



# Liquid Absorption in Composite

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**Abstract:**

This thesis work aims to study the water absorption in composite materials including wood and composites/thermosetting resin under condition of room temperatures and atmospheric pressures. The testing specimens for water absorption in composite were prepared following to the standard measurement of ASTM D570 and ISO 62. The composite laminate used in this research was built from glass fibers and the resin of vinyl-ester ATLAC E Nova M6215. The data sheet of this resin shows a noticeable value of water absorption property which need to be measured. At first, the study of water absorbed into wood samples of Balsa and Birch was conducted by immersing the samples in tap water until the saturation point. The process of water absorption in the samples of wood was found to approach the behavior of non-Fickian diffusion. The resulting data observed by the mass change during soaking time is analyzed and modeled following to the mathematical viewpoint of Fick's law diffusion and the empirical model of Peleg. The diffusion coefficient to evaluate the water uptake in two different wood materials of Birch and Balsa, were determined as  $8.23 \times 10^{-4}$  and  $5.67 \times 10^{-3}$  m<sup>2</sup>/s, respectively. Besides, the resulting parameter of non-linear regression analysis according to Peleg model was also obtained. The value of root mean square error (RMSE) demonstrates the better suitability of Peleg model for modelling the experiment data of water absorption in case of Birch wood (RMSE of 12.47 %) comparing to the case of Balsa wood (RMSE of 84.6%).

For the study of water absorption in composite/thermosetting resin samples, the alternative spectroscopic methods including UV-visible spectrophotometry and Fourier Transform Infrared Spectroscopy (FTIR) were investigated. The resulting spectra from the UV-visible-NIR spectrophotometer for specimens of vinyl ester resin indicate the effect of water molecules in the wavelength of 300 nm to 360nm. In the other hand, the outcome spectra of composite resin samples by using method of FTIR point out the evident impact of water to composite samples for a long period of soaking time. Two regions wavenumber involved to the increment of water absorption in composite resin samples include: the wavenumber from 2840 cm<sup>-1</sup> to 3500 cm<sup>-1</sup>, which is known as the region of OH stretching; and the wavenumber from 1630 cm<sup>-1</sup> to 1780 cm<sup>-1</sup> which corresponds to the bending vibration mode of water molecules existed in composite structure. Furthermore, the impact of different grinding paper grits when polishing the surface of composite samples was also performed by the FTIR spectra. In general, the intensity of absorbance peaks in OH stretching region intends to increase when increasing the polishing protocol on surface of composite samples. After 15 days of exposure in water, composite samples polished by paper grit of

4000 has a highest increase of absorbance intensity with 470% at the peak  $2924\text{ cm}^{-1}$ , while the sample polished by the paper grit of 320 has the lowest increase of intensity with 260%.

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## Equations

$\frac{dC}{dt} = \frac{d}{dx} \left( D \cdot (C) \cdot \frac{dC}{dx} \right)$ (1)	19
$J = -D \cdot \Delta x$ (2)	25
$J = -D \cdot \frac{\partial M}{\partial x}$ (3)	25
$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \cdot \frac{\partial C}{\partial x} \right)$ (4)	26
$\frac{\partial C}{\partial t} = \left( D \cdot \frac{\partial^2 C}{\partial x^2} \right)$ (5)	26
$M_t = M_0 + \frac{t}{K_1 + K_2 \cdot t}$ (6)	26
$R = \frac{dM}{dt} = \frac{K_1}{(K_1 + K_2 \cdot t)^2}$ (7)	26
$R_0 = \left. \frac{dM}{dt} \right _{t=0} = \frac{1}{K_1}$ (8)	26
$M _{t \rightarrow \infty} = M_e = M_0 + \frac{1}{K_1}$ (9)	26
$m_W = A \cdot \sqrt{t}$ (10)	31
$\frac{M_t - M_0}{M_s - M_0} = \frac{2}{\sqrt{\pi}} \cdot (S/V) \cdot \sqrt{D \cdot t} = \alpha_b \cdot \sqrt{t}$ (11)	31
$D_e = \frac{\pi}{4} \cdot \left( \frac{V}{S} \right)^2 \cdot (\alpha_b)^2$ (12)	31
$RMSE = \sqrt{\frac{\sum_{i=1}^n (M_{r,i} - M_{p,i})^2}{N}}$ (13)	32

## List of Symbols

A	Coefficient of water sorption, $\text{kg}/(\text{m}^2\text{s}^{1/2})$
C	Concentration, $\text{mol}/\text{m}^3$
D	Diffusion coefficient, $\text{m}^2/\text{s}$
$m_w$	Amount of water absorption, $\text{kg}/\text{m}^2$
$M_0$	Initial water content of material, %
$M_t$	Water content into material, %
$M_s$	Water content of material at saturation state, %
J	Diffusion flux or mass current, $\text{kg}/\text{s}$
$K_1$	Peleg rate constant, $\text{h}/\%^{-1}$
$K_2$	Peleg capacity constant, $\%^{-1}$
t	Time, hour
x	Position, m
V	Volume of sample, $\text{m}^3$
S	Surface area of sample, $\text{m}^2$
RMSE	Root mean square error

# FOREWORD

This thesis was written for my Bachelor degree of Materials Processing Technology in Arcada University of Applied and Sciences. First of all, I would like to thank to my thesis supervisor, Rene Herrmann, who not only has been guiding as well as advised me on every step regarding the thesis research but also supported me wholeheartedly so that I could bring this thesis to its finalization. Moreover, my gratitude goes also to my examiner, Stewart Makkonen-Craig, who also offered me the instructions during working in the Chemistry Laboratory and the guidance to perfect the thesis.

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# 1 INTRODUCTION

## 1.1 Background

This thesis focuses on the water absorption in different composite materials. It was studied by using Peleg model and Fick's law to figure out a mathematical model fitted to the water absorption process as function of time involving the saturation point. The experiment was conducted using wood samples as a kind of natural composite. Furthermore, the experiments to investigate water uptake in composite resin materials were carried out in this study by using the methods of UV-visible spectrophotometry and Fourier Transform Infrared Spectroscopy (FTIR).

Nowadays, composites are considered as one of the most important materials in a great number of industries because of its advantage in high-performance products. These materials are applied in many fields in life, from transportation, sports, foods, medical, construction to scientific fields such aeronautics and cosmology. Due to the advanced properties as well as the ability of being customized to a specific request, composite materials play an essential role in many applications which require the lightweight structures. One of the important application fields of glass fiber reinforced polymer composite worth mentioning here is the wind industry. To take full advantage of the energy from high wind speeds and reduce the land usage, the location to install the wind farms is ordinarily offshore. Since the cost for the installation of wind farm is expensive, it is necessary to optimize the operating capacity of the wind turbines so that the wind energy capture is maximized. This means that the turbines size needs to be increased. During the process of wind turbines design, the elastic characteristics of the turbine blades are considered as a constraining parameter because the value of strain in the turbine blades requires to be minimized to resist the degradation impacts of fatigue during their life expectancy. However, the working environment of offshore is a specific challenge to operation of wind turbines because of its high content of moisture, which can lead to the degradation of elastic properties of composite materials used for wind turbine blades. Moreover, this issue also increase the strain of turbine blades during operation and hence, the lifetime of these blades can be reduced. Consequently, to design and optimize the operation capability of turbine wind in the moisture conditions as offshore, it is important to determine and understand the influences of moisture on the properties of composite materials [1].

In this research, the composite laminas used in experiments are built from textile with a highly un-iso-tropic structure. The fibers in its structure are minerals or glass. The matrix is considered as a polymer, called as vinyl-ester ATLAC E Nova M6215. This specific resin is used for highly corrosion resistant applications due to its ability of resisting any form of liquid absorption. Thus, this composite is often used to work as the wind turbine plates. As mentioning earlier, it is necessary to study and understand the effect of water absorption in this composite material when working in wetted environment for a long time. The water absorption in this case could be explained by the diffusion mechanism. The diffusion is driven by concentration differences. This can be taken place base on the osmosis. Furthermore, it is feasible to define these other factors which affect this process.

## 1.2 Aims

The purpose of this study includes:

- Conduct the experiment of water absorption in wood materials of Birch and Balsa woods under condition of room temperatures and atmospheric pressures by using a scale to measure the data of mass change. The outcome will show the measure of water absorption rate and the saturation limit of materials.
- Analyze the resulting data based on the Fick's law and the empirical model of Peleg to calculate and appraise the diffusion of water into wood materials. It is desirable to figure out a suitable mathematical model that describes the absorption process as function of time involving a saturation point.
- Conduct the experiments of water absorption in composite of vinyl ester resin in condition of room temperature and atmospheric pressures following to the standard measurement of water absorption of composite materials in ASTM D570 [2] and ISO 62 [3]. The mass change is extremely small to be detected by laboratory scale, hence it is unexpected to measure the water absorption in composite resin of vinyl ester by the mass change.
- Analyze the water uptake in composite of vinyl ester resin samples by using the alternative spectroscopy approaches of UV-visible spectrophotometry and Fourier Transform Infrared Spectroscopy (FTIR).

- Observe the resulting spectra collecting from these spectroscopy methods; and evaluate the effect of water uptake in composite resin materials as well as the suitability of these methods when using to study the water absorption in composite resin.

### **1.3 Motivation**

The motivation of the thesis is to determine the effect of liquid absorption on composite laminates. It is widely acknowledged that setting composite materials in condition of wet environment is able to cause the liquid absorption in materials structure. The absorbed liquid components may change the composite structure. As a result, this problem may not only create alterations of chemical and physical properties but also degrade mechanical properties of materials. In the other words, this issue reduces the life cycle of materials, or the water absorption is aging. The deterioration of the three composite phases including the fibers, the matrix and the interface is the reason of the reduction in strength and stiffness of composite materials [2]. The amount of liquid absorption into composite materials is the deciding factor of the degradation which is variable following to the component structure and other inherent attributes of the composite. In some condition the degradation of composite is too significant to be neglected when calculating for a design of composite application, especially when materials are applied in a moist environment for a long period [3].

Recent researches have approached to this field of composite materials by various methods depending on distinct situations. In this thesis, the study of liquid absorption into composite structure and its effect to composite properties were carried out. The result of study was figured out by combining numerous data analysis methods. Here, a generally used natural material wood was selected as a compared material and the composite material of glass-fabric reinforced epoxy laminate of vinyl ester resin was picked up for the experiment of water absorption.

## 2 LITERATURE REVIEW

### 2.1 Composite material

The concept of composite material is defined as a material which is composed from the combination of two or more different materials to create a new better properties material than the former individual components [4]. In opposition to metallic alloys, when combining into a composite material, each constituent element maintains its specific chemical, physical as well as mechanical properties. Because of its structure, the improvement of strength and stiffness are the key advantages of composite materials. Additionally, comparing to bulk materials, composite materials have the low density which allows reducing the weight of finished product. It is comprehensible to take an example of the combination between rocks and cement to turn out concrete which have the equivalent strength of rock while it is easier to be formed in a mold than carving rock. By this way, the properties of concrete are increased in not only strength as well as ease of formation but also physical, chemical and mechanical properties with an appropriate association of materials [4] [5].

The fundamental parts of composite include a reinforcement and a matrix. High strength structure of most composites is constructed from strong fibers joined together in a matrix. Besides, the usage of particles and flakes as reinforcement are also taken place, however, they do not have as much effect in composite structure as fibers. To be considered as the natural oldest composites, wood is built up from a structure of lignin matrix of cellulose fibers while other synthetic composites originated with the usage of straw reinforced clay to create bricks and pottery in construction. The contemporary composites are provided from metal, ceramic as well as polymer binders reinforced combining with a numerous fibers or particles. The usage of polyester resin reinforced with glass fibers in producing fiberglass boats is an example of modern composite application. Additionally, there are different ways to build a composite, sometimes, distinct materials are layered to construct a higher properties product, for instance the sandwich formation where a light core material is set up by creating sandwich construction between a stiff face and strong face materials [4]. As shown in Figure 1 is the simulation of a cross-section of a cross-plyed carbon/epoxy composite laminate and a carbon/glass fiber resin composite rod.

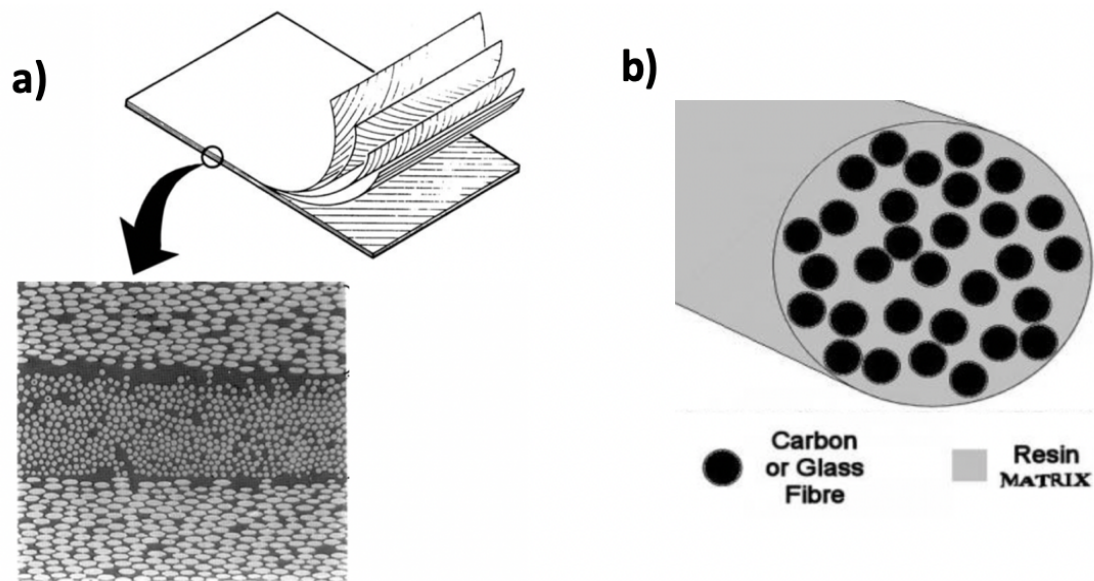


Figure 1: a) Cross-section of a cross-ply carbon/epoxy composite laminate [5];

b) Cross-section of a carbon/glass fiber resin composite rod [6]

In composite structure, the reinforced part grant the strength as well as the stiffness. In general, the reinforcement structure provides the higher strength and stiffness than the matrix. Fiber or particulate is typically used as the reinforcement. The classification of composite materials can be determined following to a variety of approaches, the key elements involved to this issue are:

- Reinforcement
  - Continuous long fibers
    - ✚ Unidirectional fiber orientation
    - ✚ Bidirectional fiber orientation (for example: woven, stitched mat, etc.)
    - ✚ Random orientation (for example: continuous strand mat)
  - Discontinuous fibers
    - ✚ Random orientation (for example: chopped strand mat)
    - ✚ Preferential orientation (for example: oriented strand board)
  - Particles and whiskers
    - ✚ Random orientation
    - ✚ Preferential orientation
- Laminate configuration
  - Unidirectional lamina: a single lamina (also called layer or ply), or several laminae (plural) with the same material and orientation in all laminae.



- Laminate: several laminae stacked and bonded together, where at least some laminae have different orientation or material.
- Bulk composites: for which laminae cannot be identified, including bulk molding compound composites, particle-reinforced composites, and so on.
- Hybrid structure
  - Different material in various laminae (for example: bi-metallic)
  - Different reinforcement in a lamina (for example: intermingled boron and carbon fibers)

## 2.2 Water absorption in composites

There are several factors effected to the water absorption ability of a composite, however the essential factors are explained based on its physical and chemical properties. Polymeric composites comprise polymeric polar groups which attract water molecules. As a result, the number as well as the position of these polymeric polar groups on a polymer chain in material structure can create the influence on water absorption. By taking full advantage of this point, chemical methods such as adding specific groups are applied to modify the sensitivity of a material [7] [8] [9].

The amount of absorbed water into material structure is depended on the accessible volume of the film. Volume of the film is able to be defined by three constituents including the occupied, interstitial and hole free volume [10, 7]. The occupied volume is considered as the volume inside material without any capacity. The interstitial volume is defined as the free space that originates in the vibrational energy of the polymer bond while the hole free volume is stems from voids caused from polymer chain relaxation. Being considered as the possibility of absorbed water as well as its transport into materials, pores are represented by these two types of free volume. So, the determined factors to water absorption is the size and density of pores [11]. Besides, in polymeric composite structure, the arrangement in the polymer chains decides the state of materials whether they are amorphous or crystalline, by this way it support to determine the size and density of the pore. Another factor worth mentioning here is film thickness which related to water absorption. Researches in thin film are shown that their behavior of water uptake is dissimilar to the bulk materials [9]. According to Bond, the description of water uptake locations and mechanisms is shown as Figure 2 [12]:

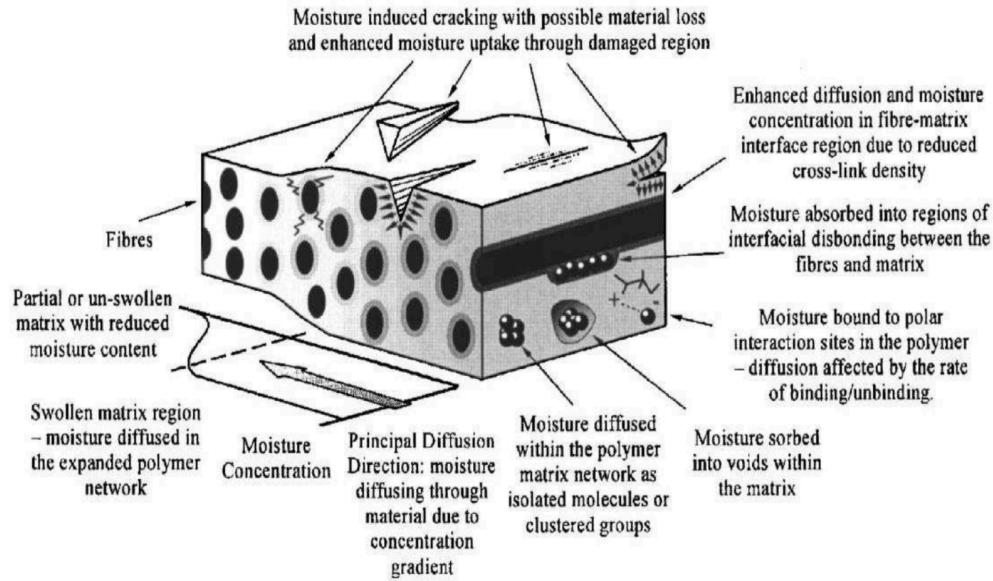


Figure 2: Water absorption mechanisms in polymeric composites [12]

In polymeric composite structure, aside from the existence of well-built bonds between its monomers in a chain formation, there are also strong bonds among its chains defined as cross-links. The hydrogel structure, known as a three-dimension network in hydrophilic polymer, allows to absorb an enormously large amount of water while remain the its structure as well as insolubility due to chemical and physical cross-links of polymeric chains. The degree of cross-link is the key aspect affected to the hygroscopic characteristic of the polymeric composite [13] [14]. By taking full advantage of this property, to modify the solubility of a polymer, the cross-linking or blending combining to a hydrophobic polymer is used [15].

Another factor affected to water absorption is temperature [11]. To explain this point, the most important definition need to be mentioned here is the glass transition temperature,  $T_g$ , which is considered as specific temperature at which the polymer chains start to move or be flexible. At this point, the transition of the amorphous region from rigid to flexible take place, this is also known at the border of the transformation from solid state to rubbery state [16]. When the temperature of a polymeric composite decreases to under  $T_g$  point, the behavior of the composite is more fragile which is considered as “glassy”. The glass transition,  $T_g$ , is regarded as a characteristic physical property pf a polymeric composite which is distinct from different composite. The water diffusion in films above  $T_g$  work generally more speedily than below. As a result, to optimize the amount of water

absorbed into materials, the aspect of temperature is referred as controllable feature based on each individual polymeric composite as well as its application [11].

Recent researches shows that the additives are added to polymeric composite materials to modify their expected properties. Several common kinds of additive used to adjust water absorbed property of a material are rheology modifier, pigments or dispersion agents [10] [11]. These additives predominantly affect the available free volume in material structure [17]. Other essential factor affect water absorption is processing conditions, for instant anneal sequence [9]. There are numerous factors involved in water uptake, however, verifying the precise details how system gets influence on this issue is also intricate. Consequently, it is necessary to carry out researches on each specific set of conditions to figure out the influence measure in water absorbed of each condition.

### 2.3 Water diffusion in composites

To explain the notion of water diffusion, it is indispensable to interpret several definitions. Firstly, the “*Absorption*” word is used to describe the uptake of water as well as vapors by a material. Additionally, the definition of “*Sorption*” is mostly used as an alternative expression of absorption, however it is preferred to be applied in case of the water uptake is in the equilibrium state. In different circumstance, the “*Desorption*” word describes the phenomenon of water or vapor losses by a material. Furthermore, the notion of *Permeation* should be also mentioned here. This phenomenon is known as the conveyance of water and vapors through a material.

The diffusion mechanism of water across a polymeric composite can occur according to Fickian or non-Fickian kinetics [11] [17]. The transport following to Fickian happens mostly in rubbery materials which allow water infiltration due to the flexibility of chains inside its structure [18]. A perfect condition is assumed that there are non-interference from the influence of polymer chain movement. This can be explained by the negligibility of the water diffusion speed comparing with the relaxation. This process is described by the equation called as FICK ‘s second law [19]:

$$\frac{dC}{dt} = \frac{d}{dx} \left( D(C) \frac{dC}{dx} \right) \quad (1)$$

where  $C$  is referred as the concentration of water,  $t$  is time and  $x$  is the position in the composite film following to the diffusion dimension, and  $D$  is the polymeric water diffusivity or considered as the diffusion coefficient which is independent of the position, time as well as the water concentration. The accumulation  $M$  of water absorption into composite material is a curve which contrast to  $t^{1/2}$  is linear. The absorbed water curve ultimately gradually reach to a saturated state,  $M_{\infty}$ . The illustrations of diffusion in different classes are showed in Figure 3 [20].

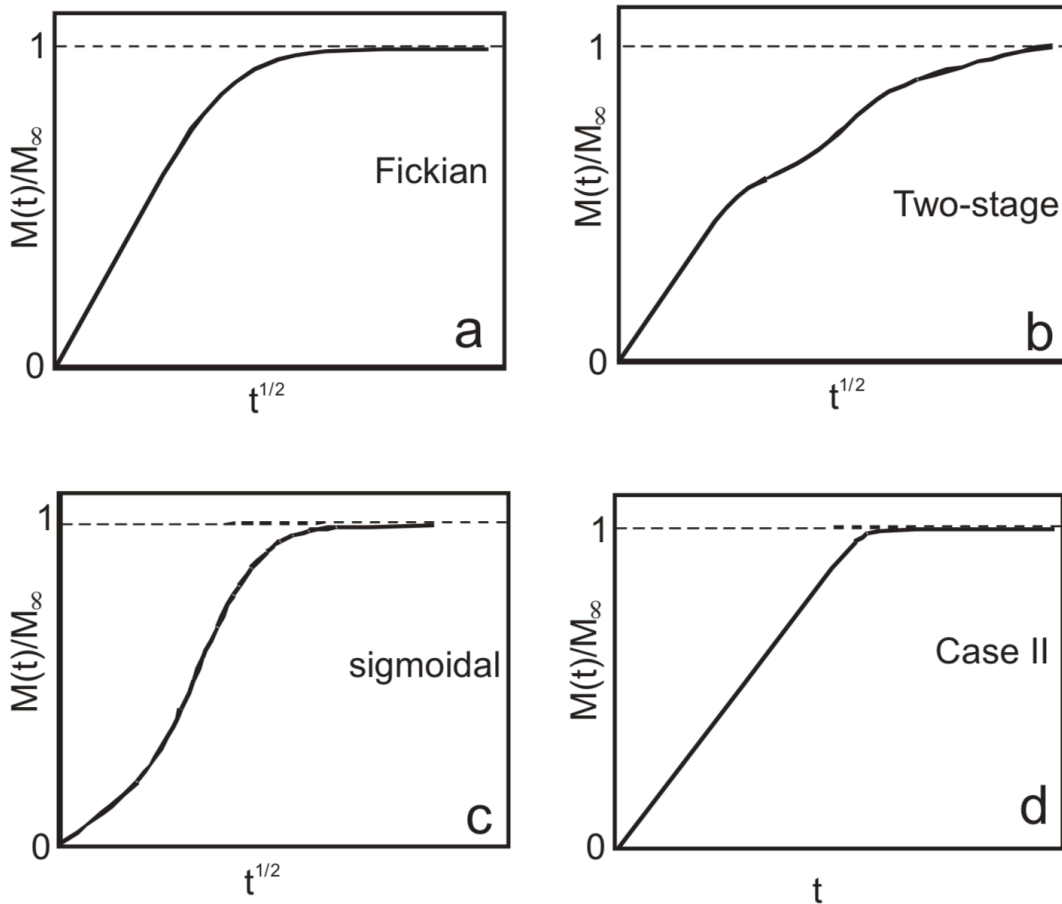


Figure 3: Classification of water diffusion, a) Fickian b) Two-stage c) Sigmoidal d) Case II [20].

Fickian diffusion is generally recognized as a common description of diffusion through an environment or a material. Nevertheless, in various polymeric composite networks, several essential assumptions in the equation are not suitable. One of the key point worth mentioning here is that when exposing to water, a polymeric composite is usually not in equilibrium due to its relaxation of polymer chains. This often takes place in glassy polymeric composites [17] [18].

In the study of Fickian diffusion aspect, water can diffuse into composite materials by atomic movement. The water molecules are supposed as spherical structure which has the approximate radius of 0.096 nm. The random movement of these molecules through the composite materials follows to Brownian motion and place to the voids of materials structure including sub-microscopic network and free volume through concentration gradient. As shown in Figure 3a is the theoretical Fickian plot of  $M(t)/M_{\infty}$  corresponding with the function of  $t^{1/2}$ .

The existence of water free volume in polymeric composites structure is considered as additive which creates the growth of total free volume of composite materials [20]. The estimated void diameter in material structure is required to be larger than  $3\text{\AA}$  so that it is possible to contain a water molecule [21]. Many researches showed that the real pore dimension for diffusion is in the range of  $3\text{-}5\text{\AA}$  [22]. This progress is known as vacancy diffusion, and the thermal energy of atomic vibrations as well as the surrounding radiate temperature are adequate to water infiltration. In the diffusion progress, the movement of free water molecules is not dependent on each other. In addition, the chemical or physical interaction between polymeric composite molecules and those of free water is not destitute [23].

On the other hand, many circumstances are mentioned as non-Fickian when the obtained plots are shown as anomalous. Several frequent non-Fickian cases in water absorption worth mentioning here are Two-stage, sigmoidal and Case II which are also illustrated in Figure 3. As being shown in Figure 3b, the illustration is referred as Two-stage diffusion which is distinguished by a speedy Fickian absorption at the beginning and slow Fickian behavior later, non-Fickian progress is activate after the occurrence of relaxation in polymeric composite matrix. It is also shown in Figure 3c as sigmoidal sorption behavior which has the curve of S-shape and an existence of inflection point. During this type of diffusion, a strain is created from the transitory swelling of the polymeric composite which involves in its diffusion [17]. As a result, this progress is called as stress-dependent diffusion.

To observe abnormalities in different water diffusion progresses, the equivalence of the water mobility in polymeric composite as well as its stress relaxation rate are considered [23]. These extraordinary things happening in these types of water diffusion are also illuminated by a combination between Fickian diffusion theory and the relaxation of polymeric composite. Many arguments stated that reducing in responses rate in polymeric

crystalline zones is the main reason for non-Fickian acting [24] and this is explained by the unbalance of swelling between upper and lower surfaces of polymer which causes the tardy processing of stress relaxation [25]. As a result, the key issue decides the speed of steady-state permeation is the rate of stress relaxation [26].

The other case of water diffusion worth mentioning here is case II absorption. As described in Figure 3d, the curve of this diffusion has the significant distinction comparing to the other non-Fickian types. The absorbed water into polymeric composites is in direct ratio to time instead of the square root of time in the other kinetics. This happened due to the significant slowdown of polymeric chain relaxation against to the stress diffusion rate which lead to the sharp fronts or “step- type” concentration profiles in diffusing process through polymeric composite films [17] [27].

## **2.4 Factors affecting to the water absorption in composite**

From George and Thomas’s point of view [28], the ability of water absorption in polymeric composites is affected by many factors including the nature of polymeric composites, the nature of cross-links, plasticizers, reinforcements and temperature.

### **2.4.1 Nature of polymeric composites**

Many researches pointed that one of the most principal factors of water transport into a material is its nature. As George and Thomas stated [28], the features of free volume in polymeric structure along with segmental mobility in its polymer chains are mentioned as the direct influences on water diffusion while the other characteristics such as saturation ability, crystalline ability, cross-links or natural substituent in polymeric structure affect indirectly to the uptake of water.

Glassy polymeric composites, for example poly-acrylamide, polyamides, polyethylene, polystyrene, polypropylene or epoxy, are stiff and fragile. The flexibility of polymer chains is restrained and there is not much void space (around 0.2-10%) in the structure with high density of polymer. Thus, the water diffusion of these composite is more complicated. As described by George and Thomas [28], the value of the glass transition temperature  $T_g$  is variable when changing the free volume in material structure at a certain temperature. This mean that blending a miscible liquid which comprises supplemental

free volume into initial polymer could adjust the  $T_g$  of material, specifically this helps reduce the  $T_g$ . Polymeric composites with lower  $T_g$  have the better segmental mobility so their diffusivity is more considerable. For the case of rubbery polymers, for example poly-(dimethyl siloxane) or polyurethane, this kind of polymers are not saturated and its segmental mobility as well as its free volume among polymeric molecules are relatively great. Consequently, these attributes facilitate the water diffusion smoothly. Furthermore, the molecular size of polymeric composites has a part in the diminution of the chain mobility which leads to the reduction of water sorption ability [28].

#### **2.4.2 Nature of cross-links**

As mentioning in the previous section, the nature of cross-links is one of indirect factors to absorbed water in diffusion. The inconsistency existing in polymeric network structure of cross-linked epoxy resins composites is the combination of highly cross-linked micro-gel particles (or known as micelles) and high density micelles along with less highly cross-linked matrix. This mixture helps intensify the water resistance of materials [29] and creates the complication of water diffusion progress. Additionally, it is also known that the higher flexibility of chain network, the higher maximum water absorption into polymeric composites. In contrast, the intensification of cross-linked density may reduce the degree of permeation [28].

#### **2.4.3 Plasticizers**

It is also mentioned by George and Thomas [28] that the segmental mobility of polymeric composites as well as its water infiltration conveyance are built-up due to the appearance of plasticizers. Therefore, by the addition of plasticizers, the diffusion coefficient of material is augmented and its solubility coefficient is decreased in contrast [28].

#### **2.4.4 Reinforcements**

Another important factor affecting to ability of water conveyance into polymeric composite is the reinforcements. The nature of polymeric structure, ability of bonding or compatibility between the reinforcements and polymers are the essential impacts on the uptake of water into a reinforced structure. According to George and Thomas, polymeric

composites with simple arranged systems could be less obstructed [28]. Generally, under the glass transition temperature  $T_g$ , the addition of filler in polymeric structure may enhance its activation energy [30]. Besides, the existence of filler causes a considerable drop in the mechanical chain flexibility because of the competitive adsorption among water molecules on filler surface. Therefore, its ability of water resistance is increased. This is reason why the materials of reinforced resin composite are reputedly impermeable with water [30] [31].

#### **2.4.5 Temperature**

In general, the impacts of temperature on the uptake water into materials are noteworthy. Specifically, the raise of temperature causes the reduction of solubility but it increases the coefficient of diffusion along with the amount of absorbed water. This happens because the decrease of solubility is negligible in comparison with the increase of driving force [21]. The relation between the diffusivity and the coefficient of permeability with temperature is followed to Arrhenius.

The researches to study the influences of temperature on water transport were carried out by Gillat and Broutman [32]. These studies on graphite/epoxy composites specimens which were immersed in water at fixed conditions in different temperatures showed the results that the rise of immersed temperature induces the increments of the maximum amount of water absorbed into specimens, the diffusivity as well as the initial gradient of sorption curve. It is also described in these studies that at the low temperatures of 25 °C and 60 °C the results of water diffusion were belong to Fickian behavior whereas non-Fickian behavior was showed at high condition of 80 °C. As high temperature could rise the relaxation of molecular chain, also reduce the glass transition temperature  $T_g$  and enfeeble the strength of molecules banding, the free spaces between molecules were formed. This leads to the intensification of water absorption amount [33].

### **3 METHOD**

To study and analysis the ability of water absorption on different kinds of composite materials, the approach is divided to three different stages: the method used for the natural composite material of woods and the other methods used for the composite resin.



With the measurement of wetting on wood specimens, several models are developed to simulate the water absorption process inside these materials of wood. Through the water sorption test of wood, the obtained resulting data is analyzed and modeled as the diffusion issue following to the mathematical viewpoint of Fick's law diffusion and three empirical equations. The water uptake kinetics are evaluated to assist to the simulation of water absorption, as a result, the appropriate absorbed conditions are predicted. The primary purpose of these experiments is to establish the water sorption coefficient and the diffusion coefficient of two kinds of wood: Balsa and Birch [34].

In the case of composite resin materials, water absorption will be negligible and the mass changes is unable to be practically observed. As a result, the analysis methods of UV-visible spectrophotometry and Fourier Transform Infrared Spectroscopy (or FTIR) were used to analyze the tested samples. The main purpose of these experiments is to study and determinate the existence of water molecules diffused through the surface of specimens immersed in water bath for different interval of time. By this way, it is possible to evaluate the absorbability of the tested composite resin.

### 3.1 FICKs law and Peleg's model

#### 3.1.1 Theory

There are two varieties of models can be used to describe the water absorption kinetics, including theoretical model and empirical model. As being mentioned in theoretical modelling, the collected results from experiments are linked to physical laws. In order to study the kinetics of water diffusion mechanism, the theories from the simplest case, Fickian diffusion to the other cases, which are more complex, of non-Fickian diffusion are referred. The diffusion of water obeys the Fick's law which describes materials flow due to concentration different. The equation is:

$$J = -D \cdot \Delta x \quad (2)$$

The first Fick's law indicates the proportion of the flow to the concentration gradient [36]:

$$J = -D \cdot \frac{\partial M}{\partial x} \quad (3)$$

However, the second Fick's law, also known as the unsteady-state law, mentions to the dependence of the diffusion on the time [36].

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \cdot \left( D \cdot \frac{\partial C}{\partial x} \right) \quad (4)$$

Or,

$$\frac{\partial C}{\partial t} = \left( D \cdot \frac{\partial^2 C}{\partial x^2} \right) \quad (5)$$

Where: the symbol of J is the diffusion flux or mass current, or it is known as the water flow through the wood in this case, measured in kg/s.

C is the concentration.

$\nabla$  is known as the gradient operator.

x is position.

D is the diffusion coefficient.

The diffusion coefficient is determined based on the understanding of the flux as well as the gradient of diffusion and absorption theory. Using the theoretical models of diffusion brings several restrictions because of its complication and involvement to many functions and parameters. Thus, it is inconvenient to apply these models as a practical tool of evaluation and computation in diffusion experiments. In many situations, the experimental models are the great solutions to compute and interpret the experiment results. Among the well-known empirical models and semi-empirical models used in modelling the uptake of water in agricultural materials, including woods, Peleg model is the most highly applicable one. According to Peleg model, the water diffusion process can be obeyed as the below equation [37]:

$$M_t - M_o = \frac{t}{K_1 + K_2 \cdot t} \quad \text{or} \quad M_t = M_o + \frac{t}{K_1 + K_2 \cdot t} \quad (6)$$

In this equation:  $M_o$  is referred as the initial water content of material (%),  $M_t$  is the water content into material (%) at the soaking time.

$K_1$  is the Peleg rate constant ( $h/\%^{-1}$ )

$K_2$  is the Peleg capacity constant ( $\%^{-1}$ )

The rate of sorption can be given by doing first derivative of the Peleg equation [38]:

$$R = \frac{dM}{dt} = \frac{K_1}{(K_1 + K_2 \cdot t)^2} \quad (7)$$

The Peleg rate constant  $K_1$  is associated to the initial sorption rate ( $R_0$ ) at  $t = t_0$  [38]:

$$R_0 = \left. \frac{dM}{dt} \right|_{t=0} = \frac{1}{K_1} \quad (8)$$

The Peleg capacity constant  $K_2$  is associated to the maximum value of attainable water content in materials. Following to the Peleg equation, when  $t \rightarrow \infty$ , the relation of equilibrium water content ( $M_e$ ) with  $K_2$  can be described [38]:

$$M]_{t \rightarrow \infty} = M_e = M_0 + \frac{1}{K_2} \quad (9)$$

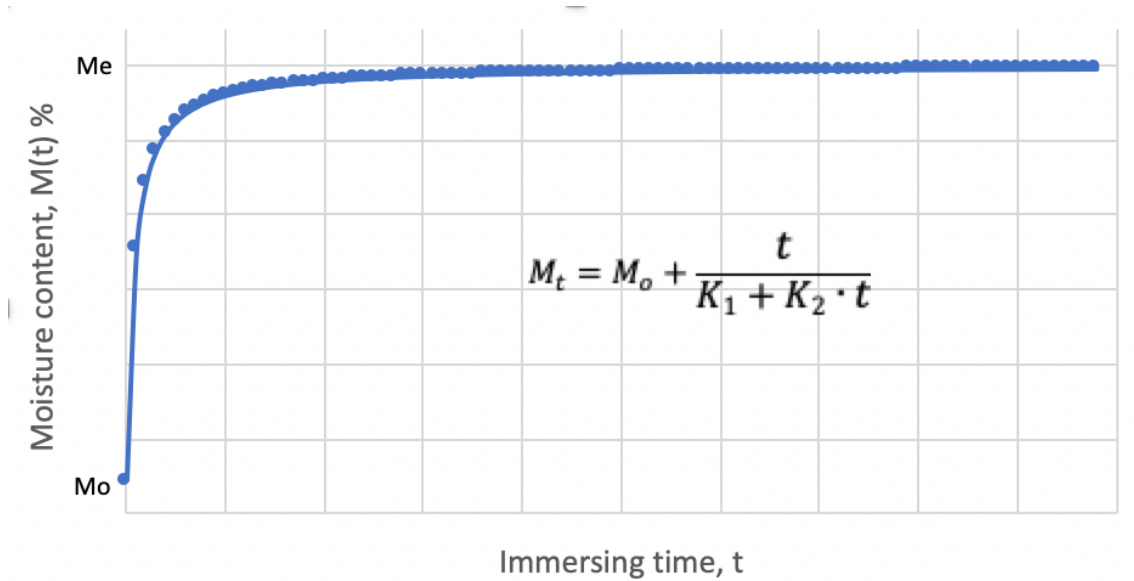


Figure 4: Graphical illustration of Peleg model (Equation 6).

### 3.1.2 Materials

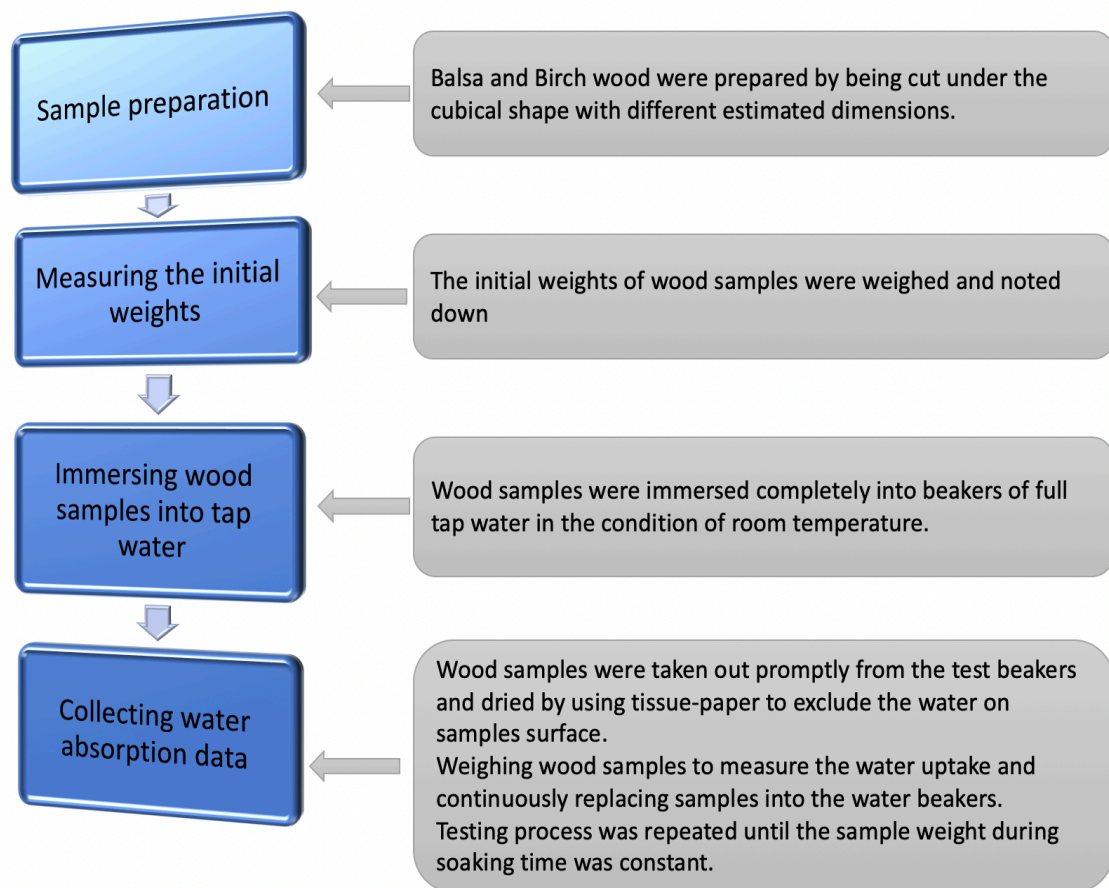
Beside of modern synthetic composites, there is a large number of natural composites in the nature. Among those, wood is considered as an excellent instance of natural composites. Natural woods are constituted from long cellulose fibers which is referred as a polymer. These cellulose fibers combine to each other by a support of an agglutinative substance called lignin. There are varying kinds of natural woods due to the variety of cellulose fibers arrangement. In addition, the construction of molecular arrangement in wood cells is illustrated through a relation of physical or mechanical features as being a composite material [39]. For that reason, woods are chosen to be examined in this study of water absorption following to the model of Fick's law.

There are two types of wood used for this investigation including Balsa wood and Birch wood.

- Balsa wood is known as a well-known wood type which has a lot of application in many fields. Its density is  $0.13 \text{ g/cm}^3$ . The outstanding features of this wood are its lightness, softness as well as its versatility. Consequently, its application is found in many industries, from producing model airplanes to the application of sport equipment producing [40].
- Birch wood is a medium-weight material which the density is  $0.65 \text{ g/cm}^3$ . This wood has many high-quality strength properties, for example, it is not principally hard however this wood still elastic and tough. Birch wood is relatively flexible to work so it is possible to be turned, profiled or carved. The features of bending are excellent while its splitting is imperfect [41].

### **3.1.3 Experiment Method**

In this method, the specimens were entirely immersed into a water container in distinct intervals of immersed time. Water absorbed inside the specimens of composite materials and could cause the alteration of sample weight. The weight changes because of water uptake were noted down.



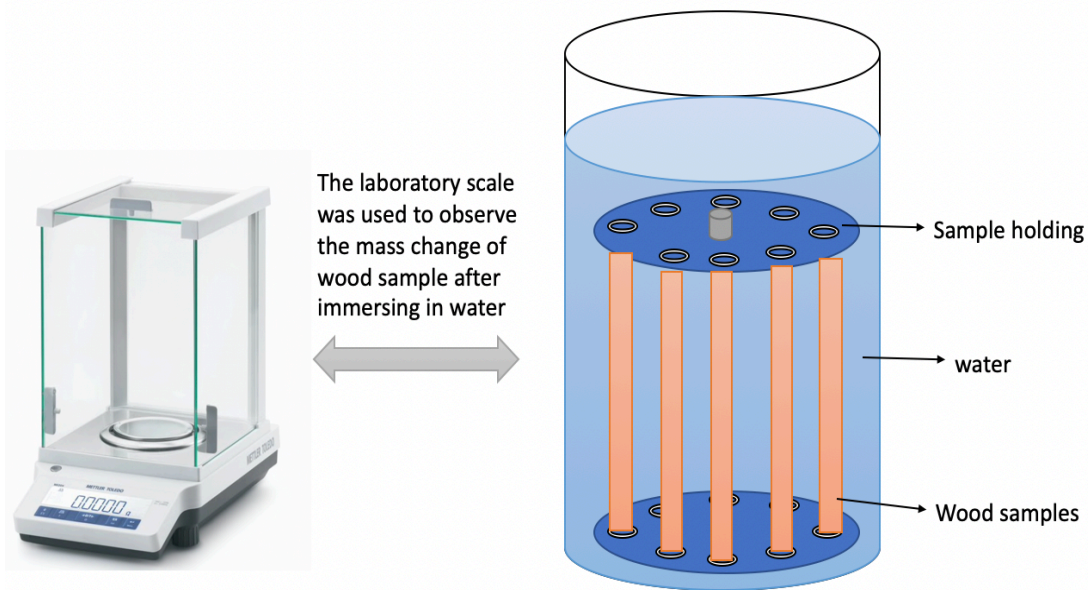
*Figure 5: Schematic set-up of water absorption test.*

The identical specimens of two species of drying wood including Balsa and Birch wood were prepared by being cut under the cubical shape with different estimated dimensions:  $L \times W \times T = 10\text{cm} \times 0.47\text{cm} \times 0.16\text{cm}$  for Birch specimens and  $10\text{cm} \times 1\text{cm} \times 1\text{cm}$  for Balsa specimens. As the wood samples used in these experiments are kiln-dried so the initial moisture content of these ones is negligible. The initial weights of these samples were weighed and noted down. Then, the absorbed water data of these woods were collected by immersing completely two kinds of specimens into two different beakers of full tap water in the condition of room temperature, around  $25^{\circ}\text{C}$ . The testing was performed for the immersed periods from 2 hours to 32 days. After being immersed in water for various interval of time, the water content of wood samples was computed by the increase of sample weight corresponding to time. Due to this intention, at regular time interval, from every 2 hours at the beginning of experiment to every 24 hours or more during the final stages of the testing, the specimens were taken out promptly from the test beakers and superficially dried by using the laboratory tissue-paper to exclude the water on samples surface. After weighing the samples to measure the water uptake, the wood samples

were continuously replaced into the water beakers. This process was repeated until the obtained water contents attained the saturated state, in which the sample weight for soaking time was constant. The experiment was carried out at least three times and the average increments of weight were collected for further analysis and evaluation [34] [42].

**Measurement Error:** there are several possible sources that cause the uncertainty in this water absorption measurement.

- Deviation due to the impact of testing conditions: Because the experiment was conducted in the condition of room temperature for a long period, there could be some fluctuations in environment that affect to water uptake data.
- The measurement error during the process of specimen preparation.
- The measurement error when applying the procedure during the actual testing: the error of manual measurement by using scale to weigh the mass change; the manner when removing the water from surface of specimens before weighing is also considered as a factor related to measurement error.



*Figure 6: Simulation of water absorption experiment in wood samples.*

Through these experiment, the results of water absorption on woods by the weight changes are plotted and studied based on the theory of Fick's law and Peleg model. The curves of cumulative weight obtained related to the square root of time was illustrated. From these curves, linear regression ones of two kinds of wood samples were calculated.

Through this way, the coefficient of water uptake in wood specimens was found out based on the equation as below [43]:

$$m_w = A \cdot \sqrt{t} \quad (10)$$

Where,  $m_w$  is considered as the amount of water absorption,  $\text{kg/m}^2$   
 $A$  is the coefficient of water sorption,  $\text{kg}/(\text{m}^2\text{s}^{1/2})$

As being described in the equation, the parameter of water absorption coefficient  $A$  is determined through the slope of the regression curve divided by contact area.

The second Fick's law of the diffusion theory was utilized to define the coefficient of the water diffusion through wood materials in this research. Following to the study of Marcovich [44], it has been shown that during immersing a material in water for a short period, the equation (11) can be used to associate the normalized water absorbed ratio  $\left(\frac{M_t - M_o}{M_s - M_o}\right)$  and the water absorbed diffusion of a material under arbitrary shape when soaking in water [44].

$$\frac{M_t - M_o}{M_s - M_o} = \frac{2}{\sqrt{\pi}} \cdot (S/V) \cdot \sqrt{D \cdot t} = \alpha_b \cdot \sqrt{t} \quad (11)$$

In this mathematical model,  $M_s$  and  $M_o$  is referred as the constants value which are dependent upon the physical properties as well as the structure of testing materials. The value of ratio  $(V/S)$ , which is known as volume-to-surface area ratio, is also counted as constant. Those factors are not affected from the water content. Thus, to obtain the value of diffusion coefficient  $D$ , the resulting data were illustrated as a plot of normalized water absorption versus the square root time,  $\sqrt{t}$ . The result of  $\alpha_b$  can be found by determining the slope of regression linear of the curve. From this value, the coefficient of water diffusion on wood samples,  $D$ , is defined according the following equation [34]:

$$D = \frac{\pi}{4} \cdot \left(\frac{V}{S}\right)^2 \cdot (\alpha_b)^2 \quad (12)$$

The knowledge of Fick's law and the empirical model of Peleg were applied for the mathematical modelling of the change in water content of wood specimens as well as its water content ratio when soaking in water. By using non-linear least squares, the essential parameters were obtained. The evaluation of accuracy or the feasibility of the model, the criteria used here are the root mean square error (RMSE) which is calculated following to the below equation [34]:

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (M_{r,i} - M_{p,i})^2}{N}} \quad (13)$$

## 3.2 UV-visible spectrophotometry

### 3.2.1 Theory

Among the analysis methods using in science researchers, using absorption spectroscopy is one of the most popular technique providing a high fidelity of results. This method operating bases on the relation between the amount of radiant energy that each atom absorbs with a variety of its structure as well as concentration and its identity. Following to the theory of electromagnetic radiation, photon is identified as a flow of a distinct energy group. Discrete atoms and molecules at different level of energy have a different energy state. If the absorption happens, the incoming radiation energy must correspond with variance of the substance energy level. As each atom and molecule is distinctive of its energy configuration, using method of absorption spectroscopy is an appropriate technique to detect the presence of components in materials [45] [46] [47].

The analysis method of UV-visible spectroscopy is constructed by the selective absorption of electromagnetic radiation in the range of wavelength from 170 nm to 780 nm. When receiving a necessary amount of energy need to create a specific transition among bonding electrons. Chromophore is considered as a functional group of atoms or molecules comprising electrons with low excited energy absorbed effectively in UV visible region. In general, Ultraviolet-visible near infrared (UV-Vis-NIR) spectroscopy is based on the electronic transition of atoms and molecules. This spectroscopy method determines the transitions from the ground state to excited state of electrons [45] [47].

### 3.2.2 Equipment

The equipment used in this method is an UV-visible-NIR spectrophotometer, specifically the V-670 optical system by JASCO (USA). This equipment is contributed from key elements including a light source, a monochromator element, a cell to contain sample and a unit of detector. There is a wide range of light sources using in this technique, the



most popular one worth mentioned are the light source from tungsten filament (300- 2500 nm of visible wavelength) or deuterium arc lamp (190-400nm of visible wavelength) or xenon arc lamp (160-2000nm of visible wavelength) or LED. A resulting spectrum from testing is obtained from the monochromator device by absorbing the light created from the light source at a specific wavelength to handle the analysis of sample in solution. The detector device is designed to evaluate the strength of light beam from the tested samples. The spectrum performed the absorbance value is shown in a computer which is connected to the UV-visible spectrophotometer. To operate and adjust the parameter for the experiment, the Spectra measurement program is used in this PC [46] [47].

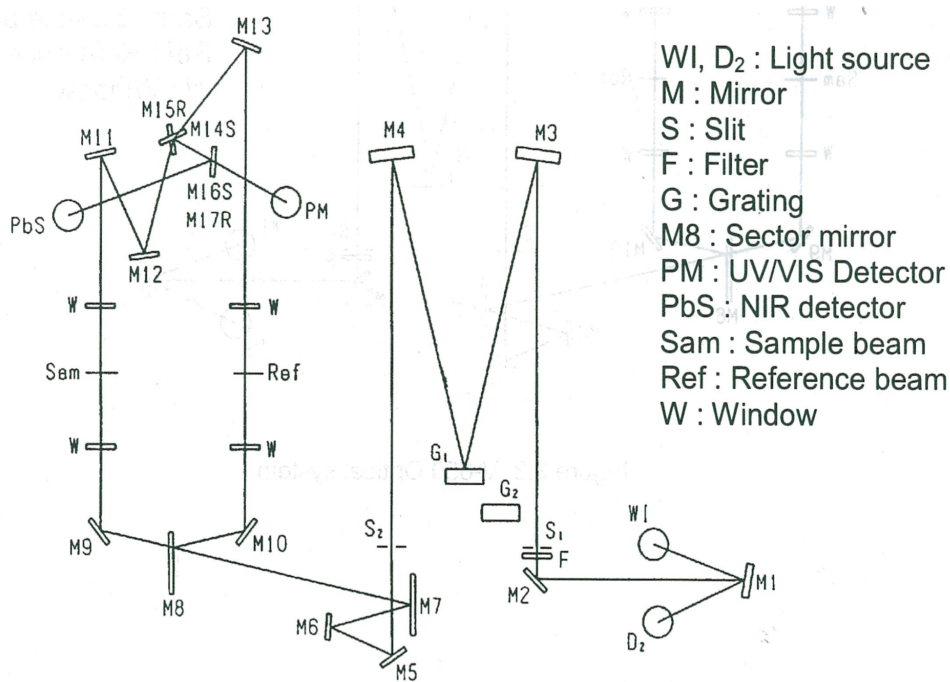


Figure 7: Schematic of V-670 Optical System [46]

### 3.2.3 Materials

The material used for this experiment is vinyl ester resin which is based on the specific polymer resin of vinyl-ester ATLAC E Nova M6215. Vinyl ester resin is considered as an important material used to enhance the properties of strength as well as chemical resistance characteristic of materials applied in commercial applications. This type of resin is created from the reaction of an epoxy resin and acrylic or methacrylic acid in

order to generate a polymer with the structure described in Figure 4. The cross-link density inside this polyester structure is lower than the basic polyester resins because of the position of reactive double bonds being at the end of the long chain. This kind of resin offers a higher failure strain and more improved mechanical as well as chemical properties than others [48].

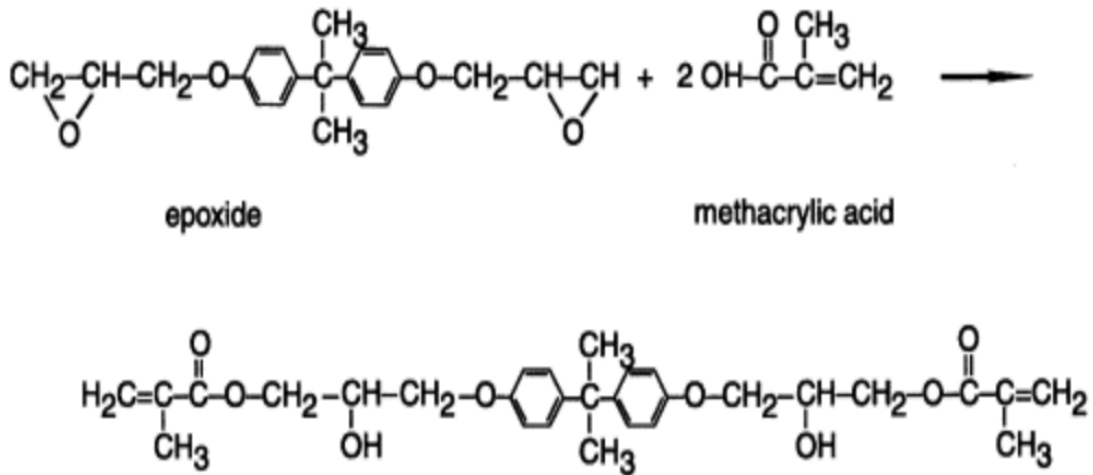


Figure 8: The reaction to create vinyl ester [48].

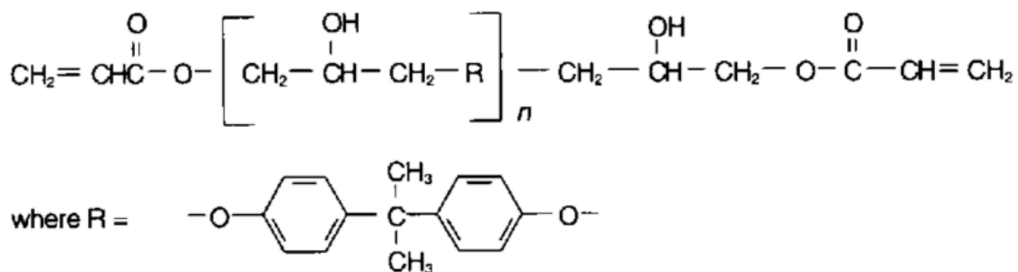


Figure 9: The structure of vinyl ester resin [49].

ATLAC E Nova M6215 is known as a type of thixotropic epoxy bisphenol-A vinyl ester modified resin which is pre-accelerated. This material provides outstanding wet out and air-release features for the production. Therefore, this can reduce the foaming creation in the step of adding peroxides which leads to lessen the air inhibition. One of the most excellent properties of this material is its higher osmotic resistance which is applied as a coat resin used in the application marine industry. Several properties of cast unfilled resin of ATLAC E Nova M6215 is shown in the table 1 as below [50]:

*Table 1: Properties of cast unfilled resin ATLAC E Nova M6215 (typical value) [50]*

Property	Value	Unit	TM
Barcol hardness GYZJ 934-1	45	Barcol	ASTM D2580
Tensile Strength	70	Mpa	ISO 527-2
Tensile E-modulus	4	Gpa	ISO 527-2
Elongation at break	2 - 3	%	ISO 527-2
Flexural strength	120	Mpa	ISO 178
Flexural E-Modulus	4	Gpa	ISO 178
Heat Deflection Temp. (HDT)	110	°C	ISO 75-A
Water absorption, 60 °C, 24 hrs	0.5	%	ISO 175

### 3.2.4 Experiment method

For the approach of UV-visible spectrophotometry, two similar specimens were prepared. One specimen was immersed into a container of full tap water and the other sample is placed in a container without water. The experiment was carried out at the condition of room temperature. By collecting and comparing the spectra from these two specimens, the uptake of water into resin was determined.

For the sampling preparation and instrument preparation [46]:

- Set up the standard parameter for this measurement in the Spectra measurement program. The parameters value need to be: Photometric mode = Abs, Response = Fast, UV/Vis bandwidth = 2.0 nm, Scan speed = 1000 nm/min, Start = 2200 nm, End = 190 nm.
- Carry out a baseline measurement without specimen in the instrument.
- Ensure to clean the inside and outside surface of specimen by using light-duty tissues. For specimen immersed into water container, dry the surface of specimen lightly with tissues before testing.

- The piece of resin specimen was mounted in the position between the magnetic cell holder of the spectrophotometer machine. The wavelength range of this testing is from 190nm to 2200 nm. Two measurements were carried out for each specimen and the average results were collected.

The procedure was repeated every 24 hours for 2 days at first, then every 48 hours or more for next 18 days to observe the spectra changes of resin specimens after 18 days being immersed inside water.

### **3.3 Fourier Transform Infrared Spectroscopy (FTIR)**

#### **3.3.1 Theory**

Fourier Transform Infrared Spectroscopy analysis method that is usually abbreviated as FTIR Spectroscopy or FTIR method, is considered as one of the most recent advanced analytical technologies which is applied to detect and identify unknown materials or components. This analysis method is also used for determining quality or consistency of a material and used as a potential method to quantify of different components in a mixture [51]. In the analysis process of the infrared spectroscopy, the instrument of FTIR sends the radiation of infrared in a range of 10,000 to 100  $\text{cm}^{-1}$  through a specimen. During this progress, several radiations of infrared are absorbed into the specimen while the others are transmitted through the sample. The radiations absorbed to the sample are transferred to the energy of molecular rotation and vibration. The outcome signal at the equipment's detector is stated as a spectrum. The spectrum received from this method stands for the transmission as well as the absorption of molecules. The spectrum also generates the sample 's fingerprint which means the identification to a unique molecule since it is impossible to exist two distinct molecular structures which create the similar infrared spectrum. Every molecule produces a typically distinctive spectral fingerprint so this why FTIR method is a useful tool of chemical identification [51] [52].

Recently, FTIR analysis method play an important role in the quality control technique, especially in the material evaluation of industrial manufacturing. This approach is usually operated as the primary stage in the process of material analysis. Obviously, the modification in the distinguished prototype of absorbed bands reveals an anomaly in the material components due to the transformation of chemical structure inside material or

the contamination influence. For industrial production process, the defective products which are detected by visual inspection are generally verified by FTIR analysis to figure out causes of product issue. It is feasible to use this analysis technique in determining the micro-size particles of chemical components as well as the large irregularity on material surface [51].

Several applications of FTIR spectroscopy used in reality [51]:

- Identification and description of extraordinary or unknown materials, for instance powders, solids, liquid or film and so on.
- Determining contamination or anomalous constituents inside material or on its surface. They can be particles, liquid or fibers.
- Identification of additives added to a polymer matrix of a composite material.
- Identification of many chemical reaction such as oxidation or decomposition, also determining the non-treatment monomers in unsuccessful analysis examinations.

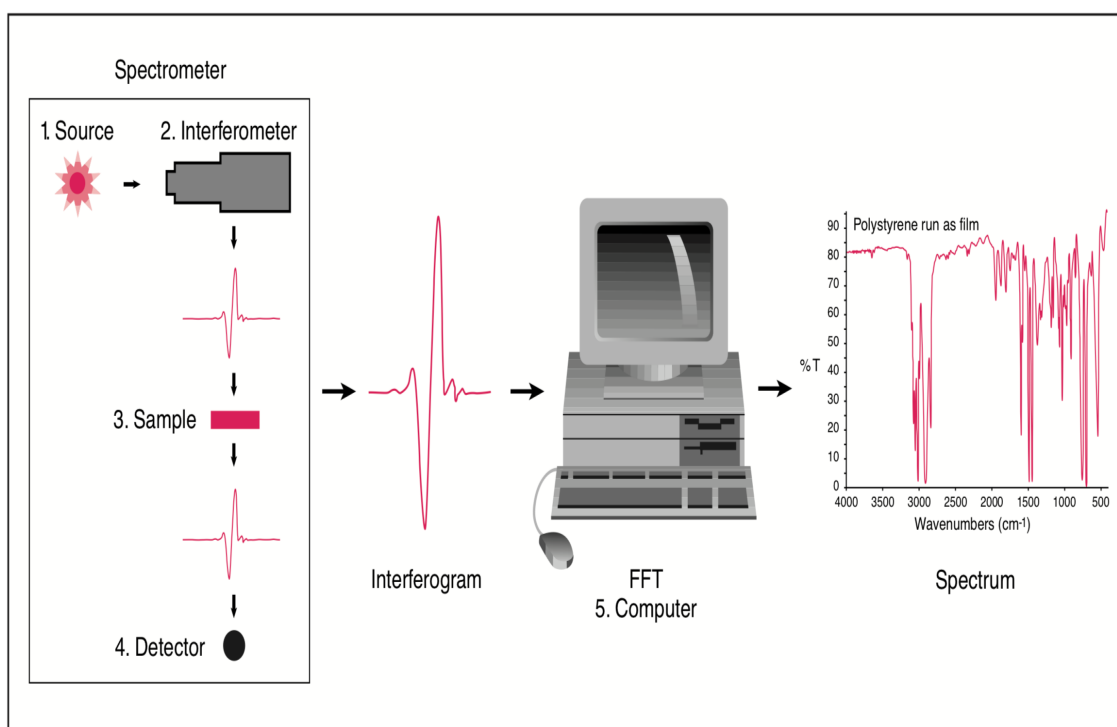
Some remarkable advantages of FTIR analysis method that over against the other infrared spectral analysis are [51]:

- With this analysis technique, it is dispensable to destroy material structure of sample. This is known as non-destructive method.
- This method has the ability of internal calibration. As HeNe laser is used as the calibrated standard of wavelength in the FTIR instruments, then without the external calibration from user this analysis still provides a high precision in
- FTIR method has high analysis processing speed. Since all frequencies are processed concurrently so the FTIR measurements are completed in several seconds instead of several minutes.
- In FTIR spectroscopy, the sensitivity is significantly developed because its detector parts are improved to achieve a much higher sensitivity and its optical throughput is much greater to lower levels of noise in resulting scan. Furthermore, the scanning speed is fast which enable combining many scans limit the noise by random measurement.
- The other improvement worth mentioning here is its mechanical simplicity which includes a single moving part to reduce the mechanical problems during operating.

### 3.3.2 Equipment

The operation of FTIR analysis instruments can be described as below [52]:

- The source: there is a glowing black-body source which generates the infrared energy in the instrument. This light goes through an aperture to handle the volume of energy transferred to samples.
- The interferometer: the light from the source goes to the interferometer and the spectral encoding process is implemented in this part. The result goes out this unit under interferogram signal.
- The sample: after leaving the compartment of interferometer, the beam keeps entering to the unit of sample. Here, this light is transmitted through the sample or reflected off the sample, according to the purpose or type of analysis method. Additionally, the absorption of characteristic frequencies of the energy is occurred.
- The detector: the resulting light is transmitted to the detector part as the last step of measurement. With a specialized design, the detector reads and processes measuring the signal from the interferometer.
- The computer: the outcome signal measured from previous stages is digitized and transferred to the computer. Here, the Fourier transformation is carried out to produce a final infrared spectrum which is represented as the unique characteristic of a sample so that user can interpret and analysis.



*Figure 10: Schematic of FTIR analysis system [52]*

It is necessary to implement a measurement of background spectrum because the measuring process needs a relative scale of the absorption intensity. In this step, a measurement without sample is taken place to compare with the normal measurement with sample so that the percent of transmittance is determined. By this technique, all noise or characteristics from equipment are eliminated. Therefore, the resulting spectra received from the measurement are totally generated by the tested samples. The step of background measurement need to be done only one time and used for several sample measuring since this background spectrum is the instrument's features [52].

In this research, the FTIR equipment used in Arcada 's chemistry laboratory is the FTIR spectrometer of Thermo Scientific Nicolet iS5 which is connected to a computer used the OMNIC™ software to drive the obtained data from the experiments.



*Figure 11: FTIR analysis equipment used for experiment in Arcada laboratory*

[53].

### 3.3.3 Material

The material used in this FTIR experiment is the composite laminate which is constructed from textile with highly un-iso tropic structure. In the laminate, the fibers used is glass and the matrix is the polymer resin, known as vinyl-ester ATLAC E Nova M6215. This composite laminate was prepared by using the technique of vacuum-assisted resin transfer molding in Arcada 's machine laboratory.

The glass fabric-reinforced laminate composite of vinyl ester is known as an essential material which has a wide usage in structural or functional applications due to its advanced performance as well as the improved properties of higher strength, stiffness or the reduction of weight. In general, most glass fabric reinforced composite materials have lots of advantages comparing to other materials such as: the low cost, the ability of ultimate strain, the impact resistance or the tolerance of damage, the excellent formability and the resistance of corrosion or fatigue. By taking full advantage of this kind of composite and combining with the characteristic of vinyl ester resin, the composite of glass fiber based on vinyl ester resin as thermoset matrix of its reinforced structure becomes an attractive material used for numerous applications in the aerospace industry or several automotive industries [54].

### 3.3.4 Experiment method

❖ **For sampling preparation:**

The purpose of this experiment is to observe and evaluate the water absorption of four different specimens during the soaking time by FTIR spectroscopy analysis. By making the reference of the standard measurement of ASTM D 570 [55] and ISO 62 [56] for water uptake when immersing in water, four specimens of composite laminate were prepared with the dimension of 40 mm x 15 mm x 3.5 mm. The cutting edges of the testing samples were made smooth to avoid cracks. Before carrying out the experiment of water absorption on composite samples, these samples were lapped and polished by a grinding and polishing machine shown in the image in Figure 8 [57]. The polishing step was conducted by using hand to hold the four samples on the wet grinding plate under different grit of SiC paper grinding which is tabulated in Table. The rotation of machine was controlled to be slow enough so that it does not heat up the surface of samples.

*Table 2: Four different progressions of grinding and polishing grit.*

Grit #	Lapping time (min)
320	1
600	1
1000	1



4000	1
------	---



*Figure 12: Example of grinding and polishing machine [57]*

The FTIR analysis was conducted with four dry composite sample under four different levels of polishing grit: 320, 600, 1000 and 4000. After that, the composite sample were immersed into four different containers of full tap water. The resulting data from FTIR of four composite samples when exposed into water during soaking time was collected. The condition of experiment was at room temperature. During testing with FTIR, to avoid error in the result, it is necessary to dry the specimens lightly with tissues before working.

## **4 RESULT AND DISCUSSION**

### **4.1 Water absorption in woods**

The pattern of water absorbed into the two varieties of woods including Birch and Balsa are illustrated in Figure 13. As being plotted in the scheme, the behavior of the water absorption in the two type of wood samples is presented. The exhibition of data from wood specimens shows that in case of Birch specimens, the initial speed of water sorption is fast and then slower in absorption in later stager which is considered as the relaxation phase [58]. The behavior of water uptake in this case is predicted as the two-stage process of diffusion, in which more than 50% of water uptake content was happened in the first 3 hours when the Birch wood samples immersed into water. After that, the

following period of water absorption process for Birch samples was uninterruptedly occurred more slowly than before but still in a slight increase until obtaining the saturated state of the samples. On the other hand, for the case of Balsa wood samples, the water absorption speed in soaking time is slower than samples of Birch and it is obviously shown in the scheme that there is no existence of a speedy uptake water mechanism in the initial stage as in the situation of the water absorption process in Birch wood samples. Although the diffusion behavior is expected as the two-stage process, it still has the different shape of graph from the one of Birch samples, in which the Birch samples rapidly reached to the point of 60% of water content level after 3 hours and the point of saturated state after 145 hours of immersed time whereas the Balsa samples gradually increased to a water level in excess, of 60% after 124 hours and achieve the saturated point after longer time, for 755 hours.

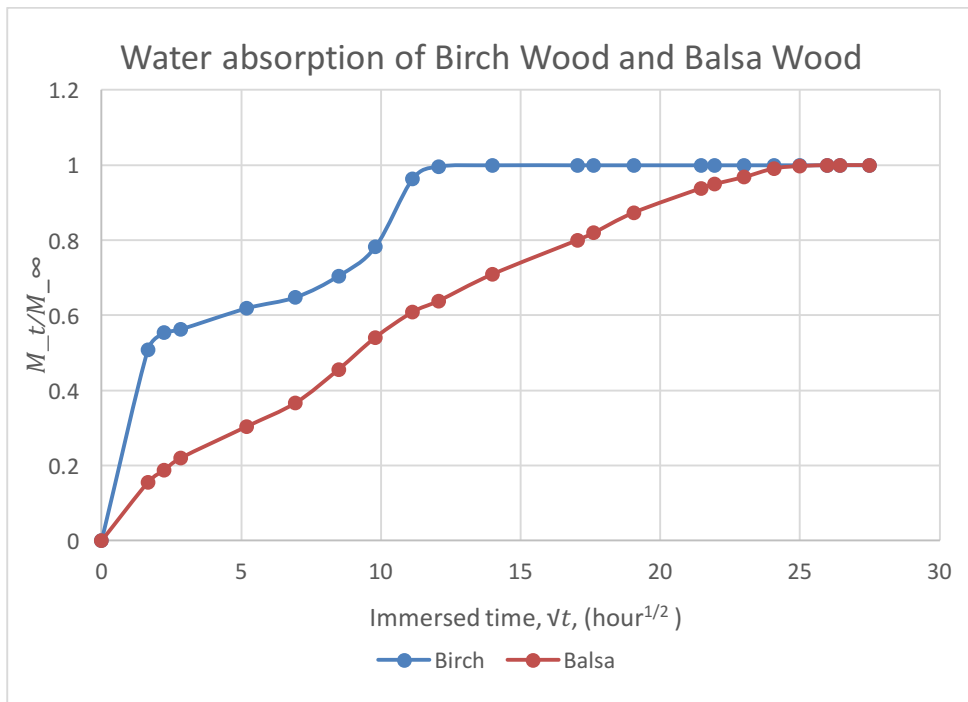


Figure 13: Water absorption curves during immersing the samples of Birch and Balsa woods.

To understand for the water absorption process in these wood materials, it is essential to know the structure built up these woods which includes numerous natural capillaries. The existence of these capillaries speed up the water uptake process to achieve the equilibrium with the hydrated environment by the mechanism of capillaries inhibition. In the initial stage of water absorption process, water molecules penetrate rapidly to the

capillaries and voids which closed to the surface of wood samples. Thus, it can be conceivable that the concentration of water on the surface is increased to the saturated level immediately. Furthermore, the movement of water molecules inside wood material is restricted because when the water absorption occurs, the water molecules transfer freely and easily through the large voids inside woods, however the movement of water molecules through the small voids is prevented from the trapped air bubbles presented in wood structure [34]. This can be obviously expressed by the plot of water absorption curve in Birch samples.

On the other hand, it is possible to explain the higher rate of water absorbed at the beginning of process based on the knowledge about the diffusion phenomenon. During the diffusion of water into wood materials, water penetrates and spreads into wood structure by vessels, capillaries as well as the cellular walls of wood samples. Water absorbed to wood is existed under two kinds including the interstitial water and the dependent water, also known as the bound water. The type of interstitial water molecules is hold in the voids while the other one is contained in the cellular wall. The main factor affected to the water uptake rate is the driving force which is known as the difference in the saturated water content and the water content at a certain immersed time. This means that the water gradient absorbed to wood samples between the surface and center causes the water diffusion phenomenon in these samples. During the process of water absorption, the amount of water inside woods increases which leads to a reduction of the driving force, hence this causes a gradual decrease in the water absorption rate. This diffusion process is accomplished when the water content reaches to the saturated point. Also being created in the water diffusion of wood materials is the distinct concentrations among numerous cellular layer inside material. Consequently, the water molecules transfer from the higher level of water concentration to the lower level [34].

Following to the equation (10), the value of water absorption coefficient of Birch wood and Balsa wood during soaking time were determined based on the plots of variation in amount of water uptake and square root of immersed time in Birch samples and Balsa samples (Figure 14 and Figure 15). As being shown in Fig.14 and Fig. 15, from the ingress linear of resulting curves, the water absorption coefficient  $A$  of Birch and Balsa wood for the whole experiment process were defined as  $3.3 \times 10^{-4}$  and  $8.35 \times 10^{-4}$   $\text{kg}/(\text{m}^2\text{s}^{1/2})$ , respectively.

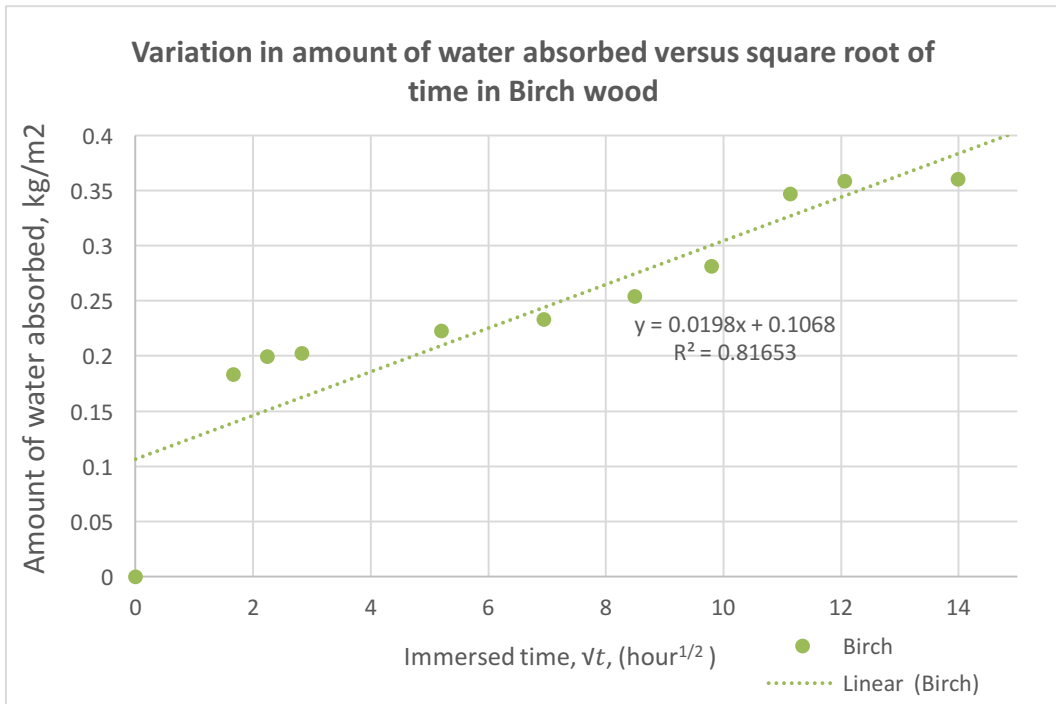


Figure 14: Amount of water absorption curves versus square root of immersed time in Birch wood.

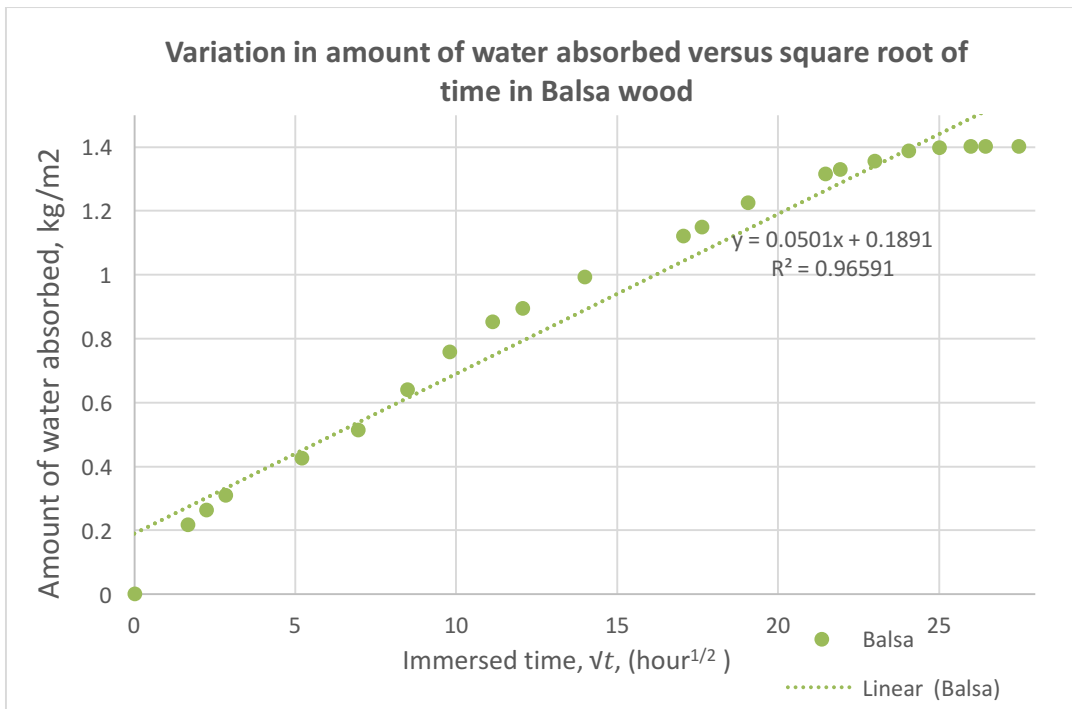


Figure 15: Amount of water absorption curves versus square root of immersed time in Balsa wood.

❖ **Determine the coefficient of water diffusion in case of Birch and Balsa wood**

Water diffusivity of a material is considered as an essential conveyance property which plays an important role in design and optimizing of a process affected by the presence of water [59]. The water diffusion coefficient of a material is known as a proportional factor which characterizes the content of matter diffused through a unit area by concentration gradient in division time [34]. This parameter of wood specimens was computed by applying the results of water absorbed data to equation (11) and (12). The resulting data was plotted as the normalized water absorption versus square root of soaking time in Figure 16. In general, to estimate the value of diffusion coefficient, the initial slope ( $\alpha_b$ ) from the plot in Figure 16 of absorbed data curves disregarding the behavior of non-Fickian was found out. The value of diffusion coefficient in case of Birch wood and Balsa wood were calculated equal  $8.23 \times 10^{-4}$  and  $5.67 \times 10^{-3}$  m<sup>2</sup>/s, respectively. From the result, it could be seen that the value of diffusion coefficient computed for Birch wood was smaller than the result obtained for Balsa wood. The potential reason of this difference between Birch and Balsa wood is the distinction of chemical component as well as the arrangement of cell wall in each variety of wood which maybe cause the impact on the transport of bound water molecules in wood during diffusion process. Another reason worth mentioning here is the density of Birch samples and Balsa samples which may affect to the diffusion process. In this study, the density of Birch wood is 0.65 g/cm<sup>3</sup> which is higher than the density of Balsa, 0.13 g/cm<sup>3</sup>. It indicates that Birch wood is denser than the Balsa which lead to less porous in its structure comparing to Balsa wood. Hence, the water diffusion in Birch wood is much smaller than Balsa wood.

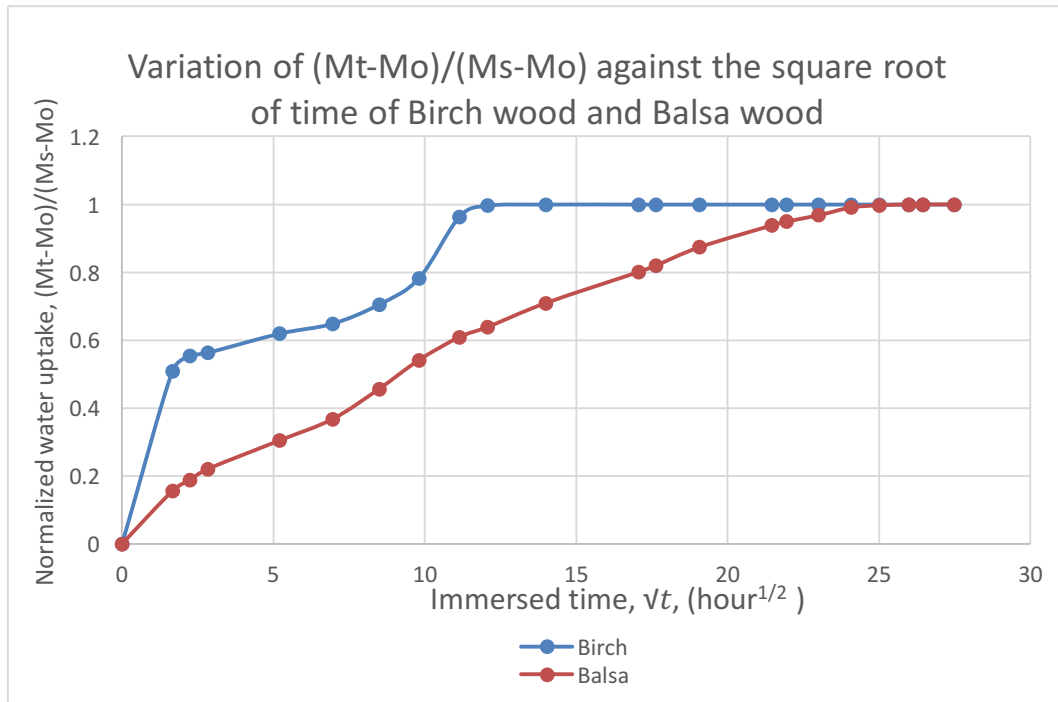


Figure 16: Variation of  $(M_t - M_o)/(M_s - M_o)$  curves versus square root of immersed time in Birch wood and Balsa wood.

❖ **Mathematical modelling following to Peleg model**

The resulting parameters of non-linear regression analysis obtained by mathematical modelling the experiment data of water absorption in wood samples during soaking time following to Peleg model is presented in Table 3. The standard to assess the ability of fit, the root mean square error (RMSE) is also performed in the Table 3. The lower values of RMSE denote better fit of the predicted model. From the results obtained from this table, the Peleg model is more fitted to describe the water absorption process of Birch wood than Balsa wood. The value of RMSE calculated of Birch is 12.47% whereas this number is 84.6% for Balsa wood. This demonstrate that Birch wood is more appropriate to the Peleg model than Balsa. The plot displayed the testing data along with the expected curves based on Peleg model in the case of Birch samples and Balsa sample is presented in Figure 17.

Table 3: The parameters and the RMSE following to Peleg model.

Type	Peleg model		
	K1 (hour/%)	K2 (%)	RMSE (%)
Birch	3.4522	0.9256	12.47
Balsa	5.2162	0.1455	84.6

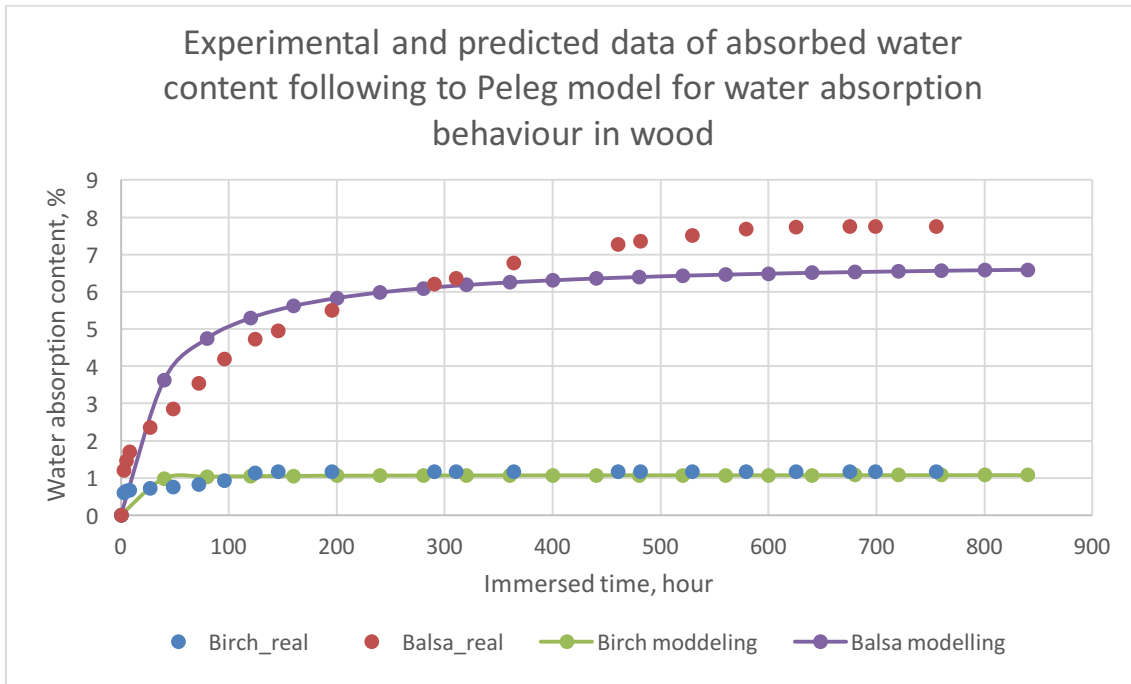
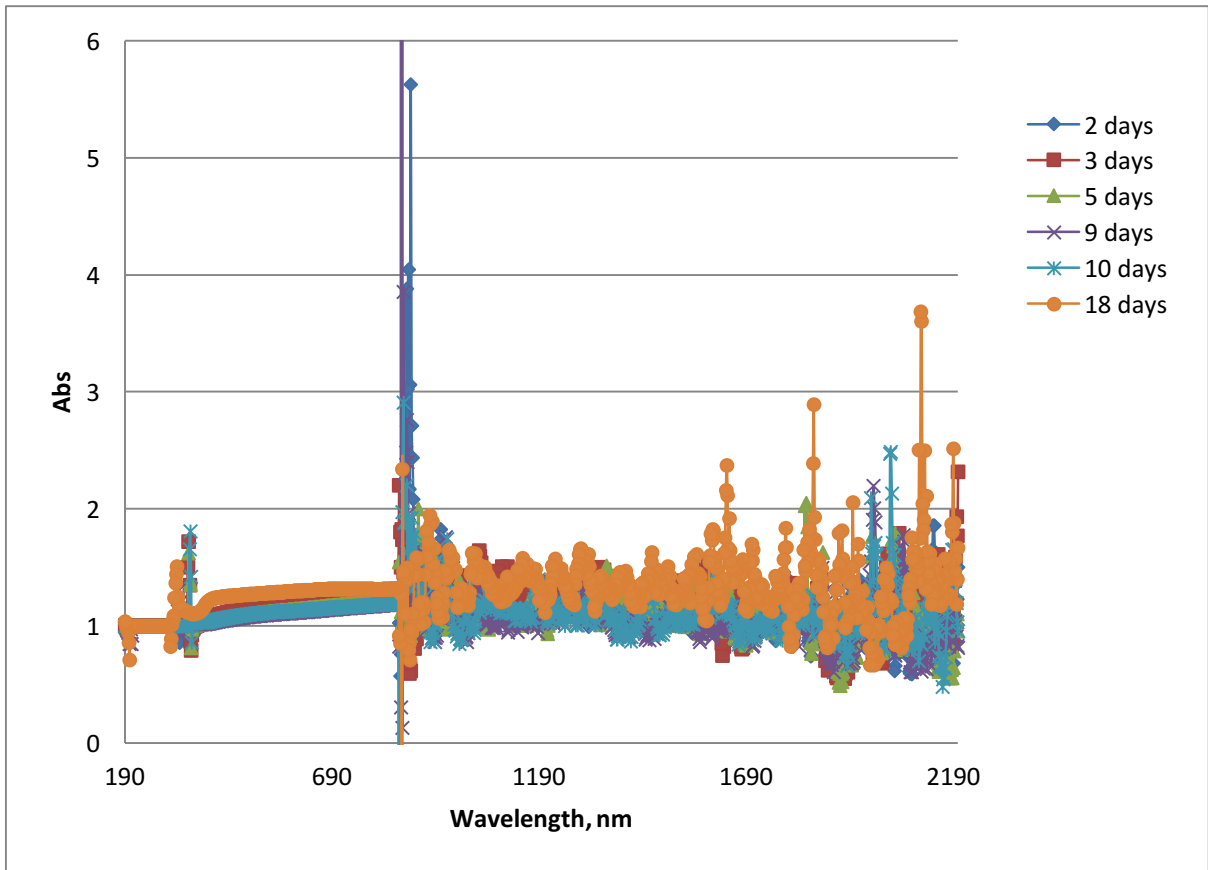


Figure 17: Experimental and expected curves of water uptake content following to Peleg model for water absorption behavior in Birch wood and Balsa wood.

## 4.2 Water absorption in resin by UV-visible spectrophotometry

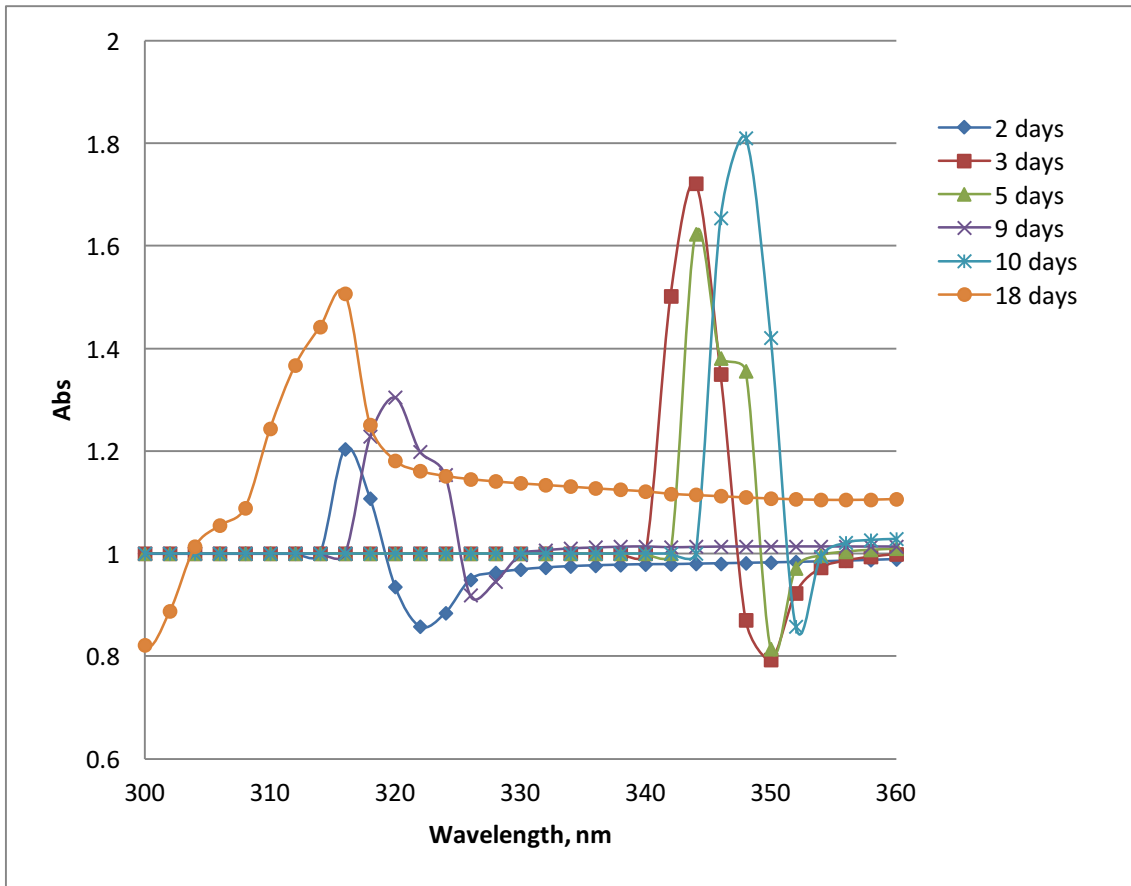
Water absorption in case of the resin samples will be small and a mass change cannot practically be observed. The specimens are studied with spectrometric methods and the changes in spectra indicate the water absorption into the resin samples. UV-visible spectroscopy is known as an easy technique which is relatively sensitive so that it is possible to apply this method to detect the presence of water molecules due to the water penetration into resin samples. Figure 18 shows the resulting UV-visible absorption spectra of solid resin specimen during 18 days of immersing in water.



*Figure 18: UV-Visible absorption spectra of resin specimens during soaking time, wavelength ranges from 190 nm to 2200 nm.*

As shown in the Figure 18, the sample of resin film does a performance of significant absorption peak in the wavelength ranges of 300 nm to 360 nm which is displayed in Figure 19. The absorption band after 360 nm in this spectroscopy method is considered as interference.





*Figure 19: UV-Visible absorption spectra of resin specimens during soaking time, wavelength from 300 nm to 360 nm.*

In the UV-visible absorption band of 300 nm to 360 nm, as can be seen that there are several appreciable differences in absorption peaks at distinct soaking time. After 18 days of being immersed into tap water, the intensity of absorbance peaks intends to be increased which performs the impact of water molecules to sample structure. However, the peaks in this band do not reflect the precise influence of water molecules on resin samples during the water absorption process. Thus, it is uncertain to determine the water uptake behavior in this case. This limitation of characterization in this method can be moderately explained that with the spectra obtained in attenuated reflectance, the definition in range of 300 nm to 360 nm is not good comparing to the definition in the transmitted mode [60].

### **4.3 Water absorption in composite by FTIR spectrophotometry**

The spectra of water absorbed to four composite samples which were modified by different grinding and polishing progression at the number 320, 600, 1000 and 4000 of

grit SiC grinding paper were obtained when being dry as well as being immersed in tap water during 23 days at room temperature by using FTIR spectrometer at the Arcada 's chemistry laboratory.

The images from Figure 20 to Figure 23 display FTIR spectral dependence on water absorbed to composite samples. The resulting spectra from four specimens have a homogeneous performance which indicates the two regions significantly impacted by the increment of water absorption into composite samples. The first zone of the peaks from the wavenumbers at  $2840\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$  corresponds to the hydrogen bonded (O-H) vibration mode. The second zone worth mentioning here is the peaks from the wavenumbers at  $1630\text{ cm}^{-1}$  to  $1780\text{ cm}^{-1}$  that match with the bending vibration mode of water molecules existed in the structure of composite samples. It can be seen obviously that the peaks in these two zone increase corresponding to the water immersing time which reveal the increment of water content in samples [61] [60].

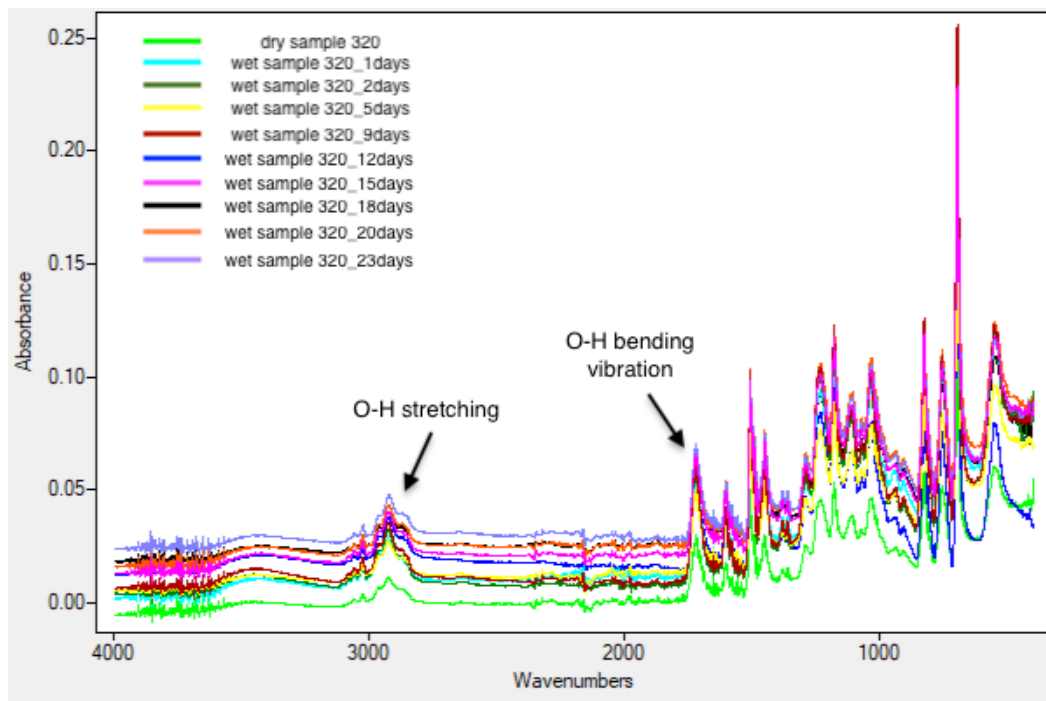


Figure 20: FTIR spectra of composite resin samples polished by #320 SiC grinding paper grits during 23 days of soaking time.

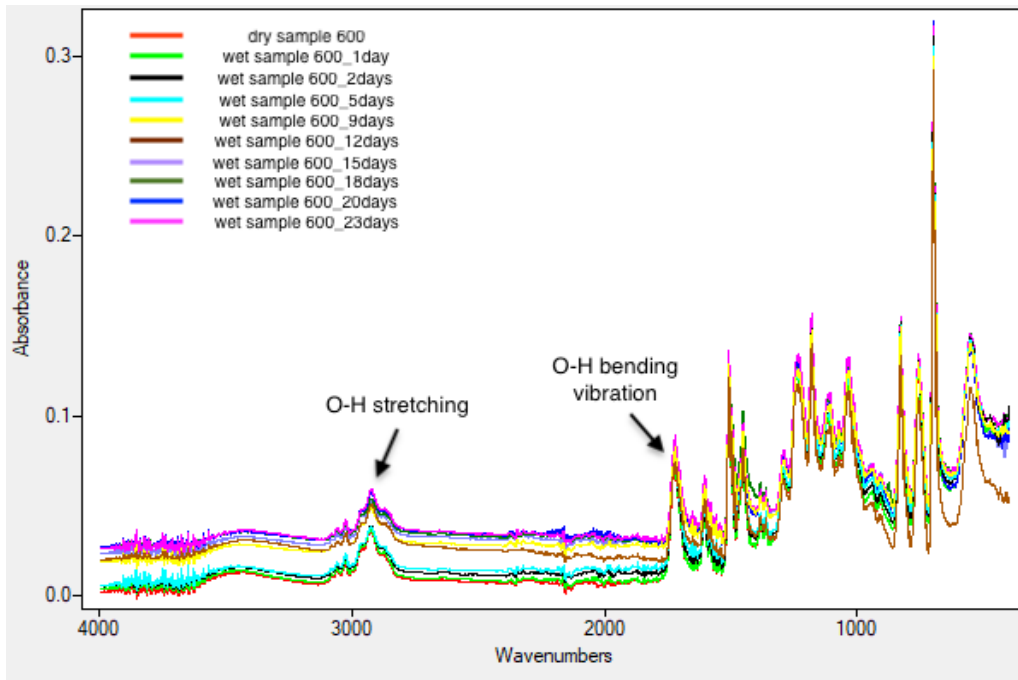


Figure 21: FTIR spectra of composite resin samples polished by #600 SiC grinding paper grits during 23 days of soaking time.

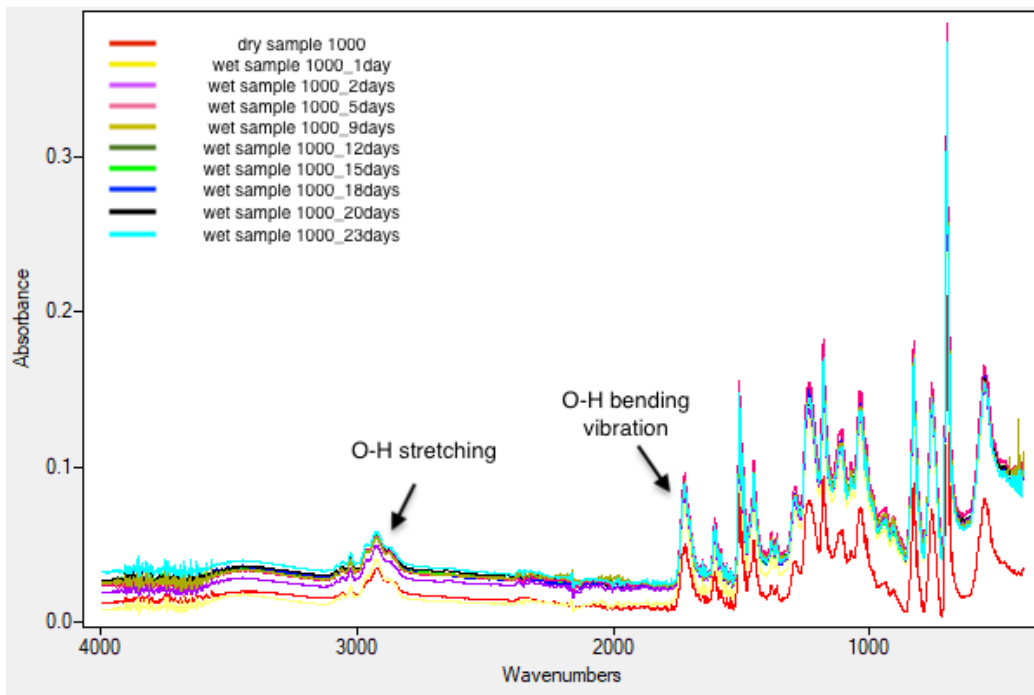
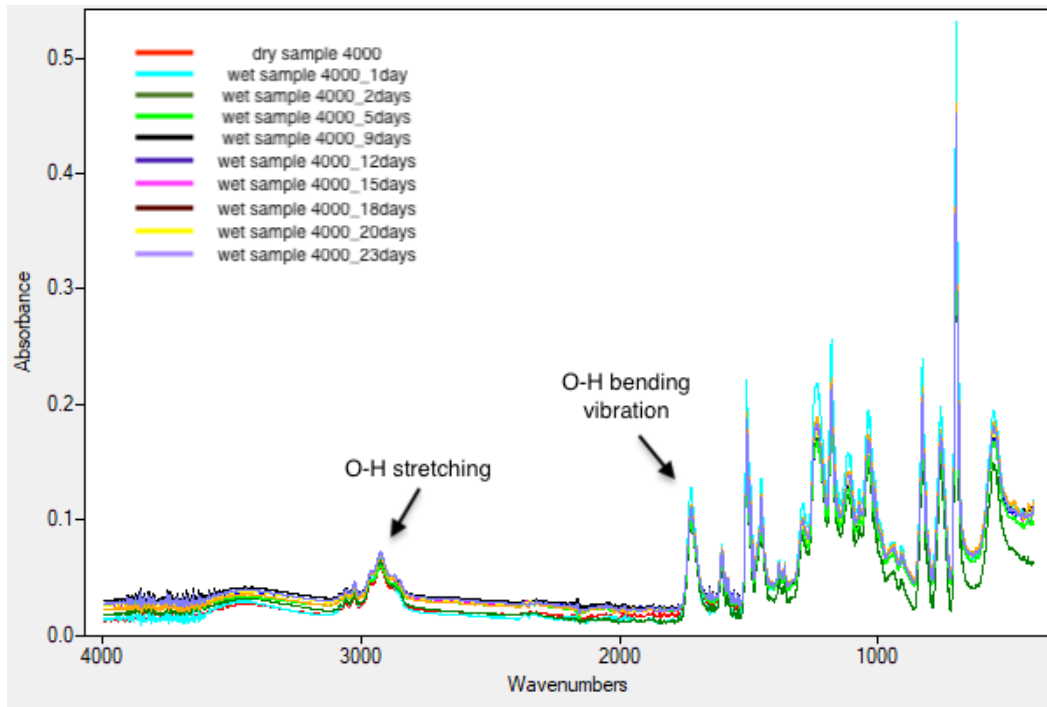


Figure 22: FTIR spectra of composite resin samples polished by #1000 SiC grinding paper grits during 23 days of soaking time.



*Figure 23: FTIR spectra of composite resin samples polished by #4000 of SiC grinding paper grits during 23 days of soaking time.*

Figure 24 illustrate the region of OH stretching (the wavelength from  $2840\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$ ) which is considered as the most sensitive zone of hydrogen bonding (H-bonding). The resulting samples mentioning here is the composite samples polished by the #320 of SiC grinding paper grits during 23 days of soaking time. Similar behavior results are observed for other specimens in different SiC grinding paper grits. The arrow in the image shows the significant increase of peak intensity corresponding to the rising of water uptake over soaking time. This can be explained based on the knowledge of the establishment of hydrogen bonding between the water molecules and the hydroxyl groups of composite constituents. The molecular positions of vinyl ester resin as well as the glass fiber constituting the testing composite samples can be mentioned here to explicate the interaction between water molecules and composite. In general, this band is correlated to the O-H stretching vibration as well as the hydrogen connection of hydroxyl groups existed in composite structures. Despite the deficiency of obvious structural shape to identify the assignment of the absorption band, numerous recent researches of the water impacted to composite materials by FTIR, for example the research by Laurie A. McDonough, resulted several suitable solutions by applying the proper deconvolution analysis methods. In the wavenumber of  $2840\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$ , hydrogen bonds of hydroxyl groups are relevant to the intramolecular and the intermolecular hydrogen bonding as well as the free

hydroxyl of polymer macromolecule in composite material. The peaks in this wavenumber are also demonstrated the contribution of the bound water and free water molecules bonded to the substrate [62] [63] [64]. In four cases of testing composite samples, the performance of spectra points out that the intensity of absorbance peaks in the band of O-H stretching increases with immersing time. This reveals the strong impact by the increment of water uptake in composite samples over soaking time. As shown in the Table 4, the intensity changes of the peak at  $2924\text{ cm}^{-1}$  after 15 days and 23 days of exposure in water.

*Table 4: Intensity changes of the peak at the wavenumber of  $2924\text{ cm}^{-1}$  when soaking composite samples in tap water.*

Sample	Absorbance			Percent of intensity changed (%)	
	dry	wet_15 days	wet_23 days	after 15 days	after 23 days
grit #320	0.011136	0.040086	0.047657	260	328
grit #600	0.035708	0.052378	0.058392	370	424
grit #1000	0.035273	0.058213	0.058909	423	429
grit #4000	0.059549	0.063423	0.072604	470	552

To describe the process of water absorption occurred in composite samples, a deconvolution on the O-H stretching band for composite resin samples polished by grit of 320 after 23 days of soaking time was performed. This band was chosen to imitate distinct kinds of water molecular environments inside composite structure [65] [66]. Four sub-bands were selected and designated as the strongly-bound, medium-bound, weakly-bound as well as free water on the resulting spectra of absorbed water into composite specimens [67] which is shown in the Figure 25. The sub-band which is observed by the lowest frequency is ordinarily considered as the appearance of the strongly-bound water molecules [65]. The obtained peak at  $2869\text{ cm}^{-1}$  in this band is formed because of the H-bonding between water molecules and precise polar of the polymer constituent network in the composite structure. The peak observed at  $2923\text{ cm}^{-1}$  belongs to the largest sub-band which is considered as the medium-bound of hydrogen bonds in the composite. The water molecules of this group still have the hydrogen bonding with the polymer chains in composite network, however these connections are not as strong as the strongly-bound group. The peaks at  $2962\text{ cm}^{-1}$  and at  $3024\text{ cm}^{-1}$  indicate the performance of the weakly-bound

and free water molecules, respectively. The groups of less-bound water molecules are commonly found in the pores of composite materials which is established from the free spaces among polymer chain to create the hole free volume in the composite structure [67].

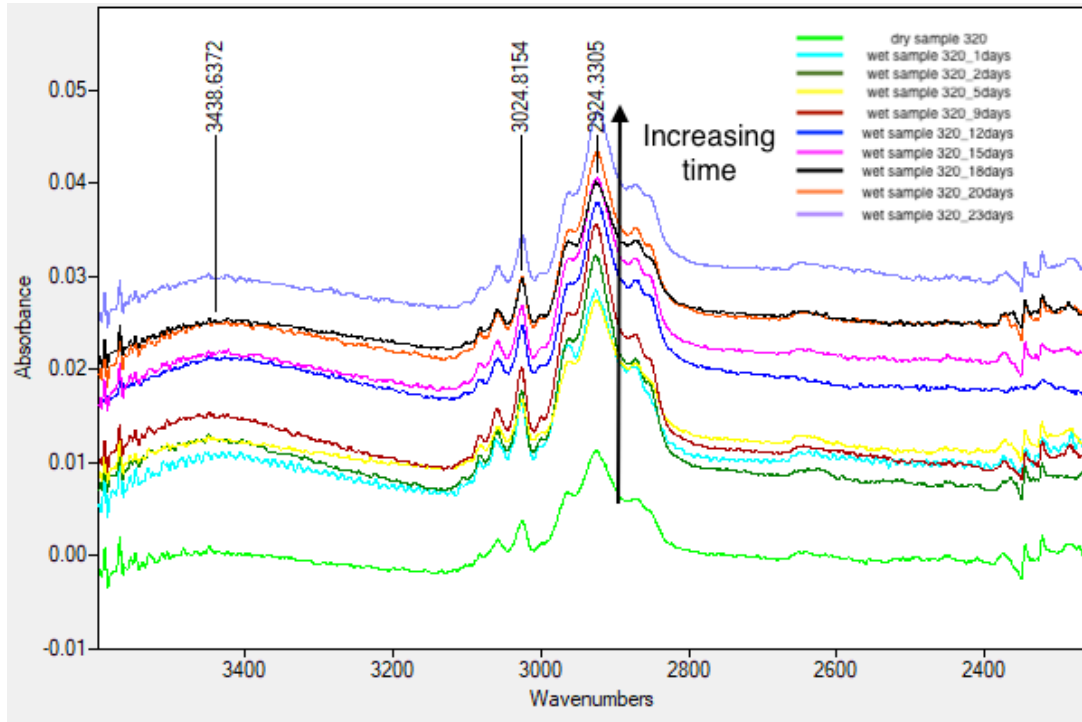


Figure 24: FTIR spectra of composite resin samples polished by #320 of SiC grinding paper grits during 23 days of soaking time in tap water and when being dry.

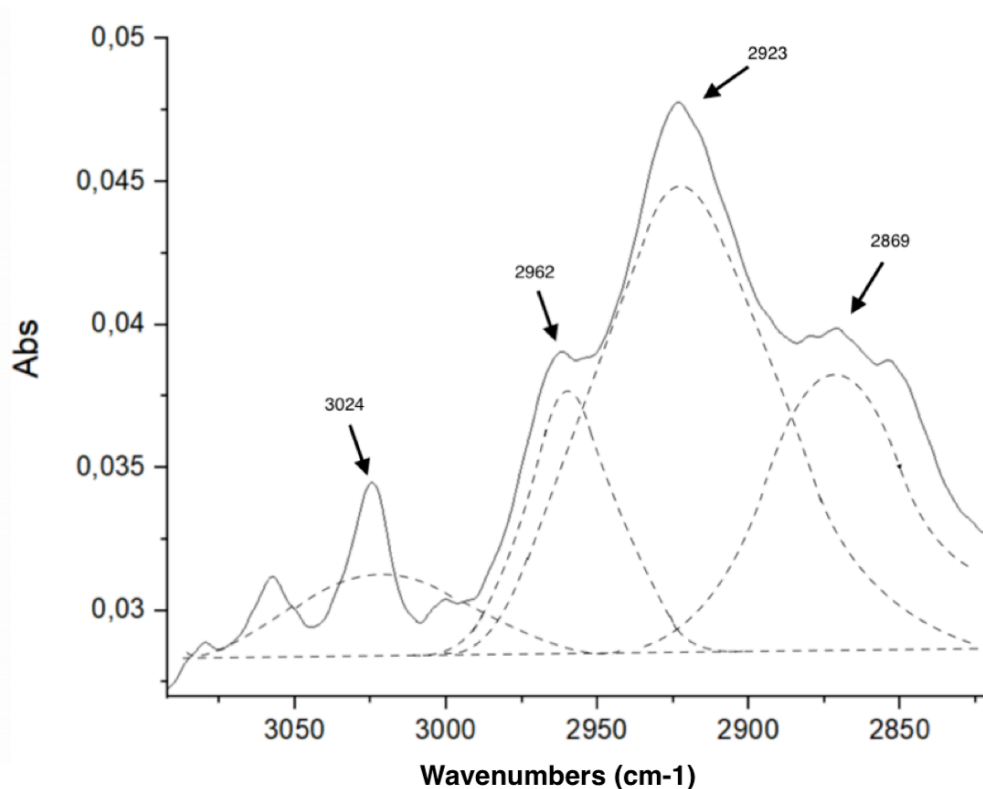


Figure 25: Deconvolution of the spectrum in the O-H stretching band for composite resin samples polished by #320 of SiC grinding paper grits after 23 days of soaking time in tap water.

The resulting FTIR spectra of the composite samples in four different SiC grinding paper grits in the polishing process when immersing into water during 15 days is also illustrated in the Figure 26. The arrow states the direction of increasing number of grit in the polishing process. Through these obtained bands, it can be seen clearly that in the region of O-H stretching band from  $2840\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$ , the demonstrations of the contribution of water molecules are impacted by different polishing protocol on surface of composite samples. In general, by increasing the value of grinding paper grits, the intensity of absorbance peaks is increased. The difference can be observed obviously in the spectrum of the paper grit of 320 compared to the other spectrum. Additionally, the Table 4 also points out that after 15 days of exposure in water, the intensity at the peak of  $2924\text{ cm}^{-1}$  of composite sample polished by the paper grit of 4000 has a highest increase of intensity with 470% while the samples polished by the paper grit of 320 has the lowest increase on intensity with 260%. This result confirms the relevance of polishing protocol to the water uptake into composite samples.

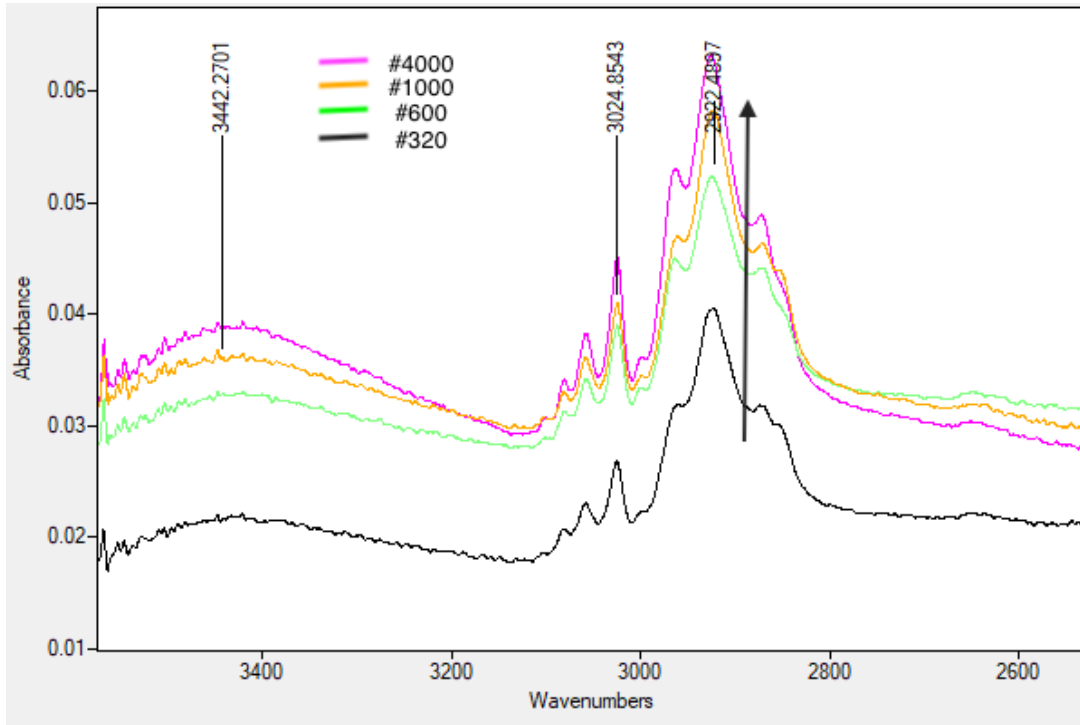


Figure 26: FTIR spectra of the composite samples in four different number of grits by SiC grinding paper of polishing process when immersing into water during 15 days.

## 5 CONCLUSION

Through this work, the study of water absorption into two types of composite materials including the natural composite, wood and the glass fiber composite of vinyl ester resin was carried out and analyzed following to different methods of qualitative analysis and quantitative analysis. The resulting data for the water absorption of wood specimens through mass changes during exposed in water was examined and modeled as the mathematical viewpoint of Fick's law diffusion as well as the empirical model of Peleg. On the other hand, the water uptake behavior of composite resin specimens was studied by using the alternative analysis methods of UV-visible spectrophotometry and Fourier Transform Infrared Spectroscopy (FTIR).

The result of water uptake into wood samples indicates the two-stage behavior of non-Fickian diffusion during water soaking time. To evaluate the water absorption process in two different wood materials of Birch wood and Balsa wood, the value of water absorption coefficient (equal  $3.3 \times 10^{-4}$  and  $8.35 \times 10^{-4}$   $\text{kg}/(\text{m}^2 \text{s}^{1/2})$ , respectively) and diffusion coefficient (equal  $8.23 \times 10^{-4}$  and  $5.67 \times 10^{-3}$   $\text{m}^2/\text{s}$ , respectively) of the wood specimens



were determined. As can be seen that the value of water absorption coefficient and diffusion coefficient computed for Birch wood was smaller than the result obtained for Balsa wood. This means that the Birch wood has lower water absorption and diffusion characteristic than Balsa wood. Additionally, the resulting parameter of non-linear regression analysis calculated by mathematical modeling the experiment data according to Peleg model was obtained. The value of root mean square error demonstrates the suitability of Peleg model for modelling the experiment of water absorption characteristic of wood materials. Specifically, the experiment data results that Birch wood has the smaller water diffusion coefficient than Balsa wood and this wood material also states the resulting data which is more appropriate with the empirical model of Peleg than Balsa wood.

In the circumstance of vinyl ester resin, water absorption behavior was observed through the alteration in the outcome spectra of specimens immersed into water for long periods by using the UV-visible-NIR spectrophotometer. The spectra of vinyl ester resin reveal the modification of the peak in the wavelength of 300 nm to 360 nm which points out the impact of water molecules to the resin samples as expectation. However, due to the limitation in the range of wavelength of this method, the changes of the resulting spectra are not clearly highlighted, therefore the influence of water molecules contribution monitoring in this case is uncertain.

By using the analysis method of FTIR, the outcome spectra for composite resin specimens indicate the significant effects of water on composite materials when immersing specimens in water for a long period. Two regions of wavelengths which are appreciably related to the increase of water uptake into composite samples include: the zone of wavenumber from  $2840\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$  which reflects the hydrogen bonded vibration mode or known as the region of OH stretching; and the other zone of wavenumber from  $1630\text{ cm}^{-1}$  to  $1780\text{ cm}^{-1}$  which corresponds to the bending vibration mode of water molecules presented in composite structure. The intensity of absorbance peaks in these ranges of wavenumber, especially in the zone of OH stretching from the wavelength at  $2840\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$ , increase corresponding to the water soaking time. This can be explained by the increment of water content in composite resin samples. Additionally, the influence of using various grinding paper grits on the water absorption process when polishing the surface of composite samples was also performed through FTIR spectra. Generally, by

increasing the polishing protocol on surface of composite samples, the intensity of absorbance peaks in OH stretching region is increased which demonstrate the relevance of polishing protocol to the water absorbed into composite materials.

## **6 LIMITATION OF EXPERIMENT METHODS AND SUGGESTIONS FOR FUTURE WORKS**

Beside of the achievements mentioning in the previous parts, this study has several limitations worth being considered here. Firstly, the experiments in this study were carried out in the assumption of non-fluctuated conditions from the environment. However, in actual experiments, there were noticeable fluctuations in the room temperature as well as the room humidity that affected the resulting data of water absorption, especially in the case of water absorption test in wood samples. Thus, it is necessary to study the effect of temperature, pressure and humidity of environment to water absorption in composite materials.

Secondly, in the water absorption experiments of composite resin samples, it is more accurate to use distilled water instead of tap water in testing so that we could minimize the error or interference in the outcome spectra from the analysis methods of UV-visible-NIR spectrophotometer and FTIR methods.

Thirdly, there should be a testing with an optical microscope to observe the microstructure on polished surface of composite resin samples that using different grinding paper grits in polishing process. From this work, it is conceivable to understand and explain the effect of the polishing protocol on surface to the water absorption.

Last but not least, to understand the impact of water absorption to mechanical properties of composite resin samples, the implementation of some mechanical tests, for example the tensile tests or the shear tests, is required.

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