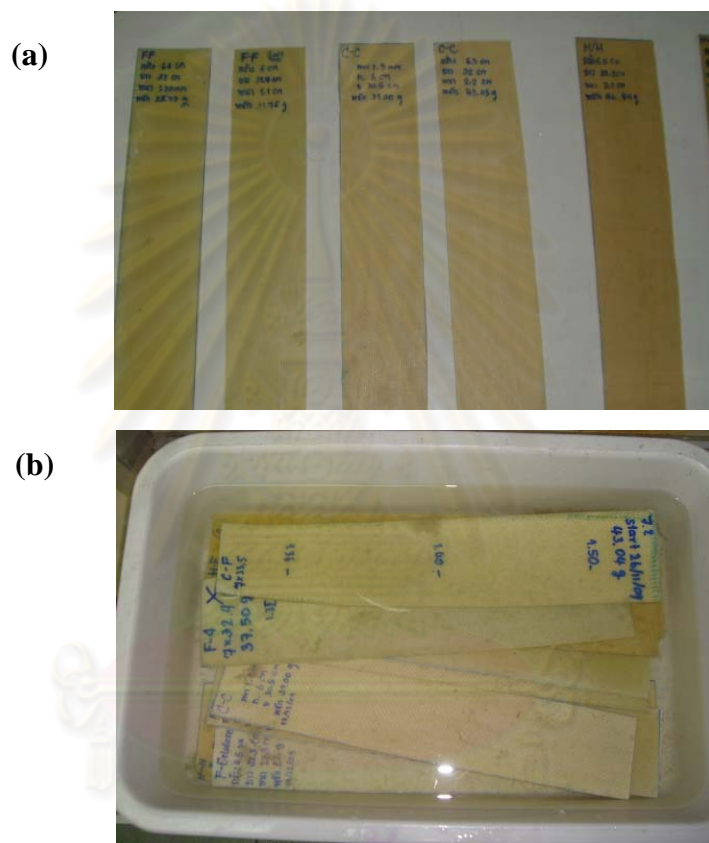


**Figure 4.14** SEM micrographs of polyurethane foam after immersion in sea water.  
(a) X50 magnification (b) X15 magnification.

## 4.4 Biocomposites Laminate Sheet

### 4.4.1 Appearance

The biocomposite laminate sheet at room temperature was rigid. The appearance of composites at room temperature and during immersion in sea water for 30 days is shown in Figure 4.15.



**Figure 4.15** Biocomposites laminate sheet (a) at room temperature, (b) during immersion in sea water for 30 days.

#### 4.4.2 Absorption-Desorption Properties

Figure 4.16 shows the absorption properties of laminate sheet with, 100% glass fabric (FF), 100% cellulose fabric (CC), 100% hemp fabric (HH) and 100% treated hemp fabric (TH/TH) reinforcement during immersion in sea water for 30 days. The composite with 100% cellulose reinforcement had maximum absorption. The composites had the decreasing absorption as following order: (High) CC>HH>TH/TH>FF (Low).

Figure 4.17 shows the absorption properties of laminated sheet with 50% hemp fabric (FH) and 50% cellulose fabric (FC) reinforcement during immersion in sea water for 30 days. The laminate sheet with 50% cellulose reinforcement had higher absorption than laminate sheet with 50% hemp reinforcement.

Figure 4.18 shows the absorption properties of laminated sheet with 100% glass fabric (FF), 50% hemp (FH), 100% hemp (HH) and 100% treat hemp (TH/TH) reinforcement during immersion in sea water for 30 days. The laminate sheet with 100% hemp had maximum absorption. The laminate composite had the decreasing absorption as following order: (High) HH>TH/TH>FH>FF (Low).

Figure 4.19 shows the desorption properties of laminated sheet with 100% glass fabric (FF), 100% cellulose (CC), 100% hemp (HH) and 100% treated hemp (TH/TH) reinforcement. The laminate sheet CC had slowest desorption. The laminate composite had the decreasing desorption as following order: (High) CC>HH>TH/TH>FF (Low).

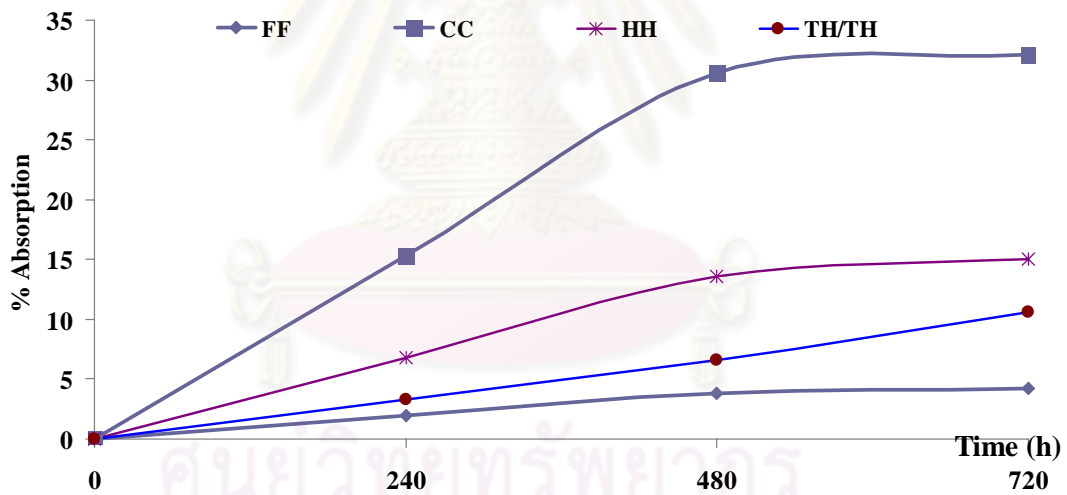
Figure 4.20 shows the desorption properties of laminate sheet with 50% hemp fabric (FH) and 50% cellulose fabric (FC) reinforcement. The FC laminate sheet had slow desorption than FH laminate sheet.

Figure 4.21 shows the desorption properties of laminate sheet with 100% glass fabric (FF), 50% hemp (FH), 100% hemp (HH) and 100% treated hemp (TH/TH) reinforcement. The HH laminate sheet had slow desorption. The laminate composite had the decreasing desorption as following order: (High) HH>TH/TH>FH>FF (Low).

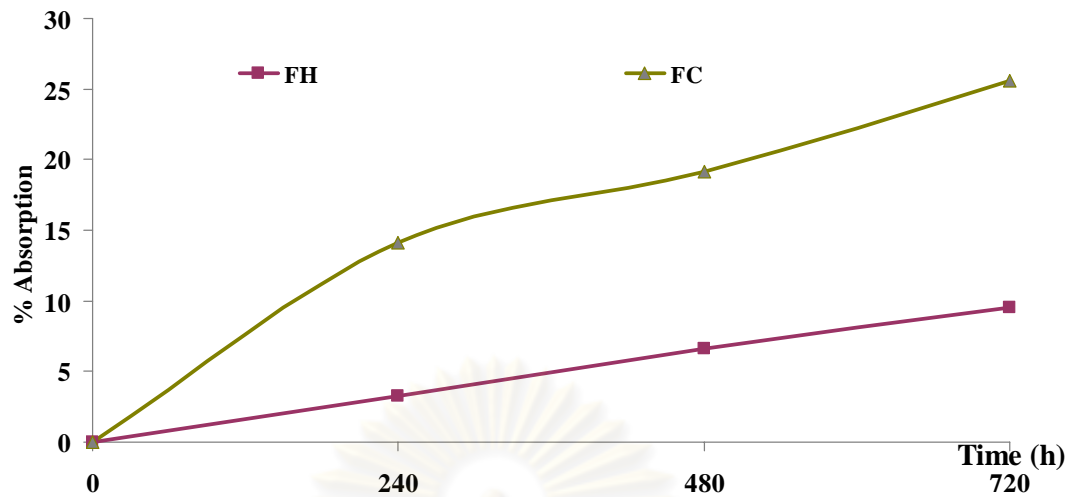
The biocomposite laminate sheets show the similar result with biocomposite sandwich. As % cellulose content increased, the composite showed

high water absorption which was not good properties for water sport products. However, the good natural fabric for reinforcement was hemp fabric with lower absorption and desorption close to traditional fabric. It can be noted that the treated hemp laminate sheet had lower absorption than the non-treated hemp composite.

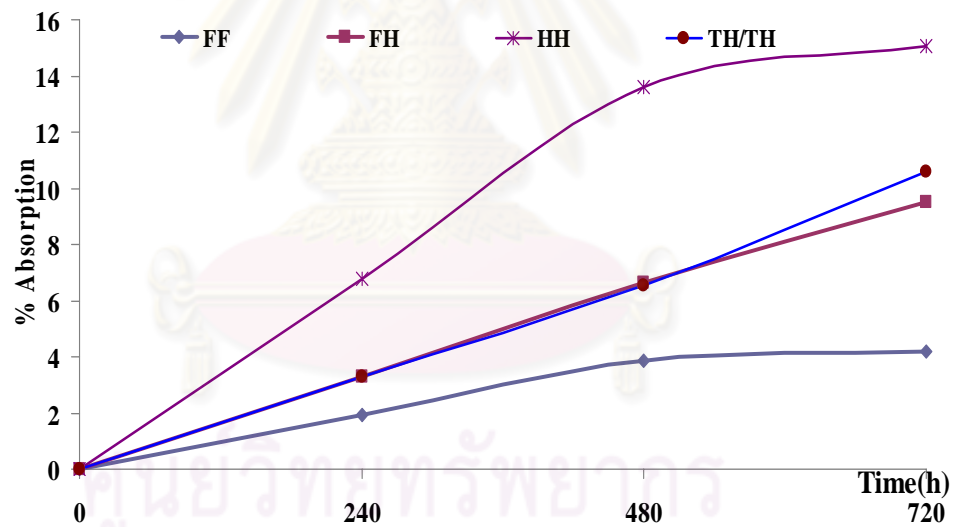
The higher moisture absorption rates can be attributed to the hydrophilic property of cellulose fabric due to the hydroxyl group ( $-OH$ ) on the cellulose molecules. Hydrogen bond may form between the hydroxyl group and water molecules [32]. The cellulose fabric composite (CC) had more hydroxyl group than hemp fabric composite (HH) that is related to high moisture absorption rate. The treated hemp (TH/TH) fabric composite had lower hydroxyl group but it improved the fiber and matrix adhesion by mercerization with NaOH that can also improve the absorption properties of composite.



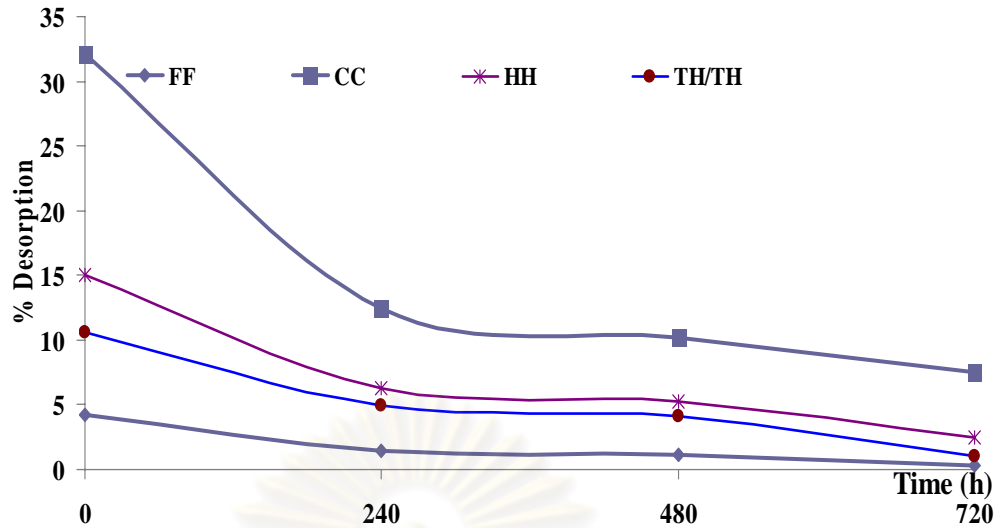
**Figure 4.16** Absorption properties of laminate sheet with, 100% glass fabric (FF), 100% cellulose fabric (CC), 100% hemp fabric (HH) and 100% treated hemp fabric (TH/TH) reinforcement during immersion in sea water for 30 days.



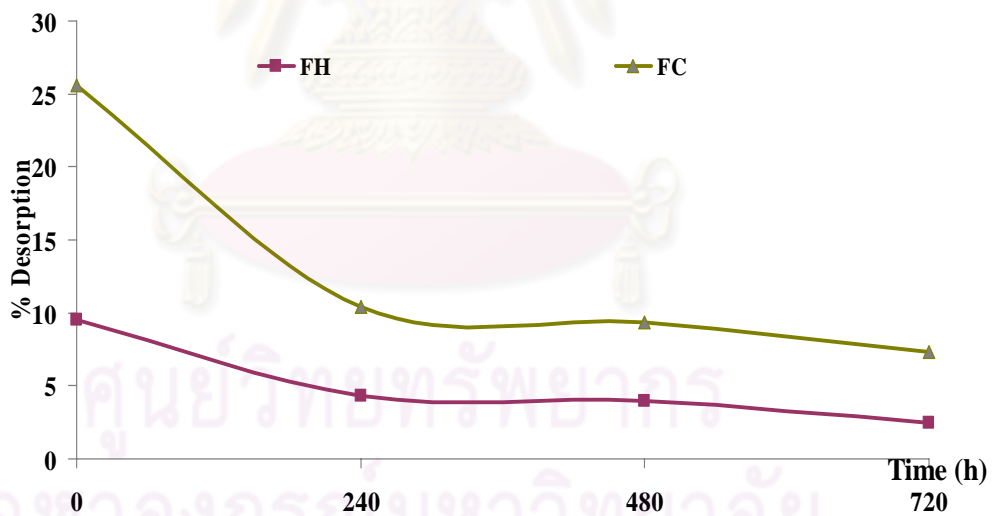
**Figure 4.17** Absorption properties of laminate sheet with 50% hemp fabric (FH) and 50% cellulose fabric (FC) reinforcement during immersion in sea water for 30 days.



**Figure 4.18** Absorption properties of laminate sheet with 100% glass fabric (FF), 50% hemp (FH), 100% hemp (HH) and 100% treated hemp (TH/TH) reinforcement during immersion in sea water for 30 days.

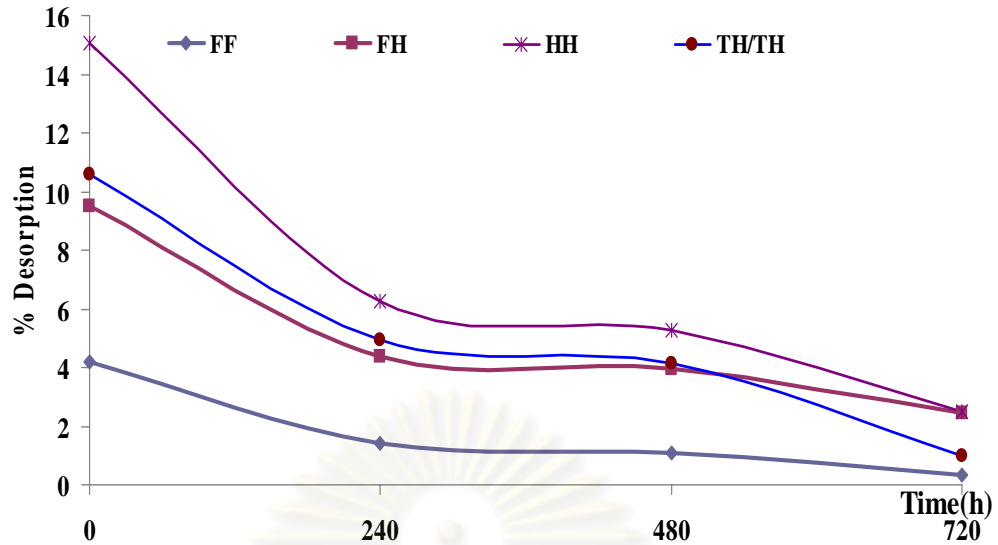


**Figure 4.19** Desorption properties of laminated sheet with 100% glass fabric (FF), 100% cellulose (CC), 100% hemp (HH) and 100% treated hemp (TH/TH) reinforcement.



**Figure 4.20** Desorption properties of laminate sheet with 50% hemp fabric (FH) and 50% cellulose fabric (FC) reinforcement.





**Figure 4.21** Desorption properties of laminate sheet with 100% glass fabric (FF), 50% hemp (FH), 100% hemp (HH) and 100% treated hemp (TH/TH) reinforcement.

#### 4.4.3 Dynamic Mechanical Analysis (DMA) for Laminate Sheet

The dynamic mechanical properties of biocomposites was studied by using dynamic mechanical analyzer (NETZSCH DMA 242) at a heating rate of 3.0K/min in the range of  $-30^{\circ}\text{C}$  to  $120^{\circ}\text{C}$ . The glass transition temperature was obtained from the maximum point of the  $\tan \delta$  curve.  $\tan \delta$  is the ratio of the loss modulus to storage modulus or the ratio of the energy loss to the energy retained during loading cycle [3].

Figure 4.22 shows the storage modulus of biocomposite laminate sheets at room temperature. FF laminate sheet had the maximum storage modulus, FH and FC laminate sheet had higher storage modulus than TH/TH laminate sheet. However, TH/TH had higher storage modulus than HH and CC laminate sheet. Figure 4.23 shows the storage modulus of biocomposite laminate sheets after sea water immersion. The storage modulus of composite after sea water immersion shows the similar result as composite before immersion (Figure 4.22.).

Figure 4.24 shows the loss modulus of biocomposite laminate sheets at room temperature. FF laminate sheet had the maximum loss modulus, FH and FC

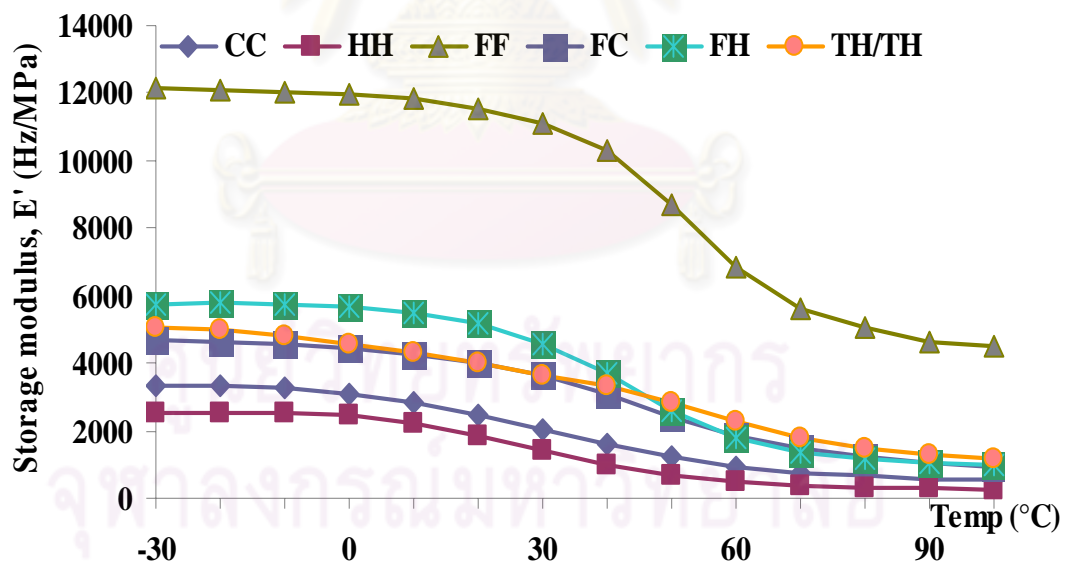
laminated sheet had higher loss modulus than TH/TH laminated sheet. The TH/TH laminated sheet had higher loss modulus than HH and CC laminated sheet. The loss modulus of biocomposite laminated sheet after sea water immersion was the same.

Figure 4.26 and Figure 4.27 show the  $\tan \delta$  of biocomposite laminated sheet at room temperature and after sea water immersion.  $T_g$  could be determined at the maximum  $\tan \delta$ . The composites had the decreasing  $T_g$  as follows: (High) TH/TH (56.6 °C) > FC (56.1 °C) > CC (51.0 °C) > HH (49.7 °C) > FH (49.0 °C) > FF (48.3 °C) (Low). However, the treated hemp fabric reinforced composites had good structural damping properties after sea water immersion and it could be used in some applications. From results of DMA, it could be concluded that:

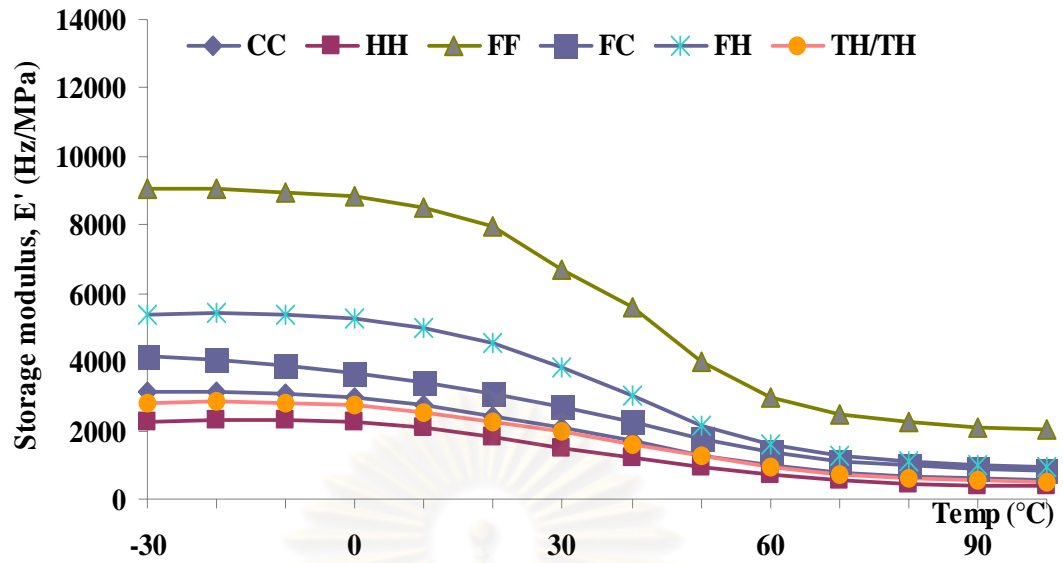
Storage modulus: FF > 50% NF reinforcement > TH/TH > 100% NF reinforcement.

Loss modulus: The similar result of storage modulus.

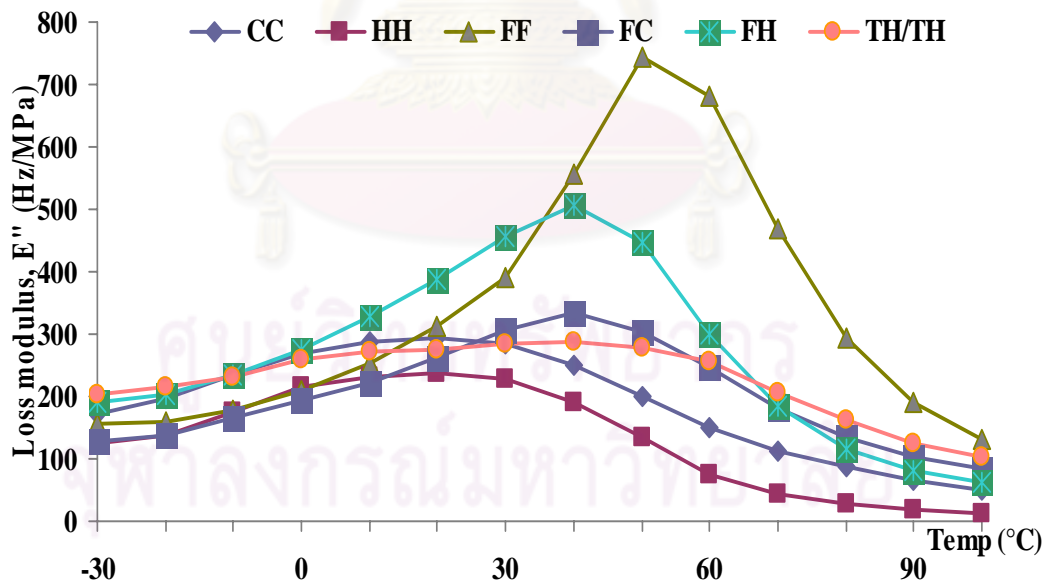
$\tan \delta$ :  $T_g$  of composite after immersion in sea water was decreased.  $T_g$  of TH/TH composite was higher than HH composite.



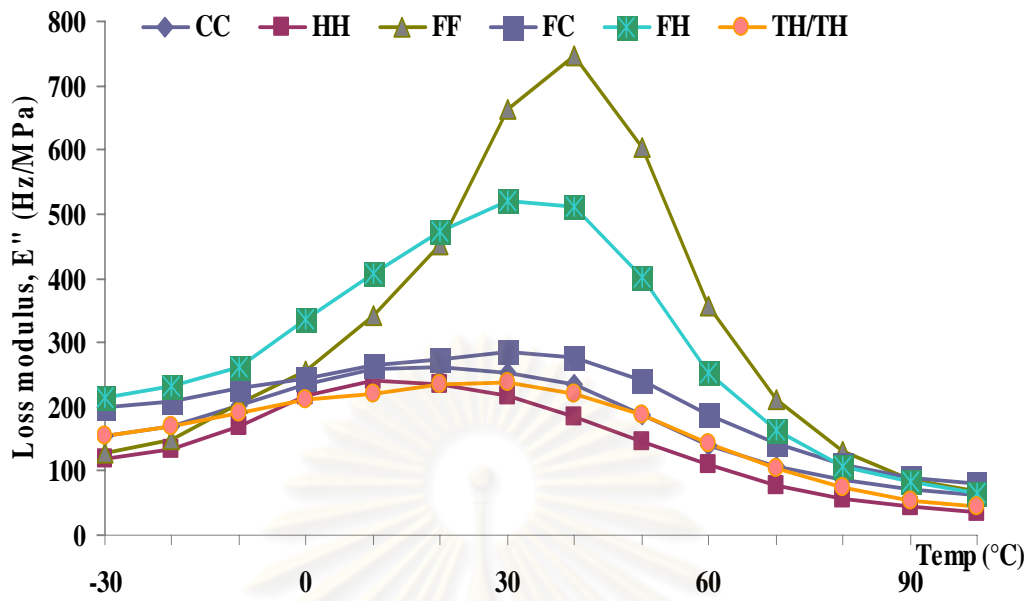
**Figure 4.22** Storage modulus of biocomposite laminated sheets at room temperature.



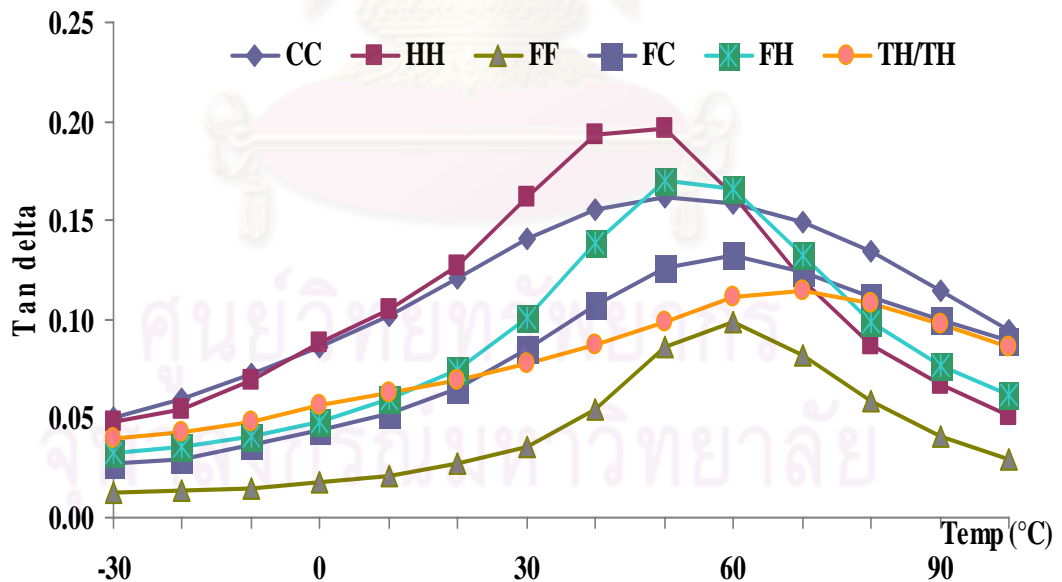
**Figure 4.23** Storage modulus of biocomposite laminate sheets after sea-water immersion.



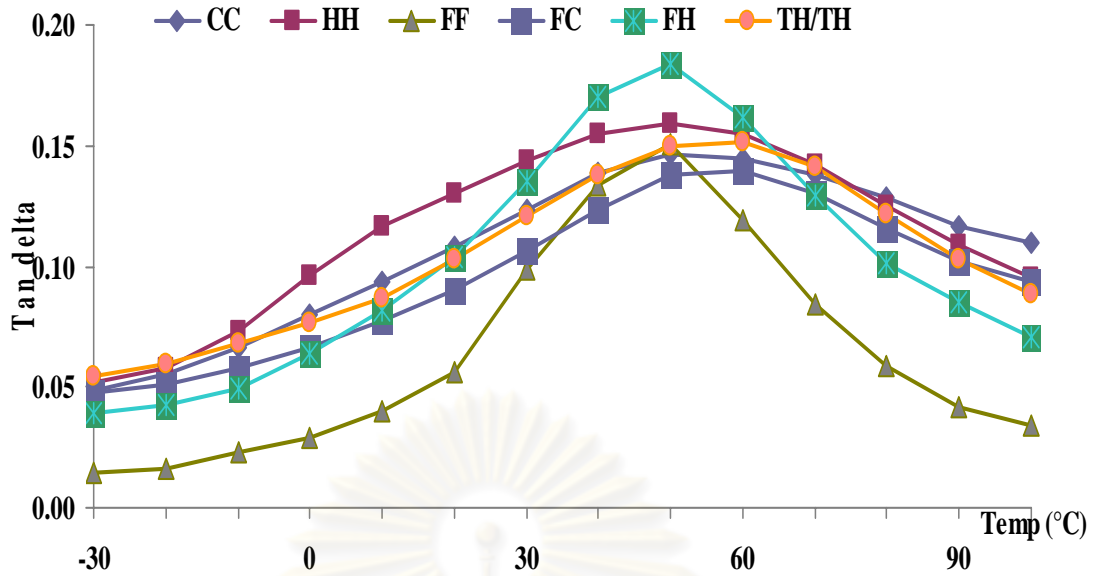
**Figure 4. 24** Loss modulus of biocomposite laminate sheets at room temperature.



**Figure 4.25** Loss modulus of biocomposite laminate sheets after sea water immersion.



**Figure 4.26** Tan delta of biocomposite laminate sheets at room temperature.



**Figure 4.27** Tan delta of biocomposite laminate sheets after sea water immersion.

#### 4.4.4 Morphology by Scanning Electron Microscopy (SEM)

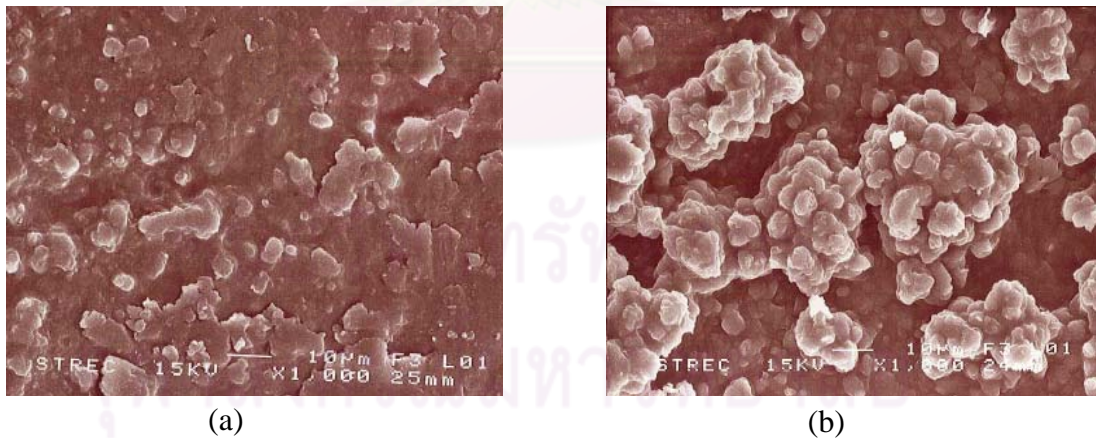
Figure 4.28 shows the SEM micrograph of FH laminated sheet. From Figure 4.28(a), at room temperature the surface of FH laminated sheet was slightly rough but not thicker surface. From Figure 4.28(b), after sea water immersion the surface of FH laminate sheet was shown the thicker surface. The biocomposite after immersion had the thicker surface due to the interaction between sea water and the natural fabric and matrix surface. This corresponded to the result of DMA that after immersion, the  $T_g$  of FH laminate sheet was decreased from 53.3°C (before immersion) to 49.0°C (after immersion).

Figure 4.29(a), shows the SEM micrograph of HH laminate sheet. From Figure 4.29(b), shows the SEM micrograph of TH/TH laminate sheet after immersion in sea water. TH/TH laminate sheet surface was smooth surface than HH laminate sheet. The treatment could improve the fiber and matrix surface interaction.

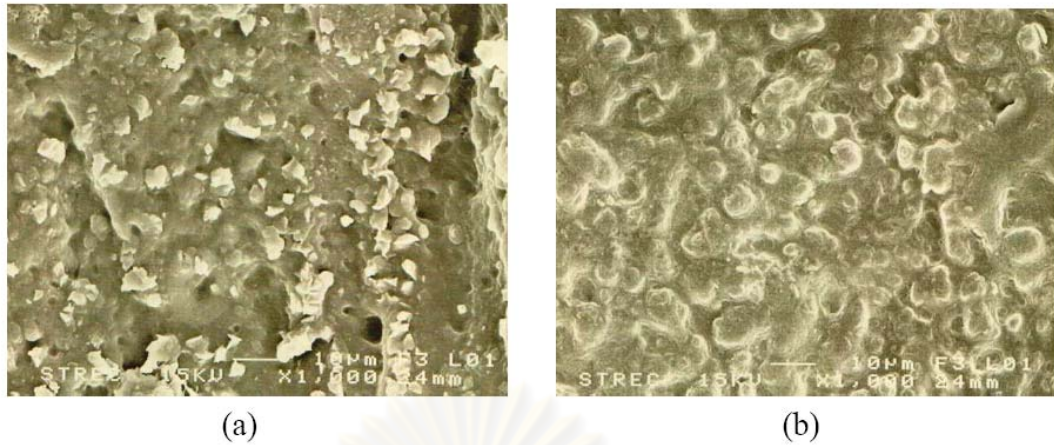
This was also confirmed by DMA results that the  $T_g$  was increased from 49.7 °C (before immersion) to 57.2 °C (after immersion).

Figure 4.30(a) and 4.30(b) show the SEM micrograph of FC laminate sheet at room temperature and after sea water immersion, respectively. From Figure 4.30(b), the surface of FC laminate sheet after immersion had the thicker surface. This corresponded to the result of DMA that after immersion, the  $T_g$  of FC laminate sheet was decreased from 60.5°C (before immersion) to 56.6°C (after immersion).

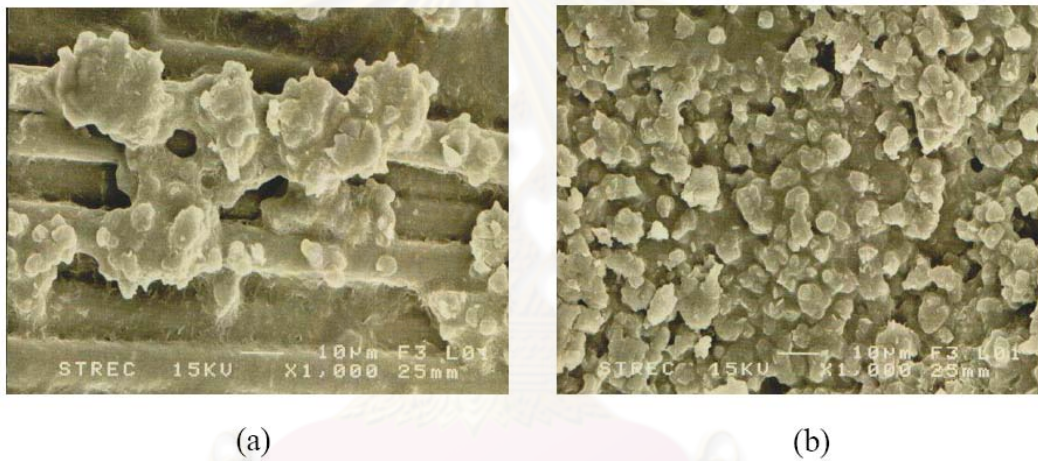
When specimens were immersed in sea water, the composite had significant moisture absorption and suffered chemical degradation of resin matrix and fiber matrix interphase region. Sea water degradation would cause swelling and plasticization of the matrix and debonding at the fiber/matrix interface that reduced the mechanical properties [28]. From the structural degradation effect in sea water environment blisters within hull laminates occurred. The defect manifest itself as a localized raised swelling of the laminate in an apparently random fashion appeared after a specimen immersed in sea water for some period of time. When blisters ruptured, a viscous acidic liquid was expelled. Because of these blisters, as the duration of immersion increased, the strength of the composite was decreased [29].



**Figure 4.28** SEM micrographs of FH laminated sheet (X1000 magnification)  
 (a) at room temperature (b) after immersion in sea water for 30 days.



**Figure 4.29** SEM micrographs of laminate sheet after immersion in sea water  
 (a) HH laminate sheet (b) TH/TH laminate sheet (X1000 magnification).



**Figure 4.30** SEM micrographs of FC laminate sheet (X1000 magnification)  
 (a) at room temperature (b) After sea water immersion for 30 days.

ศูนย์วิทยทรัพยากร  
 จุฬาลงกรณ์มหาวิทยาลัย

# CHAPTER V

## CONCLUSION

### 5.1 Conclusion

The application of natural fiber as reinforcement in composite materials requires a strong adhesion between fabric, matrix and core when used in the sea. In this work, the surface treatment was mercerization. The natural fiber /castor-oil biocomposite was successfully prepared in the form of sandwich and laminate sheet by hand lay-up technique and were immersed in sea water for 30 days. The present study could be concluded that;

1. Both sandwich and laminate sheet had similar absorption and desorption properties in sea water immersion. The absorption properties increased with increasing cellulose fabric content. The cellulose fabric was not suitable for sea water product because of high water absorption and slow desorption. The interesting finding that the hemp fabric reinforced composites showed good absorption and desorption properties and had good potential for sea water products.

2. From dynamic mechanical analysis, the composite with treated hemp fabric with 5%NaOH exhibited the higher mechanical properties due to the improved bonding of the skin and matrix bonding by the removal of impurities and wax from fabric skin. On the other hand, the mechanical properties and absorption properties could be improved by replacement of synthetic fabric by natural fabric at 50% content

3. From absorption test and DMA, the composites after immersion show the decreased Tg. Treated hemp composite laminate sheet had higher Tg than non-treated hemp laminate sheet.

The natural fiber/castor oil polyurethane sandwich biocomposite had high potential to replace the glass fabric reinforced composites in sea water sport applications, depending on strength and the environmental conditions where the part is being applied.



## 5.2 Suggestion for future work

In the area of natural fabric reinforced composite with various combination layer of hemp, cellulose and glass fabric. The polyurethane composite could be reinforce by hemp fabric treated with NaOH. The further study should be done as the following aspects:

1. The effect of long term immersion of both biocomposites sandwich panel and biocomposite laminate sheet at least 6-12 months should be studied.
2. The method of decreasing moisture absorption of treated hemp fabric to improve the interfacial adhesion between fiber and polymer matrix should be explored.
3. The effect of layer arrangement on mechanical properties and absorption properties should be studied.



## REFERENCES

- [1] Bledzki, A.K., and Gassan, J. 1999. Composites Reinforced with Cellulose Based Fibres. Progress in Polymer Science. 24: 22–74.
- [2] Silva, R.V., Spinelli, D., Bose Filho, W.W., Claro Neto, S., Chierice, G.O., and Tarpini, J.R. 2006. Fracture Toughness of Natural Fiber/Castor oil Polyurethane Composite. Composites Science and Technology. 66: 1328-1335.
- [3] Mohanty, A.K., Misra, M., and Drzal, L.T. 2005. Natural Fibers Biopolymer and Biocomposites. Taylor & Francis Publishing.
- [4] Aart van, V. 2008. Natural Fibre Composites: Recent Developments. A Powerpoint Presentation. University Leuven i-SUP . available from: [www.i-sup2008.org/presentations/...1/VanVuure\\_AW.pdf](http://www.i-sup2008.org/presentations/...1/VanVuure_AW.pdf) [2011, Feb]
- [5] Maya, J. and John, S. 2008. Biofibres and Biocomposites. Carbohydrate Polymer. 71: 343-364.
- [6] Bhagwan, D.A., Lawrence, J., Broutman, K., and Chandrashekhara, K. 2006. Analysis and Performance of Fiber Composites. John Wiley.
- [7] Wambua, P., et al. 2003. Natural Fibres: Can they replace glass in fibre reinforced plastics?. Composites Science and Technology. 63: 1259-1264
- [8] Raymond, B.S. 1992. Reinforced plastic properties & Application. Journal of Chemical Education. 69: 207.
- [9] Pcintl, Glass fiber [online]. 2011. Available from : [http://www.pcintl.com/glass\\_fiber.htm](http://www.pcintl.com/glass_fiber.htm) [2011, Feb].
- [10] Wikipedia, Polyurethane [online]. 2011. Available from : <http://en.wikipedia.org/wiki/Polyurethane> [2011, March].
- [11] Cangemi, J.M. 2008. Biodegradation of Polyurethane Derived from Castor oil. Polymer Science and Technology. 18: 201-206.
- [12] Wikipedia, Sandwich Structured Composite [online]. 2011. Available from: [http://en.wikipedia.org/wiki/Sandwich\\_structured\\_composite](http://en.wikipedia.org/wiki/Sandwich_structured_composite). [2011, April].
- [13] Sandwich Panels [online]. 2011. Available from: <http://www.sandwichpanels.org/>. [2011, April].
- [14] Mohan, M.R. Composite Materials and Sandwich Structures .A Thesis. USA
- [15] Newsurfproject [online]. 2011. Available from: [www.newsurfproject.com](http://www.newsurfproject.com) [2011, April].

- [16] O'Donnell, A., Dweib, M.A. and Wool, R.P. 2004. Natural Fiber Composites with Plant Oil-based Resin. Composites Science and Technology. 64: 1135-1145.
- [17] Xiaoming, Li. and Weitsman, Y.J. 2004. Sea-water Effects on Foam-cored Composite Sandwich Lay-ups. Composites. Part B 35: 451-459.
- [18] Kolat, K., Nesar, G., and Özes, C. 2007. The Effect of Sea Water Exposure on the Interfacial Fracture of Some Sandwich Systems in Marine Use. Composite Structures. 78: 11-17.
- [19] Silva, R.V., Spinelli, D., Chierice, G.O., and Tarpini, J.R. 2006. Fracture Toughness of Natural Fiber/Castor oil Polyurethane Composite. Composites Science and Technology. 66: 1328-1335.
- [20] Mirjana, K., Biljana, P., and Petar, S. 2008. Quality of Chemical Modified Hemp Fibers. Bioresource Technology. 99: 94-99.
- [21] Huang, G. 2008. Behaviours of Glass Fibre/Unsaturated Polyester Composites Under Seawater Environment. Materials and Design. 30: 1337-1340.
- [22] James, G.V. 2009. Effect of Water Immersion on Mechanical Properties of Polyurethane Pultruded Composites. Composite & Polycon 2009: American Composites Manufacturers Association.
- [23] Le Troedec, K., et al. 2008. Influence of Various Chemical Treatments on the Composition and Structure of Hemp Fibres. Composites: Part A 39: 514-522.
- [24] Xiaoming, Li. and Weitsman, Y.J. 2004. Sea-water Effects on Foam-cored Composite Sandwich Lay-ups. Composites Part B 35: 451-459.
- [25] Ouajai, S., and Shanks, R.A. 2005. Composition, Structure and Thermal Degradation of Hemp Cellulose after Chemical Treatments. Polymer Degradation and Stability .89: 327-335.
- [26] Berthelot, J.M. 2002. Non-Linear Behaviour of Foam Cores and Sandwich Materials. Journal of Sandwich Structures and Materials. 4(4): 297-352.
- [27] Tritron technology, What is DMA [online] 2011. Available from: <http://www.triton-technology.co.uk/> [2011, April]
- [28] Arun, K.V. 2010. Damage Characterisation of Glass/Textile Fabric Polymer Hybrid Composite in Sea water Environment. Materials and Design. 31(2): 930-939.

- [29] Kokarakis, J. and Taylor, R. 1990. Theoretical and Experimental Investigations of Blistered Fiberglass. Proceeding of the 3<sup>rd</sup> International Conference on Marine Application of Composite Materials. 19-21 Mar. 1990. Melbourne, FL: Florida Institute of Technology.
- [30] Dhakal, ZY., Zhang, M.O. 2007. Effect of Water Absorption on the Mechanical Properties of Hemp Fibre Reinforced Unsaturated Polyester Composites. Composites Science and Technology. 67: 1674–1683
- [31] Kim, H.J., and Seo, D.O. 2006. Effect of Water Absorption Fatigue on Mechanical Properties of Sisal Textile-Reinforced Composites. International Journal of Fatigue. 28: 1307-1314.
- [32] Seki, Y., Sever, K., Sarikanat, M., Sen, I., and Aral, A. 2011. Jute/Polyester Composites: The Effect of Water Aging on The Interlaminar Shear Strength , 6<sup>th</sup> International Advanced Technologies Symposium (IATS'11). 16-18 May 2011. Turkey.



**APPINDICES**

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

## Appendix A

### The Bioresin Data Sheet

**Table A-1 Bioresin properties**

Characteristic	Specification
Gel time @ 25°C	30-45 min
Mixture Viscosity 20 min	2.500-8.000cps
Hardness	60-80 shore A
Polyol/Prepolymer ratio	1:0.43
Working cure time	24 h
Total Polymerization	7-10 days
Cure Max temp (ASTM D-2471)	95°C max.
Density (20°C) (ASTM D-792)	1.0-1.1 g/cm <sup>3</sup>
Mixture Viscosity 25° C (initial)	550-750 cps
Water Absorption % (ASTM D-570)	1.0%

**Table A-2 Biofoam properties**

Characteristic	Specification
Polyol/Prepolymer ratio	1:1.63
Index	105
Cream Time	32-35 sec.
Evolution time	58-65 sec.
Density (average)	40 Kg/m <sup>3</sup>
Water Absorption (average)	0.48%
Dimension Stability (average)	0.098%
Max.Reaction Temperature (average)	>80°C

## Appendix B

### DMA Data

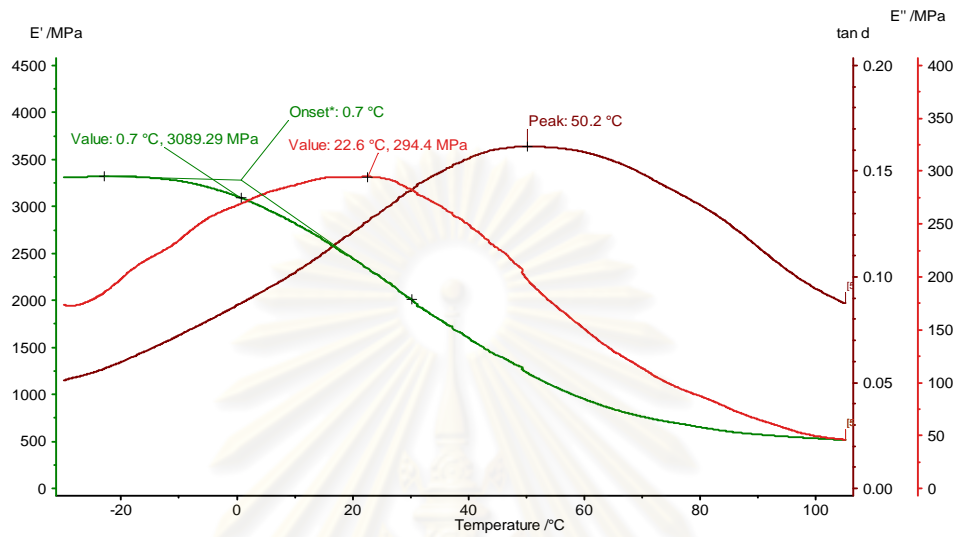


Figure B-1 FF laminated sheet at room temperature .

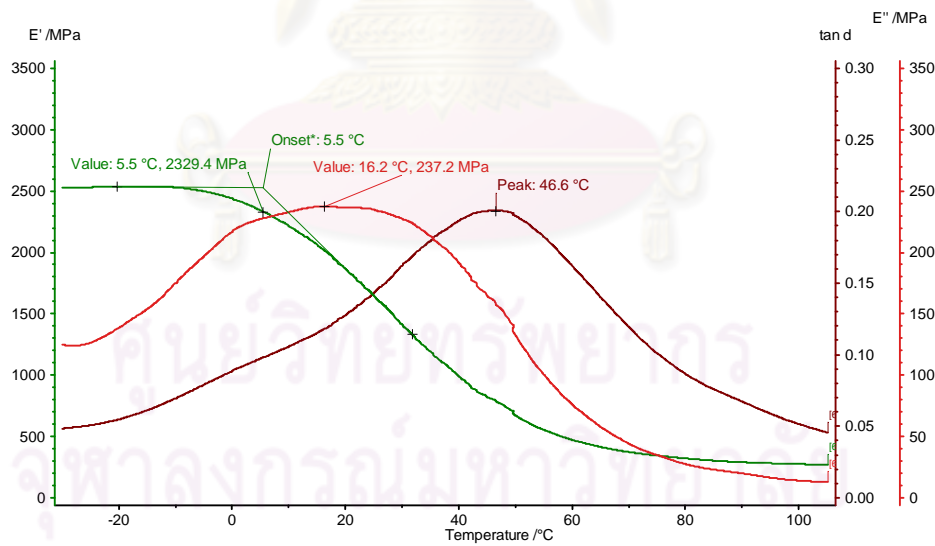


Figure B-2 HH laminated sheet at room temperature.

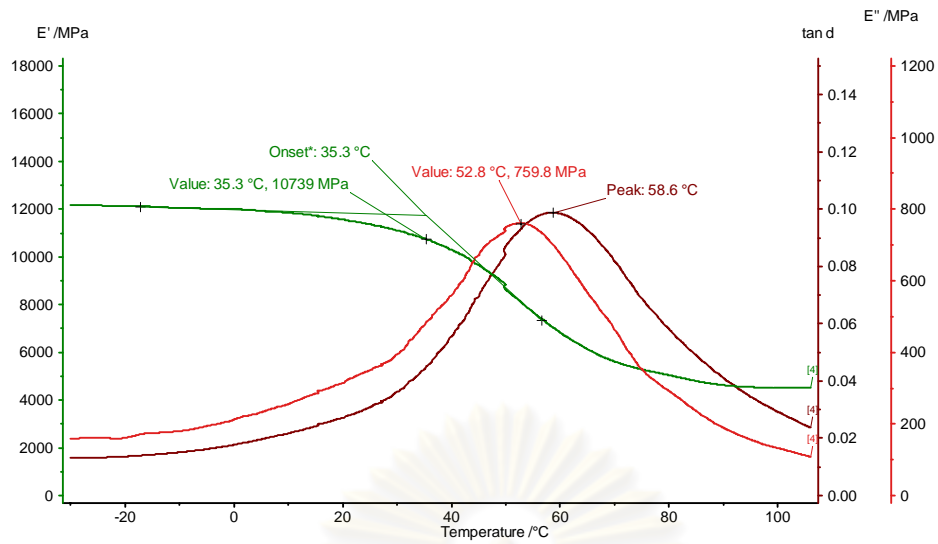


Figure B-3 CC laminated sheet at room temperature.

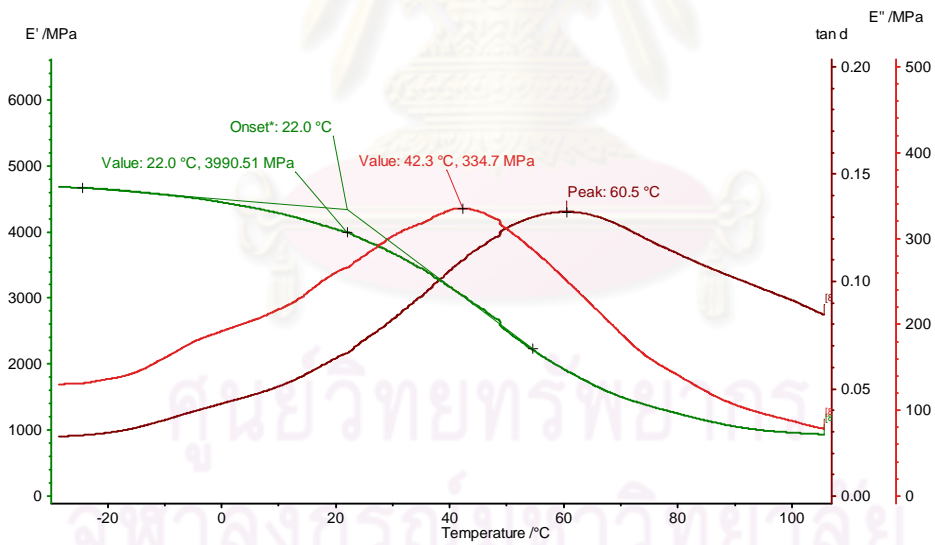
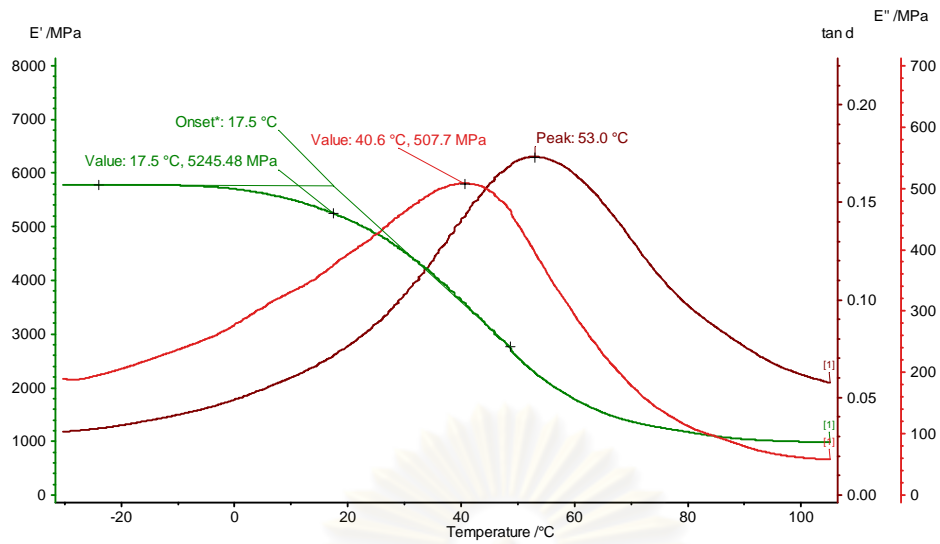
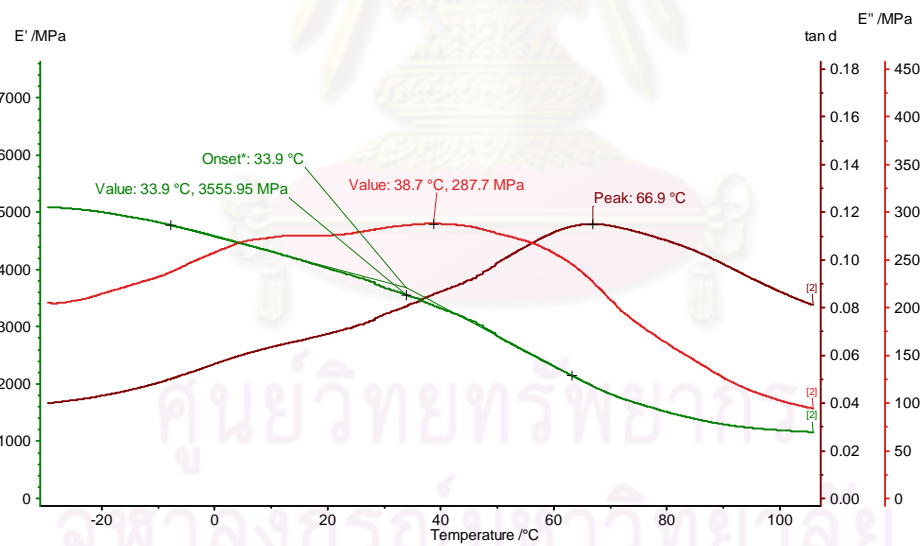


Figure B4 FC laminated sheet at room temperature.

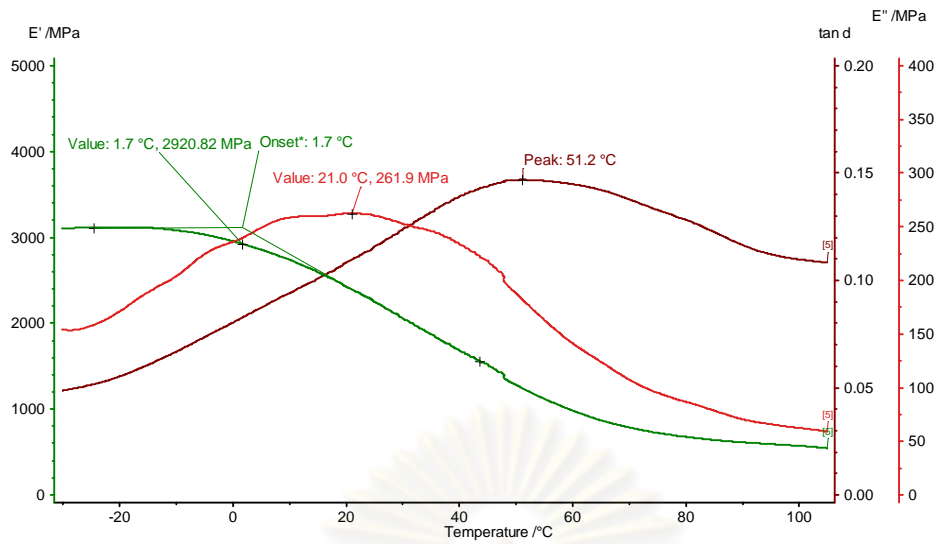




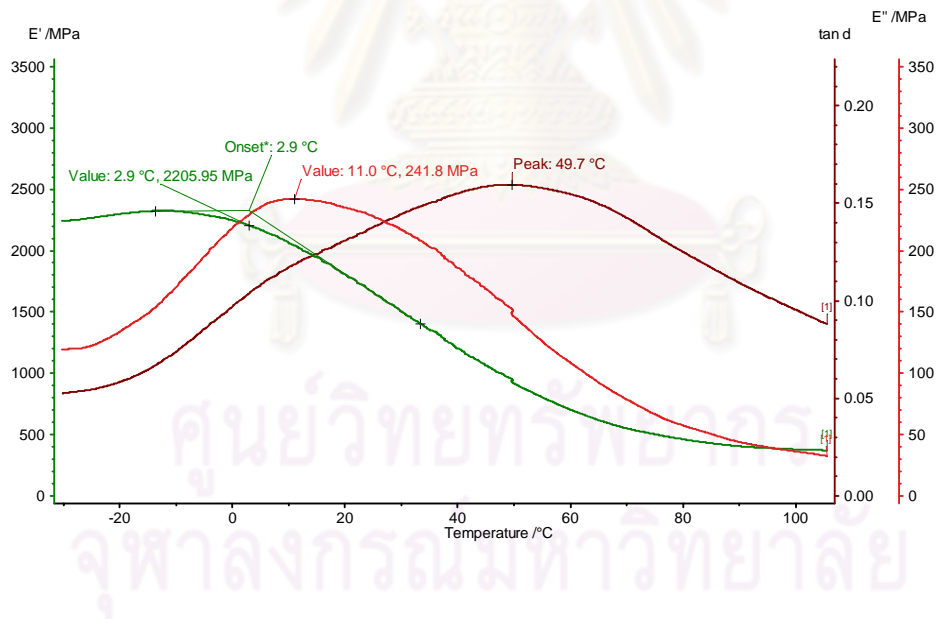
**Figure B-5 FH lamiated sheet at room temperature.**



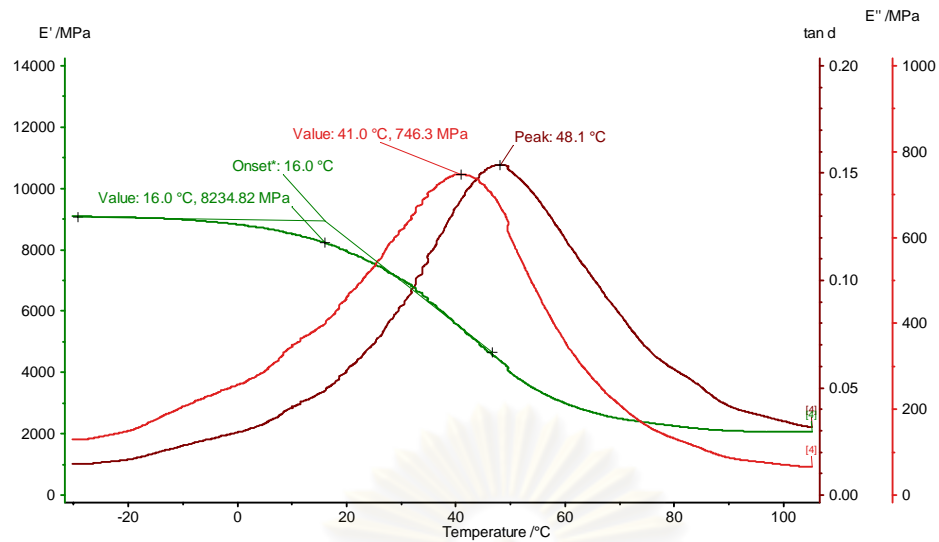
**Figure B-6 TH/TH lamiated sheet at room temperature.**



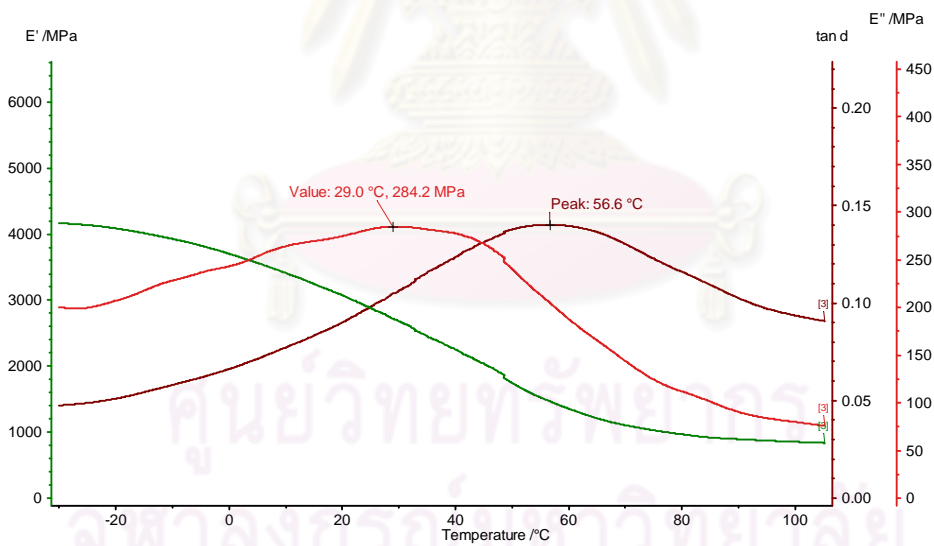
**Figure B-7 FF laminated sheet, after immersion in sea water for 30 days.**



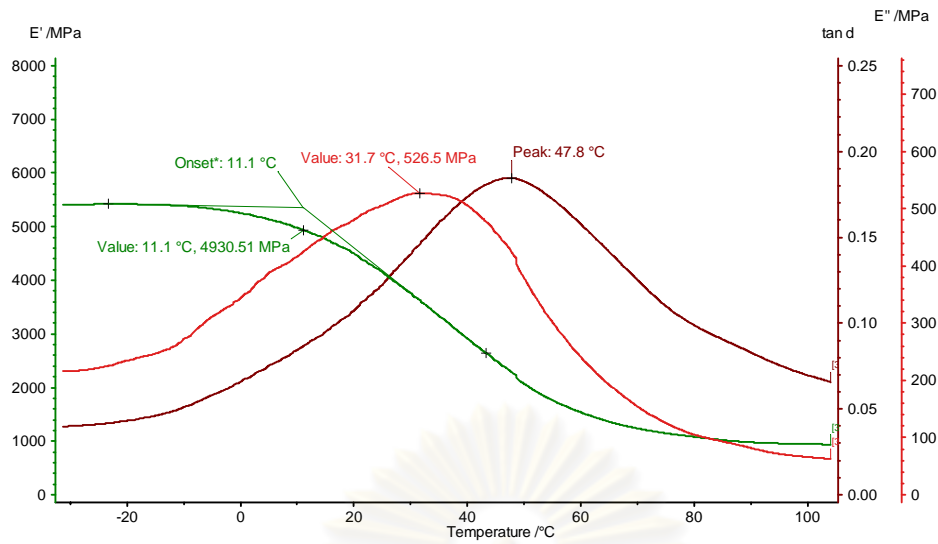
**Figure B-8 HH laminated sheet, after immersion in sea water for 30 days.**



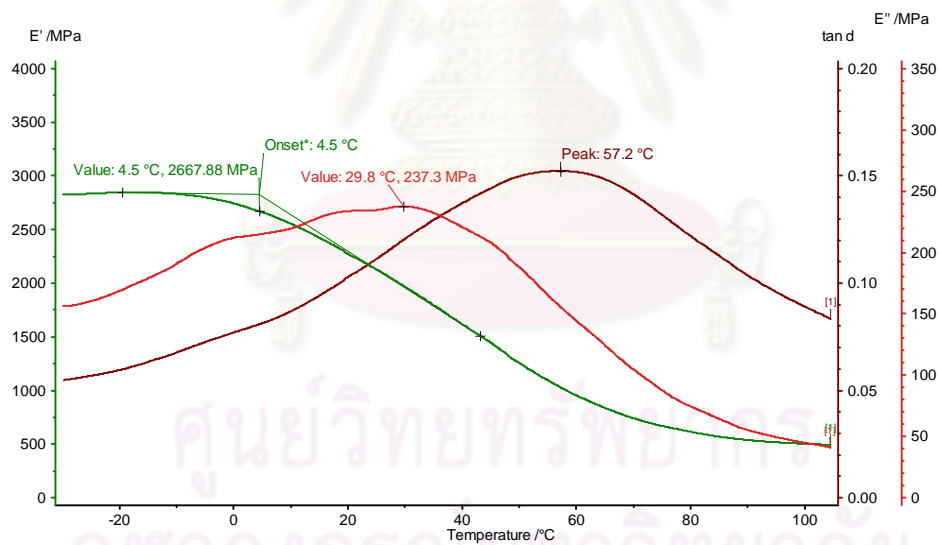
**Figure B-9** CC laminated sheet, after immersion in sea water for 30 days.



**Figure B-10** FC laminated sheet, after immersion in sea water for 30 days.



**Figure B-11 FH laminated sheet, after immersion in sea water for 30 days.**



**Figure B12 TH/TH laminated sheet, after immersion in sea water for 30 days.**

## Appendix C

### ASTM D790 Flexural Test Data

**Table C-1 ASTM D790 for sandwich panel at room temperature.**

Sample	No.	Flexural Strength (MPa)	Flexural Modulus (MPa)	Thickness (cm)	Width (cm)	Length (cm)	Weight (g)	Density (g/cm <sup>3</sup> )
FFBFF	1	4.327	63.06	5.610	6.940	33.30	232.0	0.179
	2	3.452	40.28	5.720	7.030	33.30	224.0	0.167
	mean	3.889	51.67	5.665	6.985	33.30	228.0	0.173
	SD	0.619	16.11	0.078	0.064	0.000	5.657	0.008
	3SD	1.856	48.33	0.233	0.191	0.000	16.97	0.025
HFBFH	1	2.905	49.52	5.670	7.020	33.60	222.0	0.166
	2	3.548	46.24	5.610	7.010	33.40	234.0	0.178
	mean	3.226	47.88	5.640	7.015	33.50	228.0	0.172
	SD	0.455	2.323	0.042	0.007	0.141	8.485	0.009
FHBHF	1	3.151	35.29	5.730	7.040	33.40	228.0	0.169
	2	3.092	48.68	5.550	7.000	33.30	233.0	0.180
	mean	3.121	41.99	5.640	7.020	33.35	230.5	0.175
	SD	0.042	9.465	0.127	0.028	0.071	3.536	0.008
CFBFC	1	3.720	46.02	5.820	6.980	33.20	240.0	0.178
	2	2.856	68.84	5.420	6.830	33.40	226.0	0.183
	mean	3.288	57.43	5.620	6.905	33.30	233.0	0.180
	SD	0.611	16.14	0.283	0.106	0.141	9.899	0.003
FCBCF	1	3.573	54.23	5.520	7.010	33.30	220.0	0.171
	2	3.220	38.39	5.760	7.040	33.40	228.0	0.168
	mean	3.396	46.31	5.640	7.025	33.35	224.0	0.170
	SD	0.250	11.20	0.170	0.021	0.071	5.657	0.002
HHBHH	1	2.634	31.56	5.720	6.970	33.30	220.0	0.166
	2	2.546	31.47	5.720	6.950	33.50	237.0	0.178
	mean	2.590	31.51	5.720	6.960	33.40	228.5	0.172
	SD	0.062	0.062	0.000	0.014	0.141	12.02	0.009
CCBCC	1	3.843	48.42	5.710	7.010	33.20	227.00	0.171
	2	3.985	69.92	5.730	6.950	33.30	240.00	0.181
	mean	3.914	59.17	5.720	6.980	33.25	233.50	0.176
	SD	0.101	15.21	0.014	0.042	0.071	9.192	0.007
B	1	2.555	41.74	5.280	6.950	33.50	188.00	0.153
	2	2.408	37.73	5.390	7.100	33.30	195.00	0.153
	mean	2.481	39.73	5.335	7.025	33.40	191.50	0.153
	SD	0.104	2.836	0.078	0.106	0.141	4.950	0.000
	3SD	0.312	8.508	0.233	0.318	0.424	14.85	0.000

Table C-2 ASTM D790 for sandwich panel after sea water immersion for 30 days.

Sample	No.	Flexural Strength (MPa)	Flexural Modulus (MPa)	Thickness (cm)	Width (cm)	Length (cm)	Weight(g)	Density (g/cm <sup>3</sup> )
FFBFF	1	3.596	42.97	5.510	7.050	33.30	238.0	0.184
	2	3.266	40.29	5.760	7.060	33.30	248.0	0.183
	mean	3.431	41.63	5.635	7.055	33.30	243.0	0.184
	SD	0.234	1.900	0.177	0.007	0.000	7.071	0.001
	3SD	0.701	5.700	0.530	0.021	0.000	21.21	0.002
HFBFH	1	2.977	40.17	5.640	6.970	33.40	220.0	0.168
	2	3.195	38.24	5.870	7.110	33.50	240.0	0.172
	mean	3.086	39.20	5.755	7.040	33.45	230.0	0.170
	SD	0.154	1.366	0.163	0.099	0.071	14.14	0.003
	3SD	0.462	4.098	0.488	0.297	0.212	42.43	0.009
FHBHF	1	3.146	39.17	5.770	6.960	33.50	236.0	0.175
	2	3.100	41.34	5.770	6.940	33.30	232.0	0.174
	mean	3.123	40.25	5.770	6.950	33.40	234.0	0.175
	SD	0.033	1.532	0.000	0.014	0.141	2.828	0.001
	3SD	0.098	4.597	0.000	0.042	0.424	8.485	0.003
CFBFC	1	3.538	41.17	5.760	7.020	33.30	246.0	0.183
	2	3.066	39.33	5.380	6.940	33.30	204.0	0.164
	mean	3.302	40.25	5.570	6.980	33.30	225.0	0.173
	SD	0.334	1.297	0.269	0.057	0.000	29.70	0.013
	3SD	1.003	3.890	0.806	0.170	0.000	89.10	0.040
FCBCF	1	3.359	48.63	5.460	7.040	33.30	244.0	0.191
	2	3.670	48.26	5.660	6.970	33.30	244.0	0.186
	mean	3.514	48.44	5.560	7.005	33.30	244.0	0.188
	SD	0.220	0.264	0.141	0.049	0.000	0.000	0.003
	3SD	0.659	0.791	0.424	0.148	0.000	0.000	0.010
HHBHH	1	2.827	35.75	5.590	6.970	33.50	234.0	0.179
	2	2.902	38.08	5.720	7.000	33.40	234.0	0.175
	mean	2.865	36.91	5.655	6.985	33.45	234.0	0.177
	SD	0.053	1.650	0.092	0.021	0.071	0.000	0.003
	3SD	0.158	4.951	0.276	0.064	0.212	0.000	0.009
CCBCC	1	3.032	40.58	5.680	7.160	33.50	232.0	0.170
	2	3.524	47.54	5.760	7.010	33.40	254.0	0.188
	mean	3.278	44.06	5.720	7.085	33.45	243.0	0.179
	SD	0.347	4.923	0.057	0.106	0.071	15.56	0.013
	3SD	1.042	14.77	0.170	0.318	0.212	46.67	0.038
B	1	2.215	36.61	5.290	6.760	33.30	182.0	0.153
	2	2.387	41.23	5.280	6.960	33.40	192.0	0.156
	mean	2.301	38.92	5.285	6.860	33.350	187.0	0.155
	SD	0.121	3.266	0.007	0.141	0.071	7.071	0.003
	3SD	0.364	9.798	0.021	0.424	0.212	21.21	0.008

## Appendix D

### FTIR Data

#### Characterization of Polyol and Isocyanate (MDI)

**Table D-1** IR spectrum data of castor-oil based polyol (Rescon 503 garicin) for laminate

Vibration assignments	Wave number (cm <sup>-1</sup> )
-OH stretching	3368.75
CH- stretching (C=C-H)	3008.25
C-H stretching	2925.47, 2854.34
C=O stretching	1629.49
C-O-C stretching	1167.48
C-OH stretching	1040.39
C=C stretching	909.02, 873.61, 723.81

**Table D-2** IR spectrum data of MDI (Rescon 503 proquicin) for laminate.

Vibration assignments	Wave number (cm <sup>-1</sup> )
NH stretching (Amides)	3395.47
CH- stretching	3027.14, 2908.79, 2840.72
C=O, C=N	1901.58, 1776.96, 1719.13
CO-NH <sub>2</sub>	1414.92
C-N	1232.21, 1018.38-1142.18
C-NH <sub>2</sub>	1039.48
C=C	1521.27-1608.52
Aromatic ring	811.07

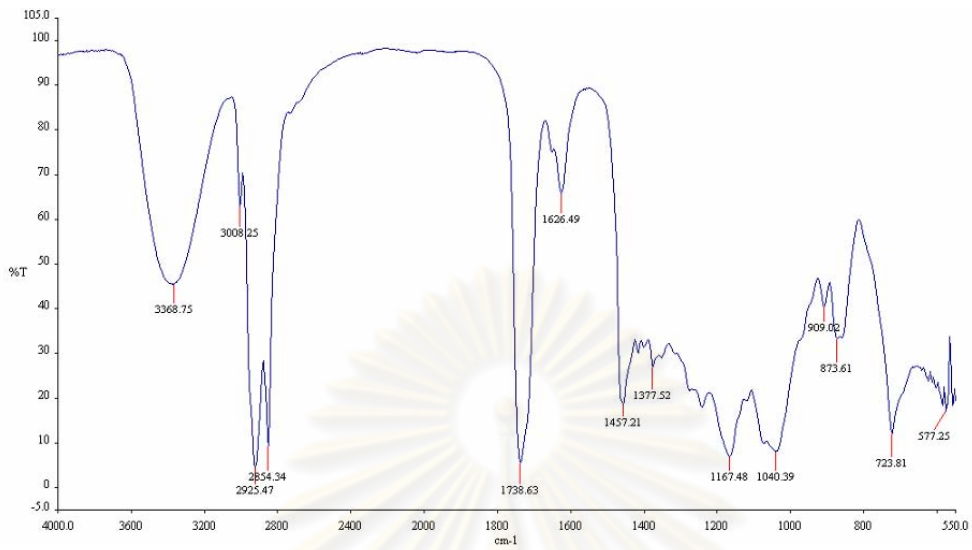
**Table D-3** IR spectrum data of castor-oil based polyol (Respan D40garicin) for foam.

Vibration assignments	Wave number (cm <sup>-1</sup> )
-OH stretching	3368.93
C-H stretching	2925.98, 2854.64, 1456.74
C=O stretching	1736.70
COO stretching	1624.49
C-O-C stretching	1260.46
C-OH stretching	1038.82
C=C (cyclic)	1568.31
-CH <sub>3</sub>	1377.52
C=CH stretching	909.25, 878.62, 803.28

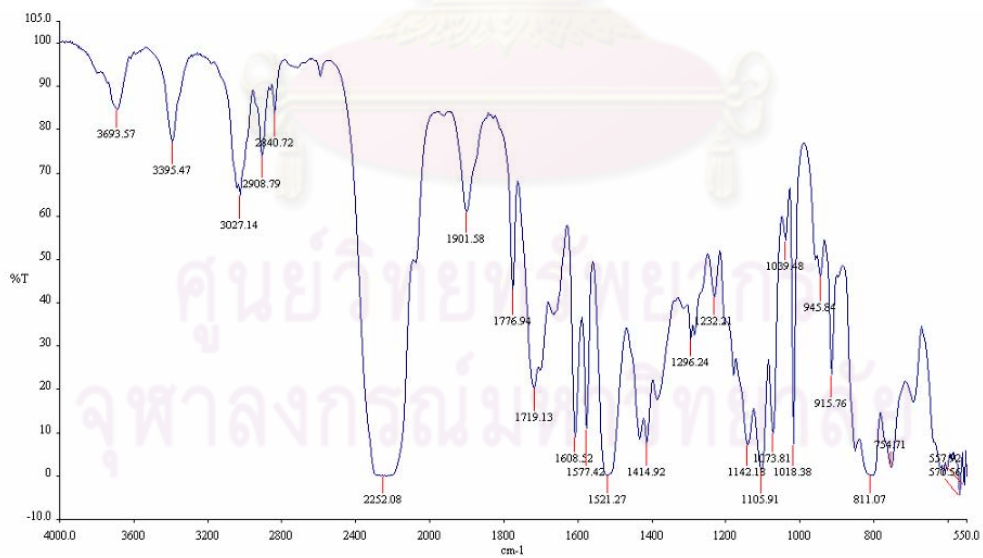
**Table D-4** IR spectrum data of MDI (Respan D40 proquicin) for foam.

Vibration Assignments	Wave number (cm <sup>-1</sup> )
NH stretching (Amides)	3395.24
CH- stretching	3027.55, 2907.83, 2840.09
C=O, C=N	1901.38, 1776.90, 1715.39
OCH <sub>3</sub>	2260.98
CO-NH <sub>2</sub>	1414.72
C-N	1296.35-1106.52
C-NH <sub>2</sub>	1041.37
C=C	1522.48-1608.15
Aromatic ring	693.28-854.05

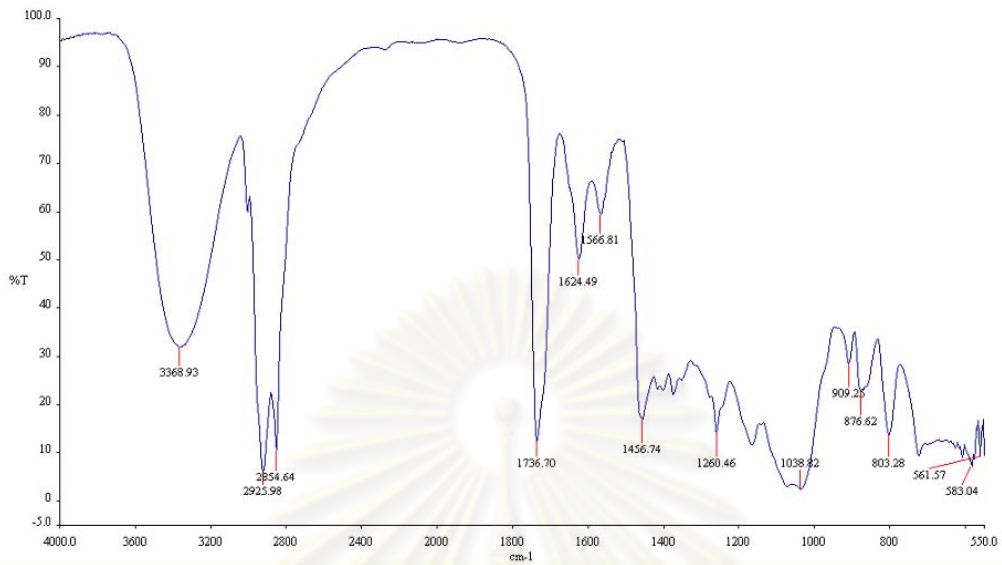




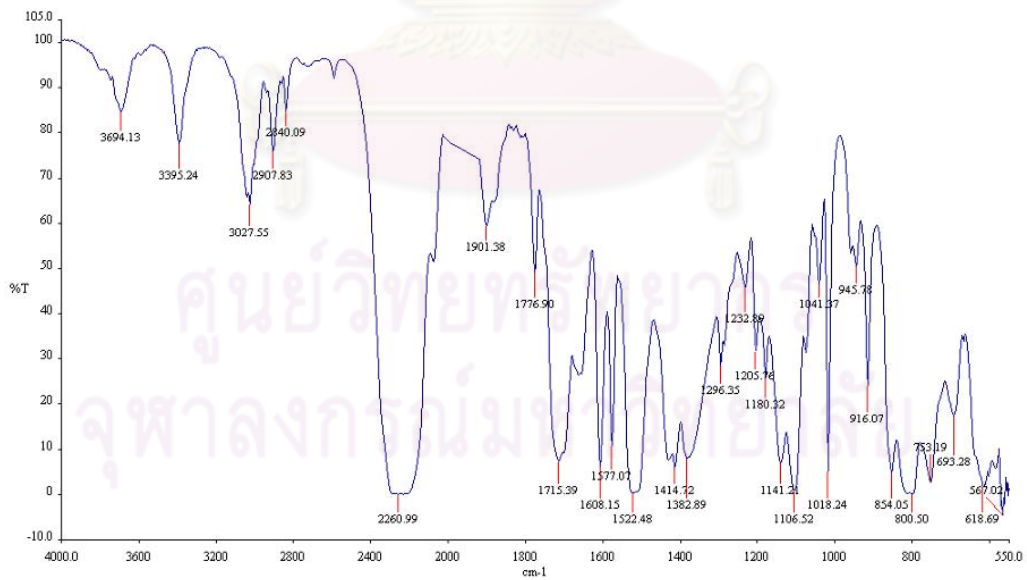
**Figure D-1** FTIR spectrum of Rescon 503 Garicin (castor oil based polyol) for laminate.



**Figure D-2** FTIR spectrum of Rescon 503 Proquicin (MDI) for laminate.



**Figure D-3** FTIR spectrum of Respan D40 Garicin (castor oil based polyol) for foam.



**Figure D-4** FTIR spectrum of Respan D40 Proquicin (MDI) for foam.

## Appendix E

### Mercerization of Natural Fabric

Table E-1 shows the weight and thickness changes of hemp fabrics (24 pieces) mercerized with 5% NaOH. The weight was reduced after treatment and thickness was increased. Wax and other impurities were removed from fabrics.

**Table E-1** Hemp fabrics mercerized with 5%NaOH

No.	% Weight change	% Thickness Change
1	7.0	13.2
2	8.1	12.5
3	7.3	17.8
4	7.0	14.7
5	7.3	14.3
6	6.3	14.7
7	7.2	15.4
8	11.2	14.1
9	8.4	14.1
10	7.0	13.0
11	6.4	18.1
12	7.5	13.2
13	7.4	18.6
14	7.3	13.8
15	7.2	15.1
16	6.0	14.9
17	7.1	15.4
18	6.2	14.1
19	6.3	15.4
20	6.6	16.7
21	6.6	14.9
22	6.7	15.4
23	6.0	14.7
24	5.4	16.0
<b>Mean</b>	7.1	15.0
<b>SD</b>	1.1	1.6

## Appendix F

### Natural Fabric Sandwich Composites

From the research work, it can be concluded that cellulose fabric can be used as reinforcement of composite compared with treated hemp fabric that was difficult to process in production. The cellulose fabric composite was fabricated into surfboard as shown in Figure F-1. In this application, the standard glass fabric was replaced by cellulose fabric. The final surfboards have excellent surface finishing, no weight increase, and very good performance. The first surfboards made of cellulose fabrics had an excitement among surfers.



**Figure F-1** Mr. Danu Chotikapanich (CEO of Cobra Groups) wins award on JEC composite asia.

## VITA

Miss Jiraporn Oupra was born on June 28, 1982 at Muang Chiangrai District, Chiangrai Province. She received her Bachelor's degree in Petrochemicals and Polymer material, Faculty of Engineering and Industrial Technology, Silpakorn University in 2004. She has pursued Master's Degree in Petrochemistry and Polymer science, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in November 2008 and completed the program in May 2011.

Presentation: "Natural Fiber/Castor oil polyurethane sandwich biocomposites" proceedings of The Polymer Conference of Thailand (PCT-1) 2010, Bangkok, Thailand, October 7 - 8, 2010.



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