DECEMBER 2018

M.Sc. in Mechanical Engineering

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UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES

INFLUENCE OF WATER AGING ON VIBRATION-DAMPING BEHAVIOR OF FIBER REINFORCED COMPOSITE LAMINATES

M. Sc. THESIS

IN

MECHANICAL ENGINEERING

BY

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Assoc. Prof. Dr. Ömer Yavuz BOZKURT

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December 2018

REPUBLIC OF TURKEY

UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES
MECHANICAL ENGINEERING

Name of thesis: Influence of Water Aging on Vibration-Damping Behavior of Fiber Reinforced Composite Laminates

Name of the student: Muhammet Enver Gökdemir

Exam Date: 21.12.2018

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Muhammet Enver Gökdemir

ABSTRACT

INFLUENCE OF WATER AGING ON VIBRATION-DAMPING BEHAVIOR OF FIBER REINFORCED COMPOSITE LAMINATES

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M.Sc. in Mechanical Engineering

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December 2018

43 Pages

This study was conducted to investigate the effect of water aging on vibration-damping properties of basalt fiber reinforced epoxy composites using experimental and analytical methods. Three different solutions (pure water, saltwater and alkaline water) were used for aging process. Specimens were immersed in solutions at constant room temperature and vibration tests were conducted for different periods of time as well as weight measurements. Water uptake ratio and diffusion coefficients were calculated via weight measurement procedure as the time progressed. Using diffusion coefficient, water uptake was plotted analytically and compared with experimental measurements. According to study, aqueous environment aging on basalt fiber reinforced polymeric composites did not cause significant change in natural frequency but led to approximately 29% increase in damping properties. According to water absorption tests, specimens aged in NaOH and saltwater solutions followed Fickian behavior at initial and saturation stages, however, pure water absorption behavior of basalt fiber reinforced composites did not show Fickian diffusion. Instead, a multi stage behavior was observed in terms of water sorption and desorption.

Keywords: basalt, diffusion, vibration-damping, water uptake, Fick’s Law

ÖZET

SU YAŞLANDIRMASININ ELYAF TAKVİYELİ KOMPOZİT LAMİNATLARIN TİTREŞİM SÖNÜMLEME DAVRANIŞINA ETKİSİ

GÖKDEMİR, Muhammet Enver

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Tez danışmanı: Doç. Dr. Ö. Yavuz BOZKURT

Aralık 2018

43 Sayfa

Bu çalışma, bazalt takviyeli epoksi kompozitlerin su ile yaşlandırılmasının titreşim-sönümleme özelliklerine etkisini deneysel ve analitik metotlarla araştırmak için gerçekleştirilmiştir. Yaşlandırma işlemi için üç farklı solüsyon (saf su, tuzlu su ve bazik su) kullanılmıştır. Numuneler, sabit oda sıcaklığındaki solüsyonlara daldırılmış ve titreşim deneyleri, ağırlık ölçümleri ile birlikte farklı periyotlarda gerçekleştirilmiştir. Zamana göre ağırlık ölçümüyle, su alım yüzdesi ve difüzyon katsayısı hesaplanmıştır. Difüzyon katsayısı kullanılarak, su alımı grafiği analitik olarak çizilmiş ve deneysel ölçümlerle kıyaslanmıştır. Çalışmaya göre, bazalt kompozitlerde sulu ortam yaşlandırması doğal frekansta önemli bir değişikliğe sebep olmamış, fakat sönümleme özelliklerinde %29 artış görülmüştür. Su absorbsiyon testlerine göre NaOH ve tuzlu su solüsyonlarında yaşlandırılan numuneler başlangıç ve doygunluk aşamalarında Fick yasasına uyan bir davranış sergilemiş fakat bazalt kompozitlerin saf su absorbsiyonu Fick yasasına uyan bir davranış göstermemiştir. Bunun yerine su alma ve bırakma açısından çok aşamalı bir davranış gözlemlenmiştir.

Anahtar Kelimeler: bazalt, difüzyon, titreşim-sönümleme, su alımı, Fick Yasası

To My Family…

ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisor Assoc. Prof. Dr. Ö. Yavuz Bozkurt for his help, encouragement and guidance in all stages of this work. I am also appreciative for his advices leading to open up my horizon.

I would like to thank Research Assistant Özkan Özbek for his advices and helps.

I would like to thank my other lecturers in Gaziantep University, for their contribution of my engineering education, expanding my point of view and transferring their experience with patience and helping their best about answering my questions.

I would gratefully acknowledge Scientific Research Center (BAP) of Gaziantep University for their financial support under grant number MF.YLT.18.15.

Special thanks to my family, friends and all people who has contribution in this thesis.

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BFRP	Basalt fiber reinforced plate
RH	Relative humidity
T_g	Glass transition temperature
CFRP	Carbon fiber reinforced plate
CF	Carbon fiber
VE	Vinyl ester
WU	Water uptake
PVB	Polyvinyl butyral
PF	Phenol
TGA	Thermogravimetric analysis
DMTA	Dynamic mechanical thermal analysis
FTIR	Fourier transform infrared spectroscopy
FFRC	Flax fiber reinforced composite
GFRP	Glass fiber reinforced composite
HDM	Hindered diffusion model
Wf%	Weight fraction
D	Coefficient of diffusion
C	Concentration of diffused substance
M_t	Moisture uptake at given time
M_m	Moisture uptake at saturation
h	Thickness
ζ	Damping ratio
$\Delta\omega$	Bandwidth
ω_n, ω_1	Natural frequency of first mode
E’	Storage modulus

E’’	Loss modulus
L	Length
ρ	Density
A	Cross-section area
I	Moment of inertia

CHAPTER 1

INTRODUCTION

1.1 Introduction

Composite structures have long history of usage in the world. It dates back around 4900 B.C. and used mostly for construction material. In 20th century, high strength fibers and adhesives were developed [1]. Therefore, composite materials have gained importance in the last decades due to superior mechanical properties [1] such as; high strength to weight ratio, high fatigue resistance, low cost and easy production compared to conventional materials [1]. Due to these advantages, they are used increasingly in critical applications such as; aerospace, marine, vehicle or military in various forms. However, their properties may degrade in moist or aqueous environments over a period of time [2,3]. In moist or aqueous environment, water molecules are absorbed by the composites over the time, resulting swelling of matrix [3,4] and change in mechanical properties due to chemical events [2,3,4]. Absorption of water is known to plasticize the polymer and reduce glass transition temperature leading to decrease the mechanical properties and durability [3]. Depending on the temperature and immersion time, longitudinal, compression, interlaminar and intralaminar properties degrade after moisture absorption [3]. Also, it causes crack nucleation by decreasing of the hydrogen bond [3] and in thermal cycling, it damages the cross-linked structure of matrix [5]. Therefore, it is crucial to understand the behavior and durability of composites in humid environment for short and long terms in critical applications requiring long term operation time.

There exist many utilization areas of composite materials and this requires several test procedures and experiment types in order to design the most convenient composite product for applications. For this reason, the studies with different aging environments such as; moist and aqueous media with different aging conditions, pure water, tap water, acidic or basic solutions at different temperatures exist in literature using natural or synthetic fibers with pure or hybrid configurations at different orientations [7]. However, the number of long-term aging studies are fewer compared to short term studies due to more time requirement for experiments depending on the material and design of composite. Also, the longer time period of aging provides more accurate results for aging. Therefore, the long-term aging studies are important for the long-term durability of composite applications.

Water uptake behavior of composites mainly depends on the material used in production. For example, natural fibers tend to absorb water either vapor or liquid form resulting change in physical, chemical and mechanical properties [7]. Synthetic fibers are less effected from the water due to water resistant properties. In addition to fibers, epoxy is also vulnerable to humid environments [2, 7,8]. Upon water diffusion into epoxy, swelling and hardening occurs and decreases the adhesion ability to fibers. Void content is also one of the important factors that effecting the water absorption behavior of composites due to allowing water to diffuse along the material and degrade the material in less time.

This study was aimed to investigate the long-term effects of pure, salt and alkaline water environment on the vibration-damping properties of basalt fiber reinforced epoxy laminates. The composite samples were prepared by stacking 12 fabric layers and vacuum assisted resin transfer molding technique. Specimens were removed from composite laminates by a 3-axis CNC router according to ASTM E756 standard for vibration tests. Three types of aging media using pure water, saltwater and alkaline water were used for all types of specimens. The specimens for vibration tests were both weighted for water uptake and subjected to free vibration tests for determining natural frequency and damping coefficient periodically.

Objectives of Research and Tasks

It is important to know the effect of long-term durability of composite laminates under aqueous conditions for reliable designs such as marine applications. The main objective of this study was the aging of the basalt fiber reinforced laminates under different aqueous solutions to investigate the change in vibration and damping properties followed by the research tasks:

I. Fabrication of basalt fiber reinforced composite laminates.

II. Aging of the basalt fiber reinforced composites under different aqueous conditions.
III. Determination of water absorption characteristics of composites at each period.
IV. Conduction of free vibration tests for each aging period.
V. Discussion of the effect of aging on the vibration-damping behavior of laminates.

1.2 Scope of Study

The main stages of this study are divided into five chapters as explained below:

- A short description of the study, introduction to research and main goals of the study was introduced in Chapter 1.
- A detailed literature survey about aging of various fiber reinforced composite materials, including natural and synthetic fibers, in aqueous environments was presented in Chapter 2.
- The properties of basalt fiber and other constituents, details of fabrication technique and the cutting of coupons from laminates using a three-axis CNC router were given in Chapter 3.
- Results obtained from experiments were reported in Chapter 4.
- Conclusions and possible further studies were expressed in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

There exist various studies including theoretical, numerical and experimental methods about the aging of composite materials under different conditions. There are many studies with carbon, glass, flax and aramid reinforced epoxies. However, aging and vibration studies related with basalt fiber reinforced plates are very limited, and therefore there is not enough data exist.

Kim and Yoon [3] studied the equilibrium water uptake of carbon/epoxy laminates under hygrothermal condition. Pure water was used for immersion at 35 °C, 60 °C, 70 °C, 85 °C, and 95 °C. The equilibrium water uptake was observed to increase with the rise in temperature.

Shen and Springer [6] presented the general mathematical expressions of diffusion procedure and conducted experiments of composites for both one and two sides, separately in constant humidity and temperature values. Graphite T-300 and Fiberite 1034 composites were used for the experiments in the range of 300-425K. Experiment and theoretical results were compatible.

Liljedahla et al. [7] examined adhesively bonded joints of aluminum and composite (CFRP) under moisture conditions and in water immersion. They used cohesive zone method for modeling the joints. Specimens were subjected to 80%RH/70 °C, 96%RH/50 °C and at 50 °C in tap water and deionized water up to 365 days. Gravimetric experiments were conducted to determine the diffusion coefficient. Deionized water and tap water results were compared and degradation was found to be faster in tap water. Pure water immersion did not alter the mechanical properties significantly after 7 years.

Zhai et al. [9] investigated the water absorption behavior of carbon fiber reinforced epoxy using electric contacts between plies in order to investigate the relationship between water absorption and resistance change in pure water at room temperature. After immersion, specimens were weighted in every 24 hours and saturation was reached after 100 days with 4.1% weight gain. Study showed no water absorption of carbon during water immersion, but the resistance of composite increased suddenly along the fiber direction after saturation was reached. The transverse resistance was observed to increase logarithmically, and an equation was derived for the determination of weight gain from transverse resistance value.

Tual et al. [10] assessed the sea water effects on the durability of carbon/epoxy composites for long term immersion. Three different specimens were manufactured using RTM (with 2.5- and 5-mm thickness), vacuum infused and prepreg methods with different orientations and immersed in sea water at 25 °C, 40 °C, 60 °C, 80 °C for 7500h. After experiments, failure strength was found to decrease between 20% and 40%, however, no significant change was found in moduli and small change in toughness was observed. The effect of thickness and orientation was also found insignificant.

Cheour et al. [11] researched effect of water aging on mechanical and damping properties of unidirectional flax fiber reinforced composites and examined the reversibility of loss factor and bending moduli by drying after aging operation. Free vibration tests were conducted for the determination of mechanical properties. Specimens were manufactured with three different lengths (240, 260 and 280 mm) and orientations (0°, 45°, 90°). Tap water was used with 4, 11 and 180 days of immersion time was conducted for aging. According to the results of experiments, fiber orientation had significant effect in water uptake. Aging resulted decrease in bending moduli and increase in damping properties for each specimen. Bending moduli was found to be partially reversible due to irreversible damage on fibers but damping properties could be reversible.

Kajorncheappunngam [12] analyzed the influence of aging and aging in sustained tension load of glass/epoxy and neat resin with four different solutions in 1 to 5 months immersion time on the mechanical properties in his PhD dissertation. 25 °C and 60 °C temperatures were used for solutions. Glass transition temperature, storage modulus, tensile strength, and strain at failure values were measured. SEM was used to examine the fracture surfaces of the specimens subjected to tensile load. According to experiments, phase separation was observed and glass transition temperature was decreased. At high temperature, T_g was observed to increase due to proceeding of resin curing. Mechanical behavior was not effected from sustained load significantly. Water was found to have greatest effect on the stiffness reduction of neat epoxy samples. Both neat resin and composite samples showed increment on T_g and stiffness.

Yan and Chouw [13] explored the aging process of flax fabric/epoxy composites in water, seawater and alkaline (5% NaOH) solution for 365 days. Tensile and three-point bending tests were conducted for mechanical properties and SEM was used for the analysis of microstructure examination. All specimens gained 8.5-9.4% weight and significant degradation occurred in mechanical properties. Alkaline had the greatest negative impact on composites and water had the least reduction effect on mechanical properties. Tensile and flexural modulus reduction was observed as higher than that of tensile and flexural strength (possibly due to stiffening because of polymerization). They also compared the results with synthetic fibers and found severe degradation in both synthetic and flax fibers after aging process.

Botelho and Rezende [14] searched the effect of moisture on the mechanical properties of polyamide 6.6/carbon fiber composites. Two different orientations ([±45] and [±0/90]) were manufactured by hot compression molding. Tests were conducted at 90% relative humidity in 80 °C temperature using environmental conditioning chamber. After 60 days of conditioning, moisture saturation was observed on specimens. Exposure to moisture environment caused decrease in both natural frequencies and elastic modulus. Elastic modulus values were found for both specimens using damping experiments and results were found similar with the modulus obtained by tensile tests. According to this results, using vibration tests to obtain the elastic modulus as nondestructive method was found as an alternative way for the determination of elastic modulus.

Kootsookos et al. [15] compared the seawater durability of the glass/polyester, carbon/polyester, glass/vinyl ester and carbon/vinyl ester composites used in marine industry. According to study, carbon composites were found to be more durable and absorbed less moisture compared to glass composites. Also, the durability of polyester based composites was found to be less durable than vinyl-ester based ones.

Menail et al. [16] outlined the effect of tap water aging on the mechanical behavior of glass and kevlar fiber epoxy composites. 1000 hours of aging was conducted. Fatigue and tensile tests were conducted to examine the mechanical behavior and the effect of aging after fatigue test. After aging, the materials become brittle and kevlar was found to be more vulnerable to tap water than glass fibers.

Li et al. [17] studied the effect of dry environment aging on the microstructures of aramid composites. Specimens were subjected in 70 °C, 90 °C, 120 °C and 150 °C of environments up to 2688 hours. Poly (vinyl butyral)/phenol formaldehyde (PVB/PF) resin was used. TGA, DMTA, FTIR analyses were conducted and ballistic limit velocities were measured. Mechanical and ballistic performance of materials were degraded after aging. Storage modulus was decreased and glass transition temperature was increased after aging.

Fitriah et al. [18] investigated the effect of aging on the compressive behaviors of glass fiber/epoxy composite pipes. Three different winding angles were used (±45°, ±55°, ±63°). Pipes were submerged to tap water at 80 °C for 500, 1000 and 1500 hours. According to results, water was found to have a significant effect to decrease on the compressive strength of materials and decrement of the winding angles resulted in increment in strength.

Amelie et al. [19] assessed the seawater aging of glass fiber reinforced epoxy and neat epoxy in determining the effect of aging on the mechanical properties. 4, 20, 40 and 60 °C temperatures of aging with 120, 300, 600 and 700 days of aging time was conducted. Decrease in strength was found as the water immersion time increased.

Apolinario et al. [20] researched the aging of flax and glass fiber reinforced composites immersing at 30 °C of water. Flax fiber reinforced composites showed higher water uptake, compared to glass reinforced plates. FFRC showed decrease in modulus by 37% and increase ultimate tensile strength by 34% but GFRP was not affected significantly. Water uptake was decreased to 9% by modifying flax fiber with silane based chemical treatment. After drying, structural changes were observed but mechanical properties were found to be similar to unaged specimens.

Miller et al. [21] studied the effect of salt water environment on the durability of unidirectional ([0°] and [90°]) glass fiber reinforced epoxy plates. 40 °C and 50 °C of immersion temperature was used. After immersion, mechanical tests were conducted. According to experiments; in 0° fiber direction, moisture leaded to decrease in tensile and compressive strength. However, in the 90° of direction, tensile strength was not effected significantly even though the compressive strength also decreased.

Muñoz and Manrique [22] researched the water aging and the effect of aging on mechanical properties of flax fiber reinforced epoxy composites. Deionized water was used for experiments until saturation. According to results, tensile stress was increased after saturation but tensile modulus and flexure properties were decreased.

Grace and Altan [23] assessed the modeling of moisture absorption of polymeric composites using three-dimensional hindered diffusion model for the long term theoretical prediction. They used incomplete experiment data for the recovery of HDM parameters. It was shown that the prediction of moisture behavior and saturation time can be accurately found with polymeric composites, using short time experimental parameters.

Bao and Yee [24] identified bismaleimide matrix carbon fiber for moisture diffusion and aging. Moisture absorption curves for both neat resin and composite were generated and compared in order to examine the interface effect. Short term absorption tests were observed to have no significant effect in terms of fiber-interface, but the in long term, diffusion was suppressed in the composites.

Karbhari and Xian [25] studied the hygrothermal effects on high volume fraction of unidirectional carbon/epoxy composites manufactured with pultrusion method. They used deionized water with three different temperatures of 23, 37.8 and 60 °C with 36 months of immersion time. Absorption, desorption, reabsorption and DMTA tests were conducted. Moisture uptake was found to be two-stage. Glass transition temperature was shown to decrease at first but after a while, increase was observed in T_g.

Assarar et al. [26] searched the mechanical properties and damage events of glass and flax fiber reinforced composites under water aging. Flax fiber was reported to absorb water about 13.5% while glass is 1.05%. After immersion, tensile stress decreased in both composites. Acoustic emission test showed that the result of degradation on the mechanical properties is matrix weakening. Water aging resulted decrease in Young's Modulus and maximum strain of flax-fiber composite, but elastic properties were hardly effected. Tension strength decreased in both composite specimens.

Menail et al. [27] examined the glass and Kevlar fiber reinforced composites in the case of fatigue, tensile test and water aging. Specimens were first subjected to fatigue loading and aged for different periods of time. After aging, tensile test was conducted.

According to study, water aging affected tensile strength compared to unaged specimens.

Verpoest and Springer [28] investigated the effect of fiber surface treatment on the moisture absorption behavior of aramid composites. 50 °C, 62 °C and 76 °C temperature in 50, 70, 100 percent humidity parameters were selected for aging. Maximum moisture content and diffusivities were determined with a new expression developed by authors to investigate the transverse diffusivities using moisture absorption data. This treatment reduced and delayed the effect of moisture on specimens.

Akay et al. [29] explored the moisture effect of Kevlar 49 epoxy laminates on mechanical and thermal properties. Autoclaving and oven-curing methods were used for manufacturing the specimens. Oven-cured specimens showed more moisture absorption than that of autoclaving specimens due to more void content.

Eslami et al. [30] assessed the temperature effect on the moisture absorption of perforated glass fiber reinforced plates in order to determine the flexural stiffness and bending loading capacity. Specimens were aged in 60% humidity with 40 °C, 60 °C and 80 °C environment temperature up to 55 days. After experiments, increment of aging temperature resulted in decrease of diffusion coefficient yielding increase of the moisture absorption and decrease in flexural properties due to degradation of matrix.

Ramesh et al. [31] studied the effect of hygrothermal aging of glass, Kevlar and glass-Kevlar hybrid epoxy laminates on the tensile and flexural performance. The specimens were immersed pure water, salt solution (30g/100 cc NaCl), 5 molar NAOH solution and 1 molar HCl solution at room temperature and 60 °C. Weight measurements were taken each month. Experiment results showed reduction in both tensile and flexure strength. Salt water had least effect on the mechanical properties, however acid solution resulted in more than 70% reduction on mechanical properties.

Alexander et al. [32] outlined the effect of hygrothermal aging on the vibration damping behavior of basalt fiber reinforced composites. Plain weave, twill weave and quadriaxial types of basalt fibers with 3- and 5-mm thicknesses were produced as specimens. They were prepared as four sets and the first set is used for vibration test without immersing water, others were immersed in pure water for 1, 2 weeks and 1 month, respectively to determine the change of vibration and damping values. The first three natural frequencies, mode shapes and damping coefficients were measured using free vibration test. According to study, various results were observed for different aging times for each types of specimens. Fundamental frequencies showed decrease at the end of 1 month, compared to unaged specimens but stiffness is increased in the case of twill weave and quadriaxial configurations. Damping coefficients were observed to increase with different ratios for each specimen.

Yu et al. [33] investigated the aging of CF/VE composites, neat VE casts, and pultruded CF/VE composites. Immersion was performed in 65 °C and 95 °C using pure water. Water absorption resulted in plasticization and high damage was occurred in interfacial adhesion. Water absorption of matrix resulted in composite swell, whereas carbon fibers did not absorb water and swelled Transverse flexural properties were decreased, however, flexural modulus were less effected.

Jiang et al. [34] assessed the aging effect of glass fiber reinforced composites and adhesive and examined the moisture characteristics. Aging conditions were selected as: 20 °C –50% RH (relative humidity), 20 °C water, 40 °C 96% RH and 40 °C water. Analytical models using 1- and 3-dimensional diffusion theories were used and compared with finite element results for determining diffusion coefficient. 3D moisture diffusion theory was found to be more reliable after comparison with FE results. Temperature increment and water accelerated diffusion process compared to humid and low temperature environments. Moreover, moisture diffusion was found to proceed along the fiber direction but not in the transverse direction.

Xiao et al. [35] analyzed the effect of aging on the mechanical properties of basalt fiber reinforced composites. They used pure water and alkaline solution for aging process at 23 °C, 40 °C, 60 °C and 80 °C. Tensile strength was measured with respect to aging time. For the 23 °C alkaline solution, tensile strength increased in the first 7 days but as the time progressed it started to decrease. Temperature increment resulted an increase in water uptake of specimens. Water was found less effective in terms of water uptake compared to alkaline solution at the same temperature.

Pandian et al. [36] examined the moisture absorption behavior of basalt fiber reinforced polyester resin composites in order to look for the alteration of mechanical properties. Sea and normal water were used in room temperature until saturation (96-120 hours) for aging operation. Woven basalt, short basalt, alkaline and acid treated basalt fibers were used for specimen preparation. Tensile, flexural and impact properties were examined for unaged and aged specimens and results were compared. According to results, all mechanical properties showed degradation after aging. Degradation level was found different depending on specimens and mechanical tests.

Kim et al. [37] researched the effect of seawater aging on the vibration-damping and fracture behaviors of basalt fiber reinforced carbon nanotube added epoxy laminates. Seawater was used for immersion up to 4 months. Damping coefficient was observed to increase 50% after immersion. Compliance and fracture load also increased but after saturation, fracture toughness decreased approximately by 20%.

Wei et al. [38] explored the artificial seawater effect on the mechanical properties of basalt and glass fiber reinforced epoxy composites. 10, 20, 30, 60 and 90 days of immersion time at 25 °C was selected. As the immersion time increased, tensile and bending strength decreased possible due to deterioration of matrix.

Tekin et al. [39] identified the effect of aging of different mediums on the bending behavior of glass fiber epoxy composites using both experimental and numerical method. Specimens were immersed to pure water, seawater, acidic water (30% HCL, 2 months) and left in room temperature without immersion up to 3 months. Young's Modulus and bending strength was observed to decrease from minimum to maximum in pure water, seawater and acidic water, respectively. Also, theoretical results showed good agreement with experiments.

Wan et al. [40] searched the carbon/Kevlar hybrid and nonhybrid composites with 3d braided configuration in terms of aging using Hank's solution at 37 °C at 1700 h. Kevlar was found to absorb the most water and carbon/Kevlar configuration was the second one following with pure carbon epoxy. Maximum reduction on shear and flexural strength was observed on Kevlar epoxy composite. Hybridization was found to lower the decrement of strength in terms of water aging.

Liu et al. [41] studied the basalt epoxy, glass epoxy, basalt vinyl ester and glass vinyl ester composites on the aging behavior. After tests, modulus of elasticity was decreased on BE, BV and GV-443. Tension strength did not reduce significantly. BV and BE has shown significant decrement on interlaminar shear strength.

Scida et al. [42] outlined the effect of aging on damage behavior and mechanical properties of flax fiber reinforced epoxy. Aging resulted in decrease both modulus of elasticity and tensile strength. Different failure modes which were fiber splitting, pulling out and explosion of microfibrils were investigated.

Alamri and Low [43] investigated nanofiller reinforced nanocomposites to examine the water absorption effect on the mechanical properties. Nanoclay platelets, halloysite nanotubes (HNTs) and nano-silicon carbide (n-SiC) particles were used for additive. Specimens were subjected to water at room temperature for 6 months. Nanoparticle addition was observed to increase flexural strength, flexural modulus and decrease the equilibrium water uptake. It can be concluded that it is possible using nanofiller to reduce water aging effect.

Batista et al. [44] assessed accelerated aging of polyetherimide/carbon fiber composites to examine effects on mechanical and chemical properties. Specimens were aged at 80 °C with 90% relative humidity for 8 weeks. Saturation was observed after 50 days with 25% of increase in weight. Fiber-matrix interface was not affected due to humid aging operation. They found to decrease of glass transition temperature after hygrothermal aging. Elastic modulus was not affected significantly, however, shear modulus was decreased from 13.27GPa to 10.50GPa.

Li et al. [45] researched the influences of both sustained tension loads and wet-dry cycles on the glass fiber fiber reinforced composites in water and saltwater conditions. Each specimen was immersed in water and dried at room temperature equally for 12 hours using 15, 30, 60, 90, 180 and 360 cycles. Applied stress was chosen to be 0%, 20% and 40% of the ultimate tensile strength of specimens. At first 15 cycles, tensile strength, modulus and rupture elongation was increased, however, after 15 cycles, these values were decreased almost linearly. Elongation at rupture was stabilized after 180 cycles of aging.

Kelverkloglou et al. [46] studied to construct a mathematical model for the prediction of moisture absorption, absorbed fluid concentration and mechanical properties after aging operation of glass reinforced cyanate ester composites. In order to compare the theoretical results, tests were conducted on the specimens for 40 °C, 60 °C, 75 °C, 90 °C for 61 days. The predicted values were found to have less than 10% error when compared to experimental results.

Mingchao et al. [47] analyzed the corrosion durability of basalt fiber reinforced composite in terms of boiling in pure water, 2 mol/L sodium hydroxide and 2 mol/L hydrochloric acid. For the chemical durability, specimens were immersed to acetone, pure water, 5% hydrochloric acid and nitric acid, 10% ammonia and 30% vitriol. After boiling, mass loss and strength reduction was found to have greatest in acidic solution, meaning basalt was more resistant to alkaline environment than acidic one. Water and acetone were found to have no significant effect up to 90 days of immersion period. Also, the mechanical properties of BFRP was compared with s2 GFRP and BFRP was found to have less tensile strength and modulus compared to GFRP.

Li and Sue [48] researched the aging behavior of unidirectional flax fiber reinforced epoxy composites. Each constituent was examined separately in terms of aging behavior. Aging temperatures were selected as 23 °C, 37,8 °C and 60 °C for the immersion in pure water up to 17 weeks. Water uptake, dimensional change and mechanical properties were measured and analyzed regularly. Also, SEM and FTIR were used for additional information about material during immersion tests. According to study, fibers and epoxy followed to Fick's law at first during immersion, but after a period of time, fiber degradation was occurred due to deterioration of flax fibers. They also showed the possibility of recovery of material, before damage and chemical alteration occurs. Aging resulted increase in plasticity of matrix, swelling of materials, significant change and damage in the structure of fibers and matrix.

Conclusion of Literature Review

Research on the previous studies have shown the following conclusions:

1. The main reason behind the composite degredation due to aging is swelling and plasticization of matrix due to water and reduction of interfacial bonding strength between matrix and fibers [3].
2. Increase in temperature leads to increases in water uptake of composite materials and decreases in water uptake equilibrium time [7]. Also, an increment in volume fraction results in higher cellulose content, therefore the percent of moisture is increased [36].
3. Pure water has the least damage to composites in terms of aquatic environmental aging. However, additives such as acid, salt or some

other substances results in increase the degradation rate of composite laminates mainly due to corrosive properties.

4. Natural fibers such as flax is more vulnerable in terms of hydrothermal aging than synthetic fibers such as carbon, glass or aramid.
5. It is possible to recover of certain composites after aging to some extend if the degradation is not high in fibers.
6. Water molecules moves along the fiber direction during immersion. Thus, the orientation of fibers affects the water uptake and saturation time.
7. Humidity reduces the natural frequency and elastic modulus.
8. Carbon fiber composites are more resistant than glass fiber composites in terms of hygrothermal aging.
9. The moisture diffusivity along the fiber direction is expected to be much higher than the bulk diffusivity in other directions (i.e., through-the-thickness of a laminate) [24].
10. Aging effects the Young's modulus and loss factor of composites either positive or negative [11,12,14,17].

CHAPTER 3

EXPERIMENTAL STUDIES

MATERIALS, EQUIPMENT, FABRICATION OF COMPOSITE MATERIALS AND CONDUCTION OF VIBRATION TEST

3.1 Introduction

In this chapter, the type of composite material and constituents, fabrication methods, test procedures and preparation of aqueous environments related with this study were presented. Properties and formation of basalt, production of basalt fibers, definition and properties of laminates, advantages of BFRE, fabrication of BFRE laminates with vacuum assisted infusion technique is explained in material section. Preparation of aqueous environment, gravimetric measurement, conduction of free vibration, definition of diffusion mechanism and construction of water uptake equation at any time using Fick's Law of Diffusion were described in tests section.

3.2 Materials

3.2.1 Basalt Fiber

Basalt is a magmatic rock formed from rapid cooling of lava, which is rich in magnesium and iron [61]. Production of basalt fibers consist of melting of basalt rocks about 1500 $^{\circ}$C, homogenizing of basalt and extracting of fibers, respectively. It is relatively new in the application of composite laminates compared to glass, carbon and aramid fibers but the usage is increasing gradually in many areas due to its advantages. It has better mechanical and physical properties than glass fiber with lower cost [37,47]. Also, it has wider temperature application range, higher oxidation and radiation resistance, higher compression and shear strength and natural fire resistance, compared to E-Glass fibers [47]. Interlaminar shear strength is reported to be higher than glass fiber reinforced plates due to better adhesion to matrix [47]. According to a moisture absorption study, conducted by Pandian et al. [36] basalt fiber reinforced composites were found to have 20% less effected in terms of mechanical properties degradation compared to glass fiber composites.

Figure 3.1 Basalt Fiber Fabric

3.2.2 Epoxy, Resin and Hardener

Epoxy resin, is the most frequently used matrix substance among the others such as: polyester, bismaleimide or cyanate ester etc. It provides excellent strength, adhesion, low shrinkage and multi-purpose usage [1]. Hardener is used as curing agent to increase the viscosity of epoxy resin for desired matrix properties such as; high viscosity, impact resistance and rigidity. Curatives start crosslinking of epoxy resin and forms three-dimensional cross-linked structure.

Epoxy (EPIKOTE Resin MGS L 160) and hardener (EPIKURE Curing Agent MGS H 160) is used for this study manufactured by Hexion and supplied by Dost Chemical Industrial Raw Materials Industry, Turkey. The properties of epoxy and hardener is shown in the table.

Table 3.1 Properties of Epoxy

Properties [**at 25^0 C**]	Epoxy Resin **MGS L 160**	Hardener Agent **MGS H 160**
Density [g/cm^3]	**1.13-1.17**	**0.96-1.00**
Viscosity [mPas]	**700-900**	**10-50**
Epoxy equivalent [gr/equivalent]	**166-182**	**550-650**
Epoxy value [equivalent/100gr]	**0.55-0.60**	**-**
Refractor index	**1.5480-1.5530**	**1.5200-1.5210**
Amine Value [mgr KOH/gr]	**-**	**550-650**

Figure 3.2 Epoxy Resin and Hardener

3.2.3 Laminate

Laminate is a type of composite material, consisting of thin layers with different types of properties. These layers consist of thin and long fibers such as glass, carbon, Kevlar, basalt etc. with different weaving types. Theses layers are superimposed with desired orientations. For example, all layers could be in the same orientation or can be rotated with a certain degree to improve the strength in other axes.

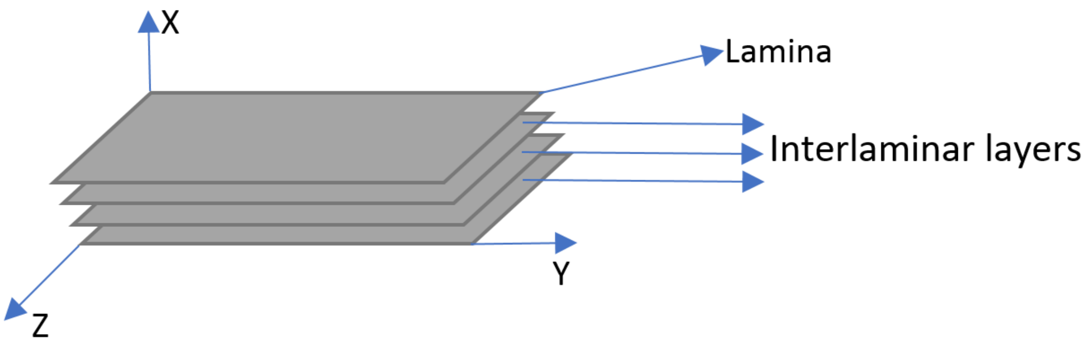


Figure 3.3 Laminate

3.2.4 Vacuum Infusion Method

This method is based on providing epoxy flow inside of fabric stacks using vacuum pressure after sealing the laminate with plastic bag. This provides the possibility of filling the voids more effectively inside of plies and fibers.

The process starts with placing the plies on the platform. After stacking is completed, the ribs were inserted at the edge of plies to prevent leakage during vacuum infusion. After this stage, the sealing is applied using vacuum bag. Two vacuum hoses were inserted to the edges of bag and the pump is started. Upon starting the vacuum pump, the resin is infused to laminate and continuous flow is provided. This flow moves the air bubbles inside of laminates and replaces with epoxy by moving toward the outlet hose. Bottom heat can be also applied according to the materials or manufacturing requirement.

Advantages of vacuum infusion process is:

- Allows higher fiber to resin ratio (up to 70% wt. of fibers).
- Provides higher strength and stiffness due to lower void content.
- Higher quality and more consistent product.
- Good surface quality and better accuracy.
- Compatibility for complex shapes of production.
- Environmentally friendly and relatively shorter application time.

Disadvantages:

- Accurate vacuum port location requirement for prevention of voids.
- Plunge, leakage or heating mistake usually results in waste of material.
- Upside surface is rougher than bottom surface. Because gravity gets the epoxy accumulated to bottom side. Thus, front and back surface quality is different.
- First installation cost is high.
- There are many disposable materials, such as; ribs, bag or valve.

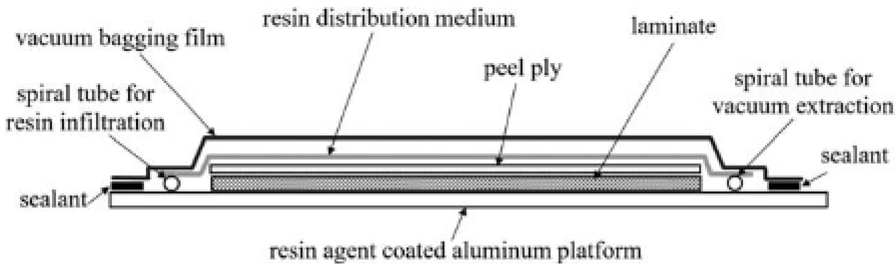


Figure 3.4 Vacuum Infusion System

3.2.5 Epoxy-Resin System Preparation

The resin is prepared according to epoxy and hardener mixing ratio, as described in the manual of manufacturer. The ratio is indicated as 100:25 by weight, meaning that 25 grams of hardener for 100 grams of epoxy. The amount of resin required for the preparation of composite laminates was calculated according to the weight of fibers for usage in experiments.

3.3 Manufacturing of Composite Laminates

The laminates were prepared by cutting the fibers in proper size (500x350 mm) for the test requirements. 12 plies were stacked for each specimen preparation. Then they were placed to the table for vacuum infusion process and the other components of sealing bags, pipes and tapes were inserted. After setup was complete, the vacuum pump was started for the operation. 6 hours later, the pump was stopped and the bottom heating on the table is switched on for curing. After 24 hours of curing, the material was removed for CNC cutting. The thickness of the specimens were measured as 2.26 mm.

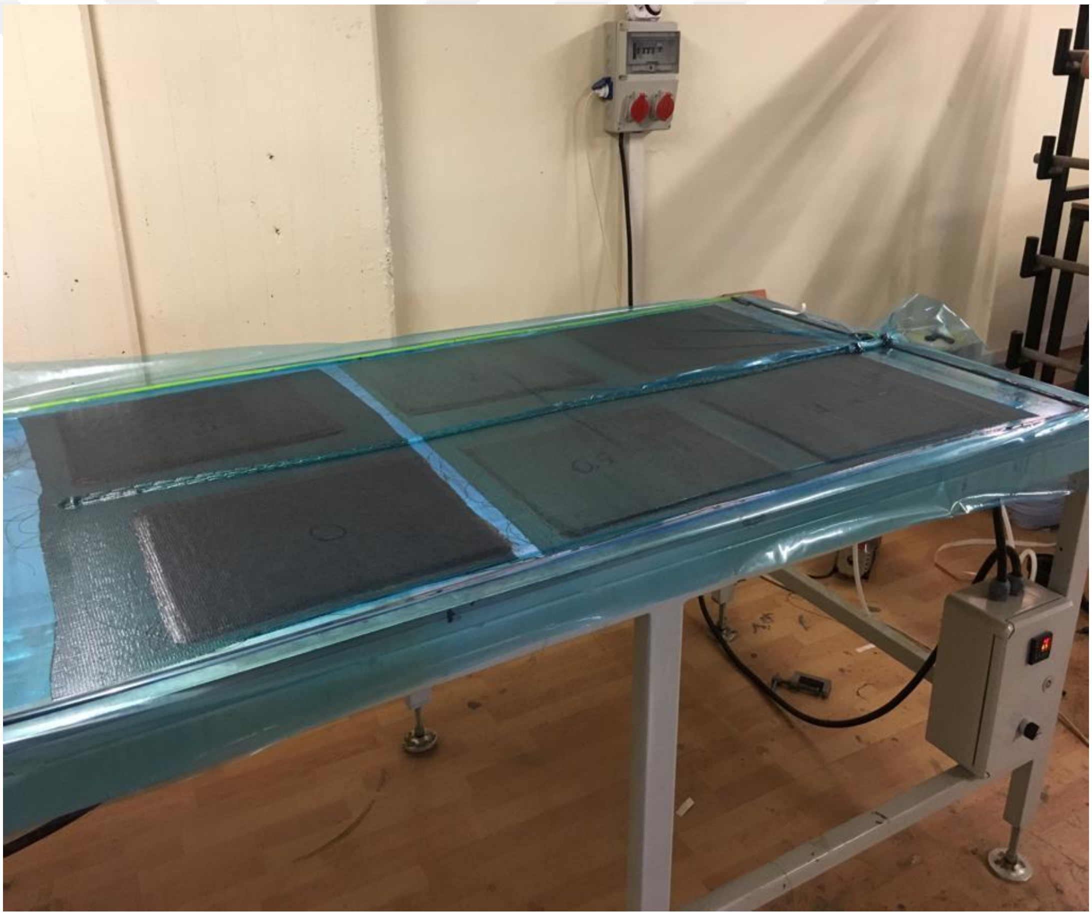


Fig 3.5 Stacking and Preparation for Vacuum Infusion Molding of Composites

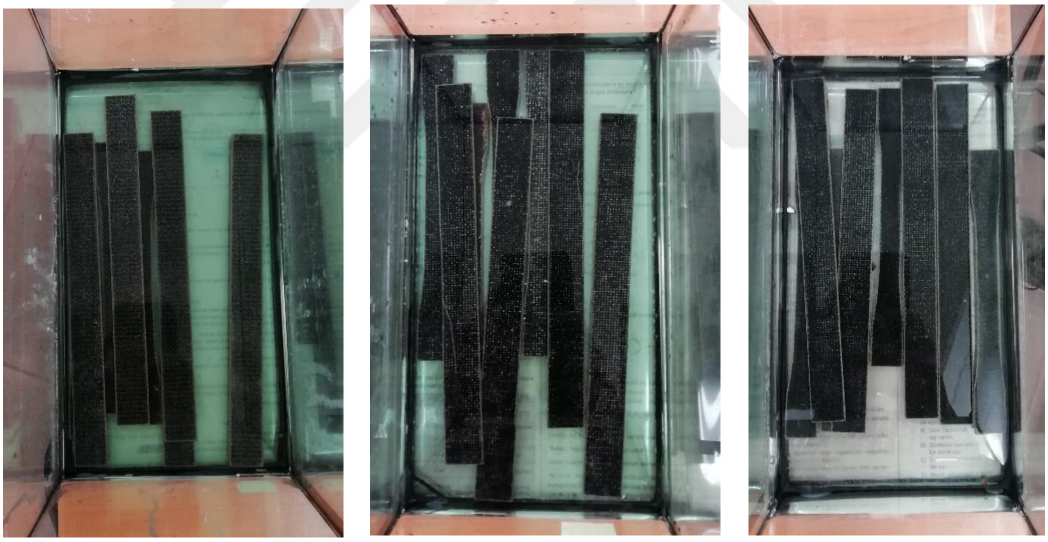
3.3.1 CNC Machining of Composite Laminates

The cutting operation of composites in proper size for experiments were performed using 3 axis CNC machine using 1 mm of cutting tool diameter for accurate cutting process.

Figure 3.6 CNC Machine for Cutting Operation

3.3.2 Preparation of Aqueous Environment

The aqueous medium was prepared using three different solutions (pure water, 1 M HCL and 30% NACI [31]) for the effect of different mediums on the aging behavior of composites. All solutions were stabilized at 25 °C of medium temperature.



a) **b)** **c)**

Figure 3.7 Aqueous Environment for Specimens; a) NAOH Solution, b) Salt Water c) Pure Water

3.4 Aging and Vibration Test

Vibration is an oscillation of solid or liquid substances about an equilibrium point. When an impact force is applied, the substance starts vibrating by moving two opposite direction until static equilibrium if force is not applied constantly. Most of machines generates vibrations in varying amounts at each location due to moving parts. To guarantee reliability, the machine parts must be designed in accordance with vibrational effects.

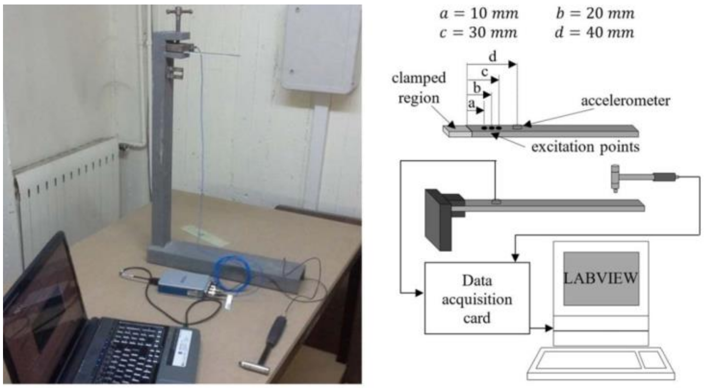


Figure 3.8 Free Vibration Device

Three types of vibration exists:

Free Vibration: The vibration of objects at it natural frequency by an excitation of a short time of force and releasing such as applying tension and releasing. An example for this phenomenon is a pendulum swinging motion.

Forced Vibration: If the input is applied constantly with a time-varying disturbance, the substance keeps vibrating until the input is removed. Working machines are good example for this situation, for example: engine of a car, electrical toothbrush etc.

Damped Vibration: During continuous input application to the system, if the vibration is compensated and ceased with some factors, this type of vibration is said to be damped vibration. Springs, dampers or shock absorbers are an effective method of elimination of vibration in most of systems.

In this study, to determine the natural frequency and damping coefficient of materials, free vibration tests were performed following the ASTM E756 standard. Vibration tests were conducted for the aging periods of 1, 3, 7, 15, 30, 60 days. Specimens were immersed to aqueous solution for the specified periods of time. Removed from tank at the measuring times and wiped out with tissue for removing the droplets, then weighted immediately and immersed back to the solution. PCB 086C03 impulse hammer for the excitation of vibrations, PCB 352C03 ceramic shear ICP accelerometer for the measurement of acceleration and National Instruments NI 9234 for data acquisition was used for the determination of vibration and damping properties of specimens.

3.5 Diffusion Mechanism

Diffusion is the transportation of matter due to random motions of molecules or atoms [3]. The diffusion speed varies with medium such as; very high in gases, slow in liquids and very slow in solids [4]. Equation of diffusion is created by Fick (1855) using heat conduction equation derived by Fourier (1822) [3]. According to theory of diffusion for isotropic materials, the transfer rate of a substance in a unit cross sectional area is proportional to the measured concentration gradient, which is normal to this area [3]. Fick's first law is expressed as:

$$F = -D\frac{\partial C}{\partial x} \tag{3.1}$$

F : rate of transfer for each unit area. Also as known as diffusion flux.

C : Concentration of diffusing substance.

x : Position of substance normal to section.

D : Diffusion coefficient.

According to this equation, diffusion occurs with the movement of molecules from high concentration area to low concentration areas.

Fick's second law of diffusion expresses the diffusion concentration change with time. In three-dimensions with variable diffusion coefficients for each axis is given by following equation:

$$\frac{\partial C}{\partial t} + \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_y}{\partial z} = 0 \tag{3.2}$$

If the diffusion coefficient is constant, then equation becomes:

$$\frac{\partial C}{\partial t} = D(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}) \tag{3.3}$$

If the diffusion is one dimensional, the equation reduces to:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{3.4}$$

The diffusion characteristics of the composite specimens can be obtained firstly via weight measurement during water immersion experiment. When the specimens were taken out from container, it is wiped out and weight is measured with a 0.1 gr sensitivity weighting device.

The weight gain data is used for the calculation of percent water uptake using the formula below [5,49]:

$$M = M(t) = \frac{Weight\ of\ immersed\ material\ at\ time - weight\ of\ dry\ material}{weight\ of\ dry\ material} x100 \tag{3.5}$$

After measurement of weight gain, one of the solutions of differential equation is used for the estimation of water concentration at given time. There exists more than one solution for each condition. In this type of studies, the solution by the method of separation of variables is used [51].

$$\frac{\mathrm{M}_t}{\mathrm{M}_m} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\left(\frac{1}{(2n+1)^2}\right)\exp\left(\frac{-(2n+1)^2\pi^2 Dt}{h^2}\right) \tag{3.6}$$

M_t : Moisture percent at given time.

M_m : Equilibrium moisture percent at saturation.

D : Diffusion coefficient

h : Thickness

This equation was calculated by Shen and Springer [6] as:

$$\frac{\mathrm{M}_t}{\mathrm{M}_m} = 1 - \exp\left[-7,3\left(\frac{Dt}{h^2}\right)^{0,75}\right] \tag{3.7}$$

Diffusion coefficient can be found using initial slope in the water absorption graphics plotted as moisture content versus square root of time [6]:

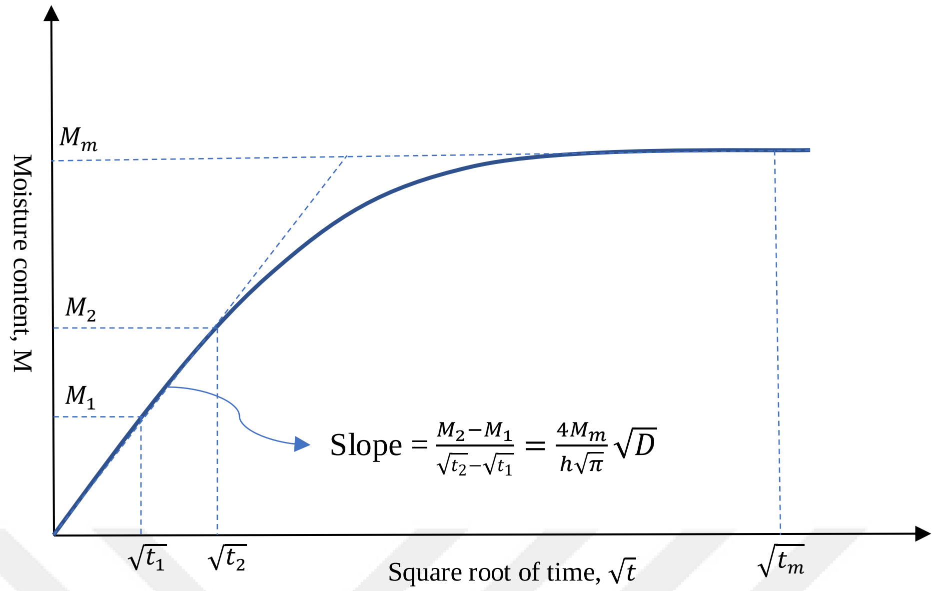


Figure 3.9 A Typical Water Uptake Graph and Calculation of D [6]

D was expressed as [11]:

$$D = \frac{\pi}{(4M_m)^2}\left(\frac{M_t h}{\sqrt{t}}\right)^2 = \pi\left(\frac{k}{4M_m}\right)^2 \quad (3.8)$$

k : slope of linear part of the curve $M_t = f\left(\frac{\sqrt{t}}{h}\right)$ which is equal to $\left(\frac{M_t h}{\sqrt{t}}\right)$ in equation 3.4.

If the diffusion occurs at the edges of the specimen, the correction factor for edge effects can be used as:

$$D_c = D\left(1 + \frac{h}{l} + \frac{h}{w}\right)^{-2} \quad (3.9)$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presented the experimental results of aging and its influence of vibration-damping behavior of basalt fiber reinforced composites. Hydrothermal aging was conducted for 52 days at room temperature and periodic weight measurements were taken using gravimetric analysis. Measured water uptake results were compared with Fick's Law. Diffusion coefficient was calculated using initial linear slope in water uptake plot for each medium separately. During gravimetric analysis, vibration tests were also conducted to examine the effect of aging on vibration and damping characteristics of specimens.

The results were unified systematically using plot visualization for each type of experiment and specimen. Theoretical and experimental aging results were both given in figures to see the fitting of curves. Natural frequency, damping coefficient, storage modulus and loss modulus results were presented and explained for each condition, separately. Also, the relations of results due to aging were explained.

4.2 Hydrothermal Aging

4.2.1 NaOH Solution

Hydrothermal aging was conducted according to ASTM standards [49-51]. Specimens were immersed to pure water, 30% NaCl and 5 molar NaOH at room temperature. Each of the samples were weighted periodically and recorded for the determination of water uptake behavior. The water uptake percent was evaluated using equation and the diffusion coefficient was obtained using the moisture content versus square root of time plot as indicated in figure 4.1.

The water uptake function of the specimens were obtained using equation (3.7) and plots were drawn for both theoretically using Fick's Law and experimental measurements.

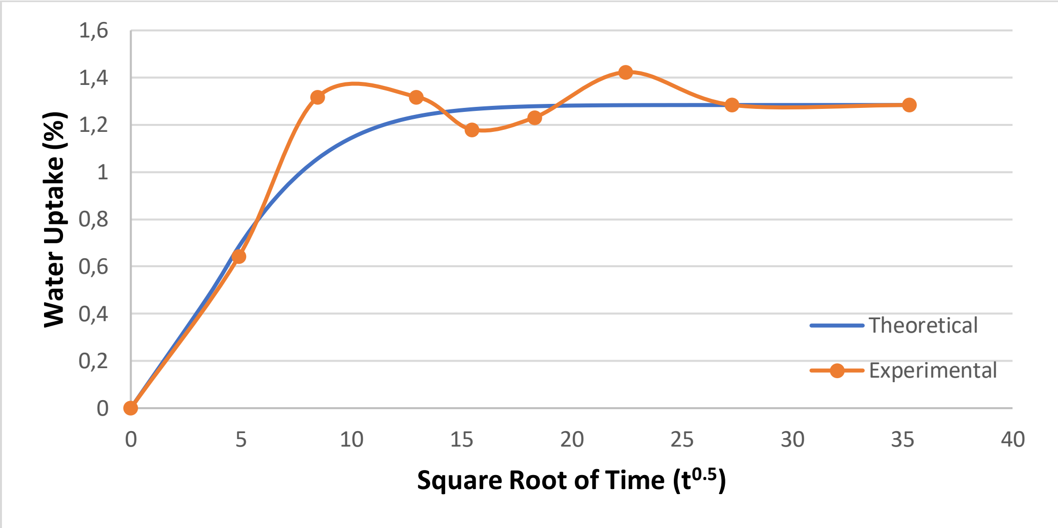


Figure 4.1 Experimental and theoretical comparisons of water uptake for NaOH medium.

Water uptake characteristics of specimens shows three different water uptake stages. First stage shows a linear increment up to some point, second stage consists of nonlinear curve concave in shape with increasing trend up to some point and sometimes decrement at the end of this stage. The third stage is the equalization of mass due to saturation, meaning no weight gain or weight loss. After this stage, the experiment was terminated, and equilibrium water uptake value was used for the determination of diffusion coefficient. The time for equilibrium varies according to the thickness of specimen, aging medium, aging temperature and material type.

In figure 4.1, experimental measurements of specimens in NaOH solution was shown. As can be seen in figure, there exists a linear increase in water uptake. After 3 days, water uptake starts to decrease until the end of 10 days and then restarts to increase until the end of 21st day. After ten days, there exists a slight decrease in water uptake and saturation occurs.

According to the specimens aged in NaOH solution, there exists a correlation between Fick's Law and experimental results at initial stage. At the end of the first stage, a rapid increase is observed during weight measurements. The water uptake percent is measured as 0.64% at the end of 24 hours. At the end of 72 hours, this value showed a 106% increase to 1.32%. After 168 hours, this water uptake percent remained at the same value. At the end of 10 days, water uptake started increase to peak point. Also, the highest water uptake is observed at the end of 21 days. As can be seen in figure 4.1, curve fit exists after 31 days of aging at saturation stage.

Table 4.1 Water Uptake Characteristics of Specimens in NaOH Solution

Days	Hours	$\sqrt{t}$	Specimen weights(g)				Mean (g)	WU (%)
			1	2	3	4		
0	0	0.00	14.55	14.51	14.24	14.33	14.41	0.00
1	24	4.90	14.68	14.57	14.36	14.39	14.50	0.64
3	72	8.49	14.75	14.70	14.42	14.52	14.60	1.32
7	168	12.96	14.75	14.70	14.41	14.53	14.60	1.32
10	240	15.49	14.72	14.66	14.42	14.51	14.58	1.18
14	336	18.33	14.73	14.66	14.43	14.52	14.59	1.23
21	504	22.45	14.76	14.70	14.46	14.53	14.61	1.42
31	744	27.28	14.72	14.69	14.41	14.55	14.59	1.28
52	1248	35.33	14.73	14.66	14.42	14.56	14.59	1.28

4.2.2 Saltwater Solution

Saltwater absorption tests also show similar behavior compared to NaOH solution at first and second stage. First two measurements show a linear water uptake with respect to square root of time. However, the absorption progresses until the next measurement which is at the end of 7 days. At the end of the first stage, the water uptake was measured as 1.08. After 4 days, the uptake raised to 1.166 and started to decrease after this point. After 21 days, the minimum value of 0.870 was observed. After this, specimen started to gain weight and maximum water uptake was reached at the end of experiment.

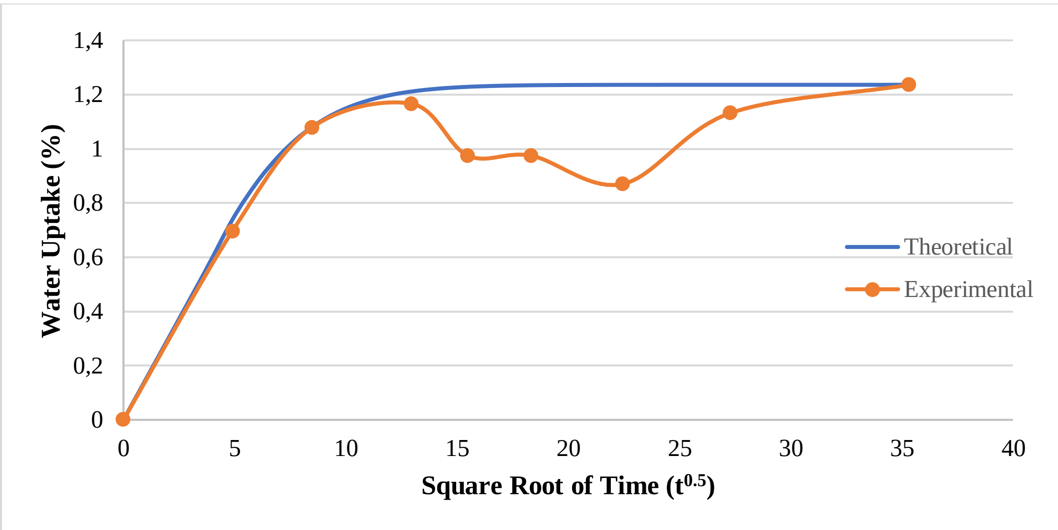


Figure 4.2 Experimental and theoretical comparisons of water uptake for NaCl medium

As can be seen in figure 4.2, water uptake continuously decreases unlike NaOH solution after 7 days until at the end of 21 days and starts to increase again. However, saturation was not observed on this specimen at the end of experiment.

Similar to NaOH solution, salt solution also shows good agreement at first initial stage. However, the second stage shows a high amount of decrement and fluctuation which was far above prediction and not compatible with Fick's law. After 21 days of aging, the material starts gaining weight, however, saturation was not achieved completely, and prediction was not close to experimental results.

Table 4.2 Water Uptake Characteristics of Specimens in Saltwater Solution

Days	Hours	$\sqrt{t}$	Specimen(g)				Mean (g)	WU (%)
			1	2	3	4		
0	0	0.00	14.24	14.21	14.62	14.39	14.37	0.00
1	24	4.90	14.34	14.31	14.70	14.51	14.47	0.70
3	72	8.49	14.39	14.36	14.78	14.55	14.52	1.08
7	168	12.96	14.40	14.36	14.80	14.57	14.53	1.17
10	240	15.49	14.39	14.35	14.75	14.53	14.51	0.98
14	336	18.33	14.39	14.35	14.75	14.53	14.51	0.98
21	504	22.45	14.35	14.34	14.76	14.51	14.49	0.87
31	744	27.28	14.39	14.38	14.79	14.55	14.52	1.13
52	1248	35.33	14.40	14.40	14.81	14.56	14.54	1.23

4.2.3 Pure Water Solution

Pure water experiments show different water uptake behavior compared to NaOH and NaCl solutions. The water uptake starts with linear increment and follows to second stage, however, after second stage, the third stage does not start and repeating starts the same sequence similar to first and second stage. It can be seen in figure 4.3 that the stage 1 and 2 is repeated two times. This situation is expressed by Flory as "Two Stage Theory". According to this theory, during water uptake, the polymer swells, and elasticity is increased leading to enhance the chemical potential. This induces the decrease the water uptake ability of polymer chains. This stage is similar to saturation phase. After a while, the swelled polymers start relaxation leading to decrease in chemical potential, resulting a new stage of water uptake [6,58]. Between 14 and 21 days, a constant water uptake did not change significantly, however, as the time progressed, swelling starts again and maximum uptake was measured at the end of 52 days.

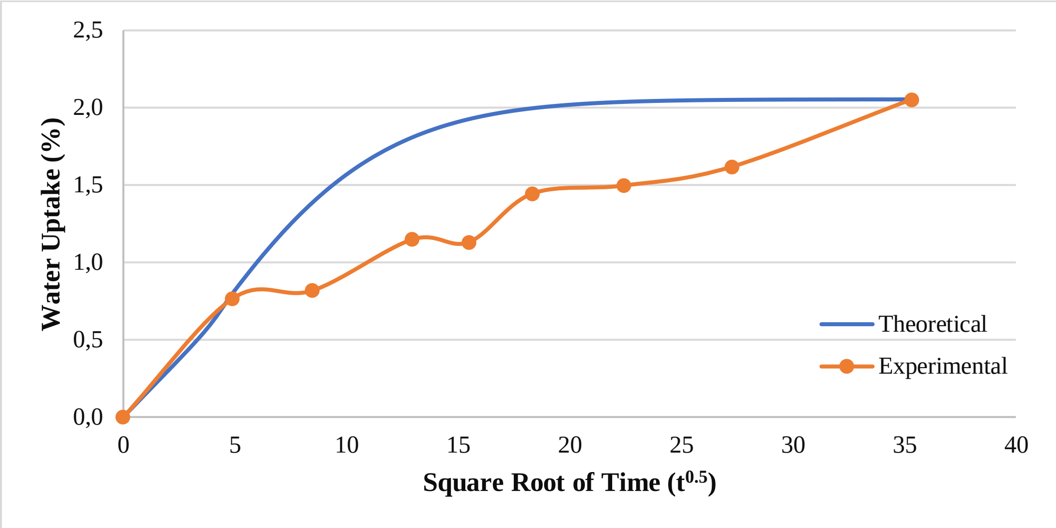


Figure 4.3 Experimental and theoretical comparisons of water uptake for pure water medium

Due to fluctuations on pure water uptake, the diffusion is not in agreement after linear stage. Because saturation was not achieved, the correlation was not achieved after linear stage. The effect of different aging media on the diffusion of basalt fiber reinforced composites both shows different water uptake behaviors and gives different mass gain percent results for each solution. This can be attributed to different effects of media due to distinctive properties of the molecules inside the solutions for example; molecular weights, sizes and interactions with epoxy.

During weight measurements, the mass of specimens decreases in some points, especially at saturation. The reason, behind the weight loss is attributed to the occurrence of chain scission due to water aging [53-55]. This event results in breakage of polymer chains, leaching out of residual monomers and degraded products to out of the resin [56,57].

Table 4.3 Water Uptake Characteristics of Specimens in Pure Water Solution

Days	**Hours**	$\sqrt{t}$	**Specimen(g)**				**Mean (g)**	**WU %**
			1	**2**	**3**	**4**		
0	0	0.00	14.23	14.38	14.48	14.36	14.36	0.00
1	24	4.90	14.34	14.47	14.56	14.52	14.47	0.77
3	72	8.49	14.36	14.46	14.59	14.51	14.48	0.82
7	168	12.96	14.41	14.51	14.64	14.55	14.53	1.15
10	240	15.49	14.43	14.56	14.61	14.50	14.53	1.13
14	336	18.33	14.44	14.59	14.68	14.57	14.57	1.45
21	504	22.45	14.46	14.58	14.69	14.58	14.58	1.50
31	744	27.28	14.48	14.59	14.71	14.60	14.59	1.61

52	1248	35.33	14.55	14.65	14.77	14.66	14.65	2.05

Table 4.4 Diffusion Coefficients of Specimens

NaOH Solution (mm^2/s)	Saltwater Solution(mm^2/s)	Pure Water Solution (mm^2/s)
2.87E-06	3.64E-06	1.61E-06

Diffusion coefficients of specimens in different medium was calculated using linear part of water uptake. According to results, diffusion coefficient was found lowest in pure water solution and highest in saltwater solution.

4.3 Free Vibration Test Results

4.3.1 NaOH Solution

According to free vibration tests, the natural frequency was found highest on the unaged samples as shown in figure 4.4. After first days of aging, the lowest natural frequency value was observed. In the following days, a slight increase was measured until 7 days. The highest natural frequency was 50.05 Hz on unaged sample, while the lowest one was 47.15 on the first day of aged specimen. Natural frequency is sensitive in terms of aging due to change in density or Young's modulus [37]. According to Meirovitch's continuous beam model [63], the natural frequency of isotropic beam can be described as:

$$f = \frac{1}{2\pi}\left(\frac{1.875}{L}\right)^2\sqrt{\frac{EI}{\rho A}} \tag{4.1}$$

where L, ρ, A and I are the length, density, cross-sectional area and moment of inertia of a specimen. According to this equation, natural frequency depends on density and Young's modulus. Decrement in Young's modulus and increment in density results in decrease of natural frequency. Because water uptake is in very low amounts and no significant density change was detected, the only variable effecting to natural frequency was modulus of elasticity. Another possible reason could be reduction of stiffness due to plasticization of matrix [20].

Damping ratio of specimens were calculated using half -power bandwidth method. This method is based on finding bandwidth of frequency response amplitude for each vibrational modes. For the first mode, the following formula was used:

$$\xi = \frac{\Delta\omega}{2\omega_n} \tag{4.2}$$

Storage and loss modulus of specimens were calculated using Euler-Bernoulli beam theory [62] as indicated in following equation:

$$E' = \left(\frac{2\pi L^2 \omega_1}{1.875^2}\right)^2 \frac{\rho A}{I} \tag{4.3}$$

$$E''(\omega) = 2E'(\omega)\xi(\omega) \tag{4.4}$$

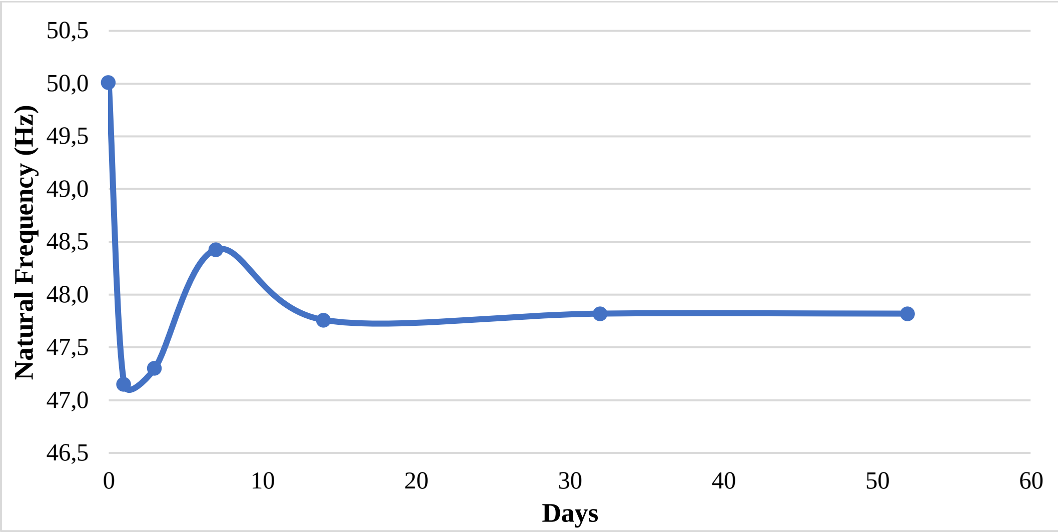


Figure 4.4 Natural frequency of aged and unaged samples in NaOH solution

From figure 4.5, it is shown that damping coefficients of specimens are more affected than that of natural frequency. First specimen had an average damping coefficient of 0.01820. After 1 day of aging, this value was measured as 0.01396 which was the highest damping coefficient value during aging operation. This means that there was a 29% of increase in damping coefficient, after swelling of NaOH solution of samples.

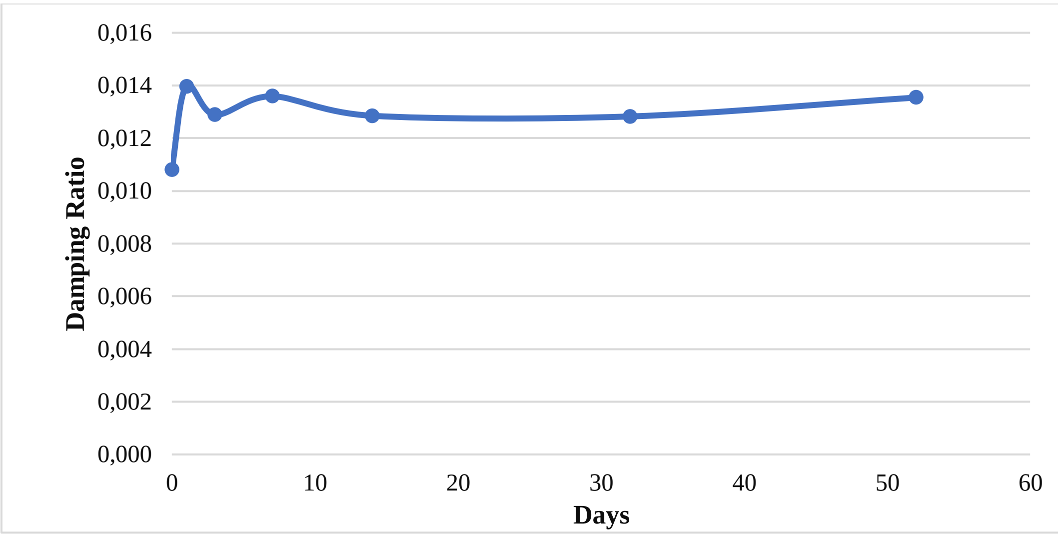


Figure 4.5 Damping coefficient of aged and unaged samples in NaOH solution

Storage modulus, shown in figure 4.6, have a similar trend when compared to natural frequency. With the start of aging process, specimens began swelling water and storage modulus showed a reduction.

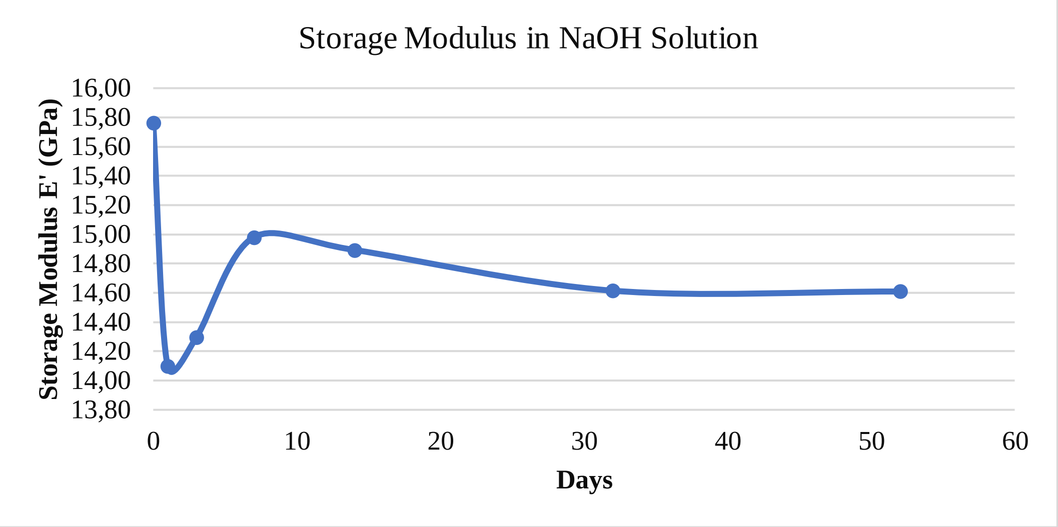


Figure 4.6 Storage modulus of aged and unaged samples in NaOH solution

Loss modulus was observed to have inverse trend of storage modulus. Therefore it was expected to increase after aging as indicated in literature [11]. The loss modulus of unaged specimen was in minimum value and as the aging was progressed, it started to increase. Because of fluctuation on water uptake, uniform increase in loss modulus was not observed. Similar to water uptake, fluctutations in loss modulus was measured as in the figure 4.7.

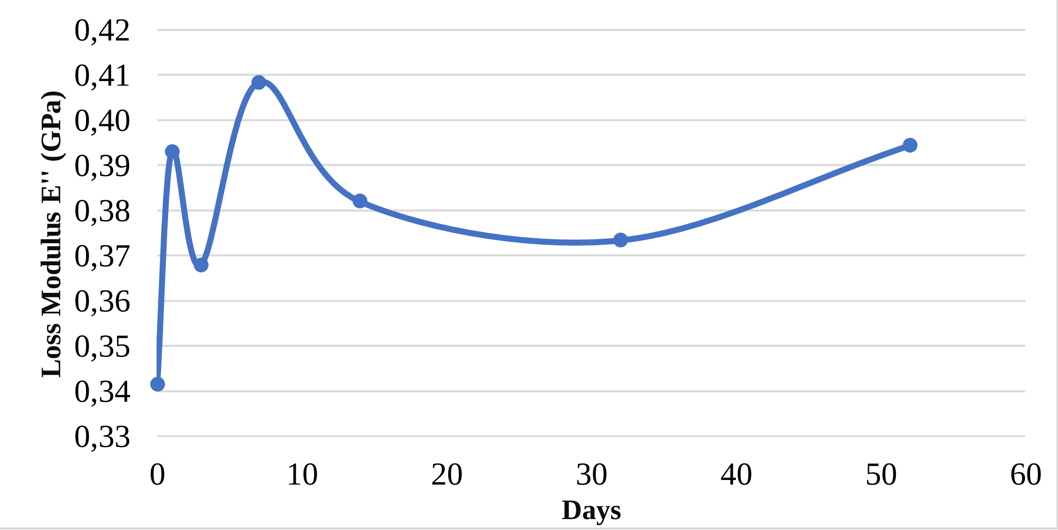


Figure 4.7 Loss modulus of aged and unaged samples in NaOH solution

4.3.2 Saltwater Solution

In saltwater solution, the natural frequency of the specimens were found on an average of 49.31 Hz. The smallest value was found at the last measurement as 48.26 as shown in figure 4.8. Considering the difference between the lowest and the highest values, there was no considerable difference among the natural frequency values. This means that, there was no significant effect of saltwater aging on the natural frequency of basalt composites.

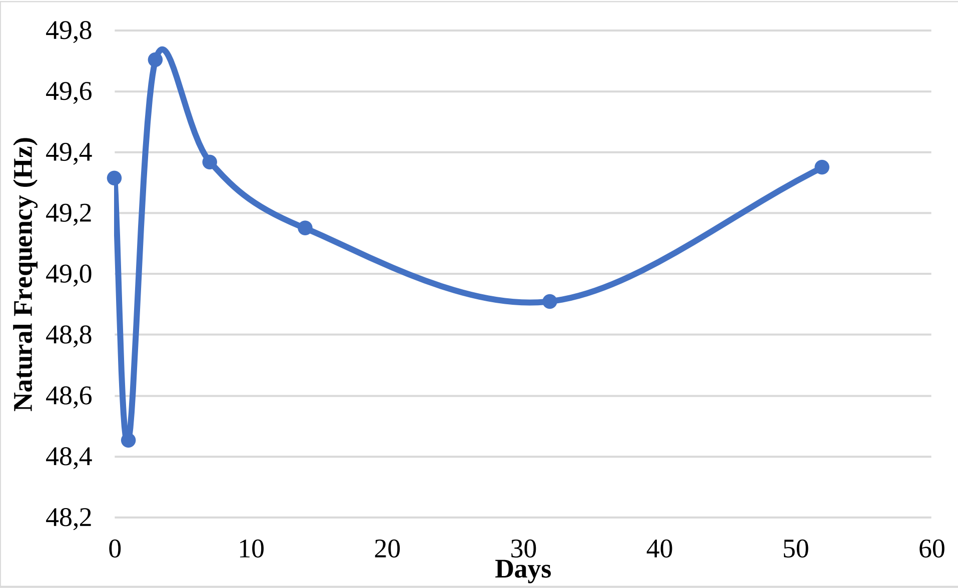


Figure 4.8 Natural frequency of aged and unaged samples in saltwater solution

Damping coefficient of specimens are found maximum on the 7 days of aged samples as 0.01092 and lowest on the first day of aged samples as 0.0951. When compared with unaged samples, there existed approximately 10% reduction on damping coefficient of specimens. However, fluctuations were observed on the damping values and this is possibly due to sorption and desorption of water from the environment of specimens as can be seen in figure 4.9.

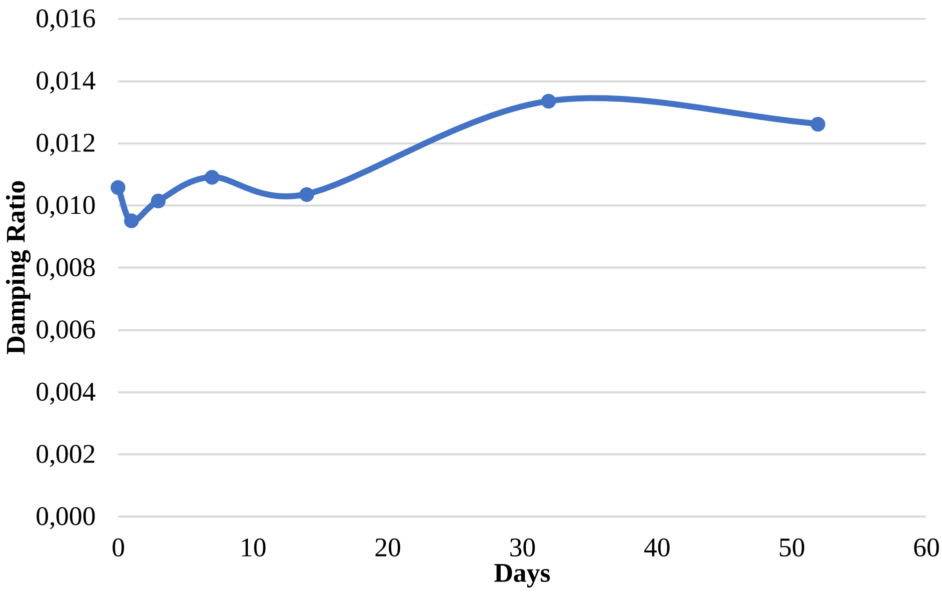


Figure 4.9 Damping coefficient of aged and unaged samples in saltwater solution

Storage modulus of the specimens that aged in saltwater solution showed similar values during aging. At 3rd day, there exist a significant decrease in storage modulus, however, a sudden increase is observed and the values remained similar. The possible reason of sudden drop at 3rd day was high amount of water swelling and plasticization, resulting in less storage ability of energy. In figure 4.10 a high amount of sudden drop can be seen, however, it is only 7% of reduction compared to unaged specimen.

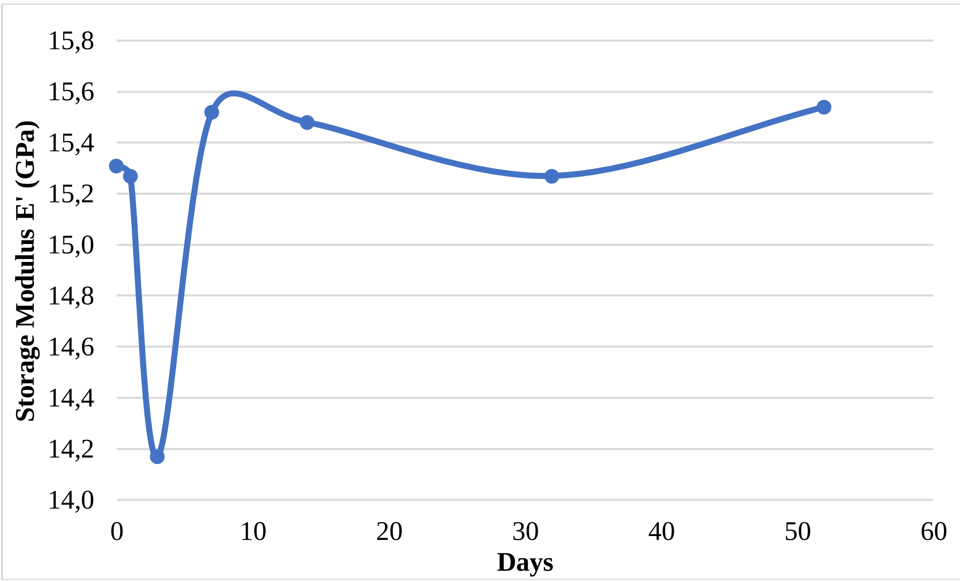


Figure 4.10 Storage modulus of aged and unaged samples in Saltwater solution

Loss modulus was observed to decrease upon moisture ingress as shown in figure 4.11. Usually, it is expected to increase due to cross-linking of matrix due to cross-linking. However, room temperature was not enough for cross-linking. Instead, the solution weakened the hydrogen bonds and reduced stiffness, resulting decrease in loss modulus upon increase the water uptake.

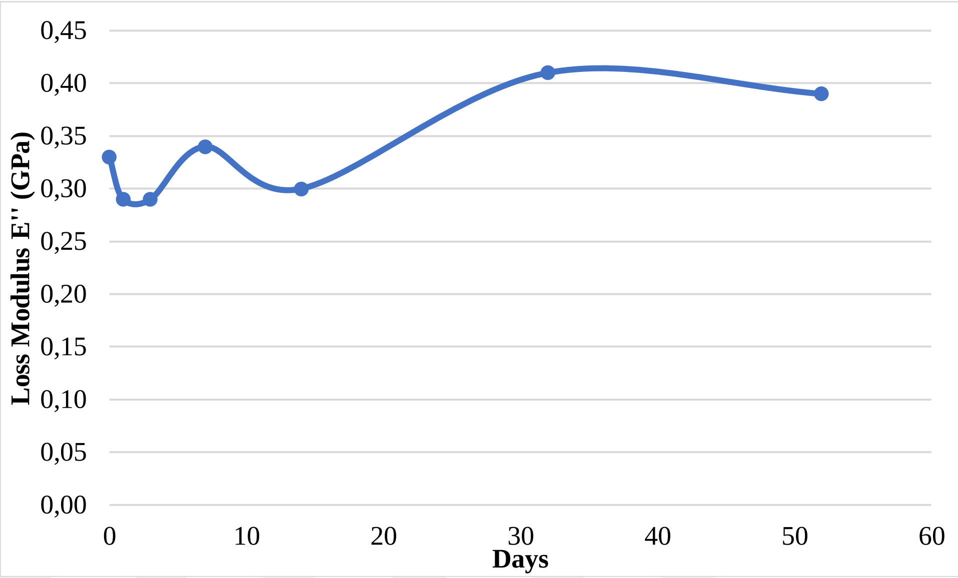


Figure 4.11 Loss modulus of aged and unaged samples in NaOH solution

4.3.3 Pure Water Solution

Specimens aged in pure water showed no significant variations in natural frequency after aging in 52 days compared to unaged samples as indicated in figure 4.12. Because specimens are thin, pure water has no relatively penetration and corrosive ability to epoxy and no significant water uptake is measured, the small change in natural frequency is considered as normal due to imperfection of specimens. Having less water permeability of basalt fibers have also contribution to this situation.

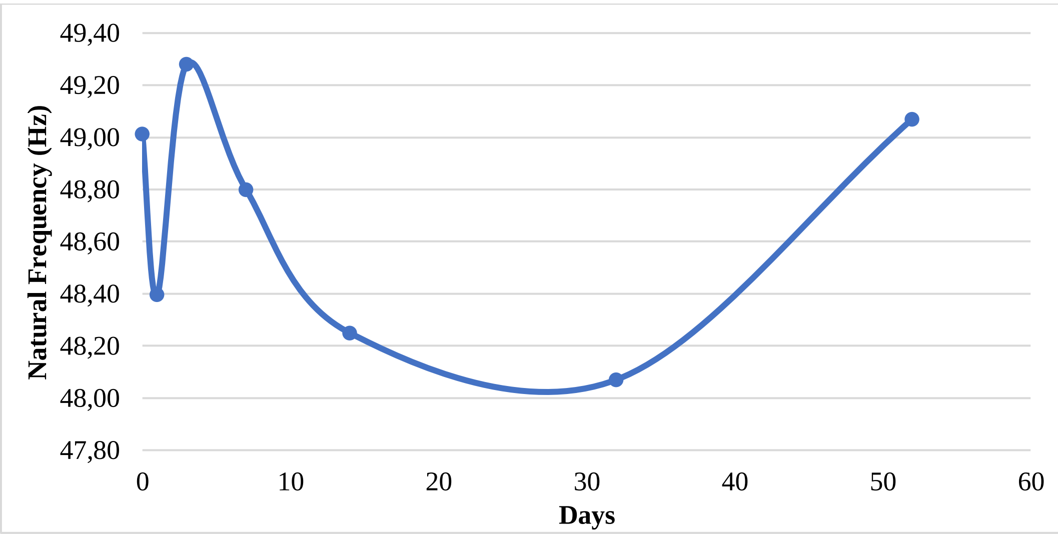


Figure 4.12 Natural frequency values of aged and unaged samples in saltwater solution

As can be seen in figure 4.13, damping coefficient seems to not affected from pure water aging. Even if there is a significant increase at the 52th days, all other coefficients were measured as same. It can be concluded that, pure water has no significant effect on damping behavior in this period of aging.

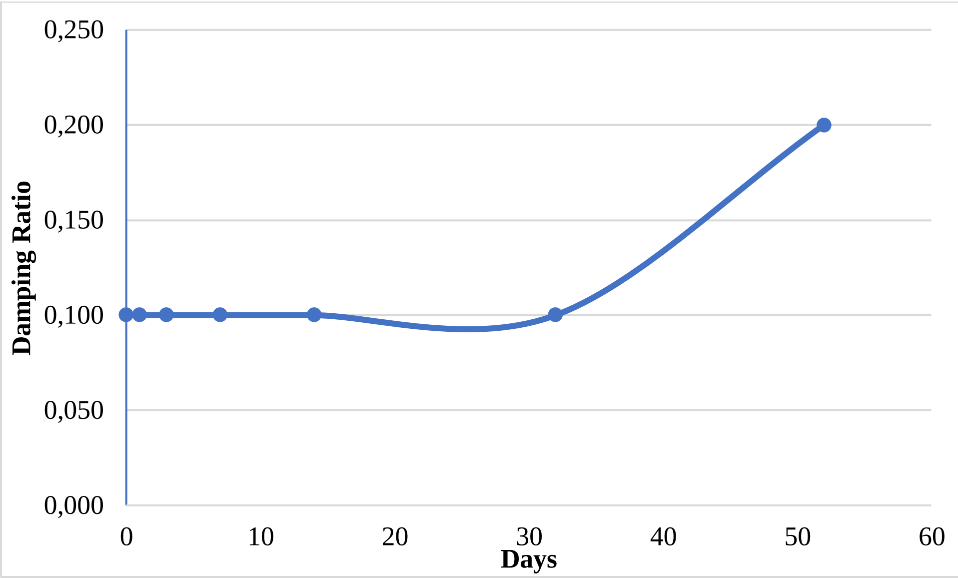


Figure 4.13 Damping ratio values of aged and unaged samples in pure water solution

In figure 4.14 storage modulus versus aging time was shown. Storage modulus values show irrelevant results in comparison with water uptake. Although water uptake had always increasing trend, storage modulus does not seem to be affected due to aging. Because there was 4% difference between the highest and lowest values, it can be concluded that this variation is due to imperfection of material.

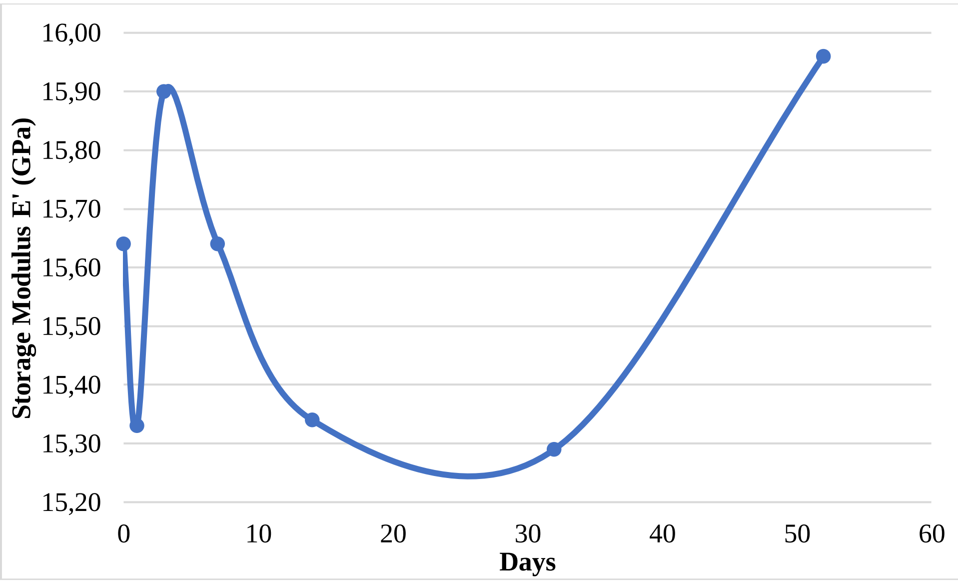


Figure 4.14 Storage modulus of aged and unaged samples in pure water solution

In terms of loss modulus, there exists a correlation between aging and loss modulus variation. 71% of increase could be observed in figure 4.15 between first and last values.

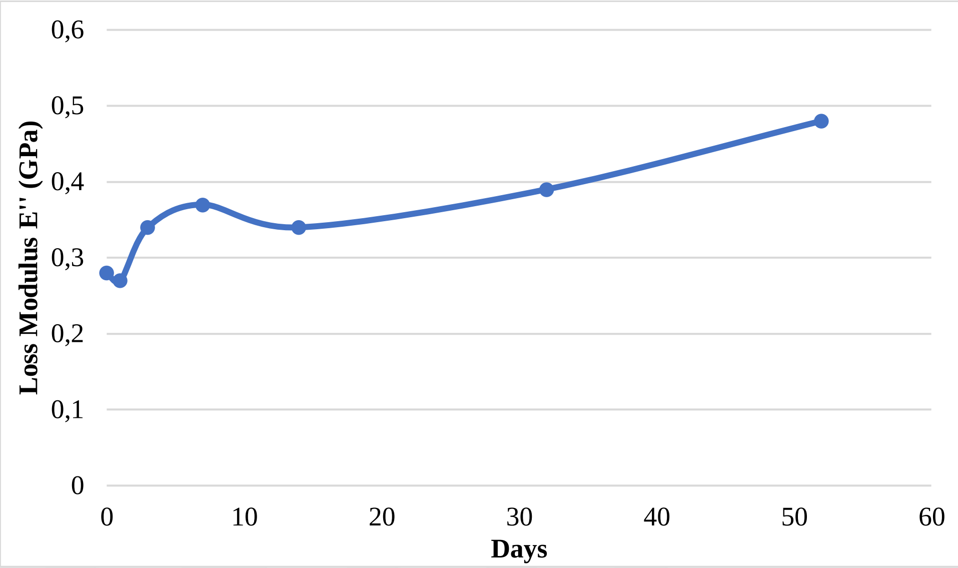


Figure 4.15 Loss modulus of aged and unaged samples in pure water solution

CHAPTER 5

CONCLUSIONS

This study was intended to investigate the effect of aging on vibration-damping characteristics of basalt fiber reinforced composites. According to water uptake measurements, basalt fiber reinforced composites are not perfectly in correlation with Fick's Law of diffusion. For each types of aging media, water uptake behavior of specimens showed good fit at initial stage, however at the end of linear stage and from the beginning of exponential increase, theoretical and experimental values were separated. Even though there was an approximation of these values, especially in pure water solution, saturation stage was not achieved as a continuous form in NaOH and NACI solution as in pure water solution aging. Fluctuations during water uptake was attributed to polymer swelling and relaxation phases and decrease in mass after peak point was explained with leaching out of unreacted monomers and chain scission.

In terms of natural frequency, the results showed that hydrothermal aging has no significant effect on natural frequency of basalt fiber reinforced composites. However damping properties were highly affected from hydrothermal aging in NaOH and NaCI solutions compared to unaged ones. Because basalt fiber has low water uptake capacity and due to low thickness of the composite samples, it can be accepted as normal to have small amount of effect due to aging.

According to the study; basalt fiber reinforced composites were very resistant to aging in aqueous media in terms of water uptake and vibration-damping characteristics. Most of the structural applications are subjected to humid or aqueous conditions for different periods of time, it is very important to be affected from this environment in minimal degree without any extra operation during manufacturing such as coating. To determine the water effect more deeply, the effect of longer terms of aging with wider temperature range can be assessed to provide detailed information to the literature.

REFERENCES

[1] F.C. Campbell, (2010). Structural Composite Materials. ASM International Materials Park, Ohio 44073-0002.

[2] Barber, J. R., Klarbring, Anders. (2014). Solid Mechanics and Its Applications. Volume 208. Springer Dordrecht Heidelberg New York London. DOI: 10.1007/978-94-007-7417-9.

[3] Suh, D.-W., Ku, M.-K., Nam, J.-D., Kim, B.-S., & Yoon, S.-C. (2001). Equilibrium Water Uptake of Epoxy/Carbon Fiber Composites in Hygrothermal Environmental Conditions, *Journal of Composite Materials*, **35(3)**, 264–278. DOI: 10.1177/002199801772662253.

[4] C.D.M.Liljedahl, A.D.Crocombe, M.A.Wahab, I.A.Ashcroft. (2007). Modelling the environmental degradation of adhesively bonded aluminium and composite joints using a CZM approach, *International Journal of Adhesion & Adhesives* **27**, 505–518. DOI: 10.1016/j.ijadhadh.2006.09.015.

[5] Mikols, W. J., J. C. Seferis, A. Apicella and L. Nicolais. (1982). Evaluation of Structural Changes in Epoxy Systems by Moisture Sorption-Desorption and Dynamic Mechanical Studies, *Polymer Composites*, **3**, 118–124. DOI: 10.1002/pc.750030304.

[6] Shen, C.-H., & Springer, G. S. (1976). Moisture Absorption and Desorption of Composite Materials, *Journal of Composite Materials*, **10(1)**, 2–20. DOI: 10.1177/002199837601000101.

[7] H. Mehrer. (2017). Diffusion in Solids - Fundamentals, Methods, Materials, Diffusion controlled Processes. Springer Berlin Heidelberg New York. DOI: 10.1007/978-3-540-71488-0.

[8] J Crank. (1975). The Mathematics of Diffusion. Second edition. Oxford: Clarendon Press.

[9] Z. Zhai, L. Feng, Z. Liu, G. (2016). Water absorption test for carbon fiber epoxy resin composite based on electrical resistance, *Li. Polymer Testing* **56**, 394-397.

[10] N. Tual, N. Carrere, P. Davies, T. Bonnemains, E. Lolive. (2015). Characterization of sea water ageing effects on mechanical properties of carbon/epoxy composites for tidal turbine blades. *Composites: Part A*, **78**, 380–389.

[11] K.Cheour, M.Assarar, D.Scida, R. Ayad, X.-L. Gong. (2016). Effect of water ageing on the mechanical and damping properties of flax fibre reinforced composite materials, *Composite Structures*, **152**, 259–266.

[12] S. Kajorncheappunngam. (1999). The Effects of Environmental Aging on the Durability of Glass/Epoxy Composites. Morgantown, Phd dissertation. Virginia University.

[13] L. Yan, N. Chouw. (2015). Effect of water, seawater and alkaline solution ageing on mechanical properties of flax fabric/epoxy composites used for civil engineering applications, *Construction and Building Materials*, **99**, 118–127.

[14] Botelho, E. C., & Rezende, M. C. (2010). Evaluation by Free Vibration Method of Moisture Absorption Effects in Polyamide/Carbon Fiber Laminates. *Journal of Thermoplastic Composite Materials*, **23(2)**, 207–225.

[15] A. Kootsookos, A.P. Mouritz, (2001). N.A. St John. Comparison of the Seawater Durability of Carbon- and Glass-Polymer Composites. ICCM-13 Beijing, China.

[16] Y. Menail, A. El Mahi, M. Assarar, B. Redjel, A. Kondratas. (2009). The effects of water aging on the mechanical properties of glass-fiber and kevlar-fiber epoxy composite materials. ISSN 1392 - 1207. MECHANIKA.. Nr.**2**(76).

[17] Li, C. , Huang, X. , Yan, L. , Zhou, H. , Shen, Z. and Fan, X. (2017), Effect of thermal aging on microstructures of aramid composites. *Polym. Compos.*, **38**, 252-259.

[18] S.N. Fitriah, M.S. Abdul Majid, M.J.M. Ridzuan, R. Daud, A.G. Gibson, T.A. Assaleh. (2017). Influence of hydrothermal ageing on the compressive behaviour of glass fibre/epoxy composite pipes, *Composite Structures*, **159**, 350–360.

[19] Boisseau, A., Davies, P. & Thiebaud, F. (2012). Sea water ageing of composites for ocean energy conversion systems: Influence of glass fibre type on static behaviour. *Appl Compos Mater*, **19**, 459. DOI:10.1007/s10443-011-9219-6.

[20] Apolinario, G., Ienny, P., Corn, S., Léger, R., Bergeret, A., and Haudin, J.M. (2016). Effects of water ageing on the mechanical properties of flax and glass fibre composites: Degradation and reversibility. In RILEM Bookseries, (Kluwer Academic Publishers), pp. 183–196.

[21] Miller D, Mandell JF, Samborsky DD, Hernandez-Sanchez BA, Griffith DT (2012) Performance of composite materials subjected to salt water environments. In 2012 AIAA SDM Wind Energy Session, Hawaii.

[22] E. Muñoz and J. A. García-Manrique. Water Absorption Behaviour and Its Effect on the Mechanical Properties of Flax Fibre Reinforced Bioepoxy Composites. vol. 2015. *International Journal of Polymer Science*. DOI: 10.1155/2015/390275.

[23] L.R. Grace, M.C. Altan. Characterization of anisotropic moisture absorption in polymeric composites using hindered diffusion model, *Composites: Part A*, **43**, 1187–1196.

[24] L.-R. Bao, A.F. Yee. (2002). Moisture diffusion and hygrothermal aging in bismaleimide matrix carbon fiber composites—part I: uni-weave composites. *Composites Science and Technology*, **62**, 2099–2110.

[25] V.M. Karbhari, G. Xian. (2009). Hygrothermal effects on high VF pultruded unidirectional carbon/epoxy composites: Moisture uptake. *Composites: Part B*, **40**, 41–49.

[26] M. Assarar, D. Scida, A. El Mahi, C. Poliâne, R. Ayad. (2011). Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: Flax–fibres and glass–fibres. *Materials and Design*, **32**, 788–795.

[27] Menail Y, Mahi AEL, Assarar M (2015) Effect of Fatigue Testing and Aquatic Environment on the Tensile Properties of Glass and Kevlar Fibers Reinforced Epoxy Composites. *J Aeronaut Aerospace Eng,* **4**, 150. DOI:10.4172/2168-9792.1000150.

[28] Verpoest, I., & Springer, G. S. (1988). Moisture Absorption Characteristics of Aramid-Epoxy Composites. *Journal of Reinforced Plastics and Composites*, **7(1)**, 2–22. DOI:10.1177/073168448800700101.

[29] Akay, M., Kong Ah Mun, S., & Stanley, A. (1997). Influence of moisture on the thermal and mechanical properties of autoclaved and oven-cured Kevlar-49/epoxy laminates, *Composites Science and Technology*, **57(5)**, 565–571. DOI:10.1016/S0266-3538(97)00017-1.

[30] Eslami S., Taheri-Behrooz F., Taheri F,. (2012). Effects of Aging Temperature on Moisture Absorption of Perforated GFRP, *Advances in Materials Science and Engineering*, vol. 2012, Article ID 303014. DOI:10.1155/2012/303014.

[31] Ramesh, C., Arumugam V., Stanley, J., & Kumar, V. (2013). Effects Of Hydrolytic Aging On Glass/Epoxy, Kevlar/Epoxy, And Hybrid (Glass/Kevlar/Epoxy) *Composites*, **2(5)**, 1589–1596.

[32] J.Alexander, B S M.Augustine, Sai Prudhuvi, Abhiyan Paudel. (2016). Hygrothermal effect on natural frequency and damping characteristics of basalt/epoxy composites. *Materials Today*: Proceedings, **3**, 1666–1671.

[33] Yu, Y. , Li, P. , Sui, G. , Yang, X. and Liu, H. (2009), Effects of hygrothermal aging on the thermal–mechanical properties of vinylester resin and its pultruded carbon fiber composites. *Polym Compos*, **30**, 1458-1464. DOI:10.1002/pc.20712.

[34] Xu Jiang, Henk Kolstein, Frans Bijlaard, Xuhong Qiang. (2014). Effects of hygrothermal aging on glass-fibre reinforced polymer laminates and adhesive of FRP composite bridge: Moisture diffusion characteristics. *Composites: Part A,* **57**, 49–58.

[35] Xiao, B., Li H., Xian, G. (2010). Hygrothermal Ageing of Basalt Fiber Reinforced Epoxy Composites. JCICE 2010 - *The 5th International Conference on FRP Composites in Civil Engineering,* September 27-29, Beijing, China.

[36] Pandian A., Vairavan M, Thangaiah W. J. J., Uthayakumar M., (2014). Effect of Moisture Absorption Behavior on Mechanical Properties of Basalt Fibre Reinforced Polymer Matrix Composites, *Journal of Composites*, vol. 2014, Article ID 587980.

[37] Kim M. T., Rhee K. Y., Jung I., Park S. J., Hui D. (2014). Influence of seawater absorption on the vibration damping characteristics and fracture behaviors of basalt/CNT/epoxy multiscale composites, *Composites: Part B*, **63**, 61–66.

[38] Wei, B., Cao, H., & Song, S. (2011). Degradation of basalt fibre and glass fibre/epoxy resin composites in seawater. *Corrosion Science*, **53(1)**, 426–431. DOI:10.1016/j.corsci.2010.09.053.

[39] Tekin A., Esendemir Ü., Öndürücü A., (2016). Experimental and Theoretical Analysis Bending Behaviors of Composite Materials Subjected to Different Environmental Conditions. *C.B.Ü. Soma MYO Tek. Bil. Der*. 2016 – Sayı 21 Cilt I.

[40] Y.Z. Wan, Y.L. Wang, Y. Huang, H.L. Luo, F. He, G.C. Chen. (2006). Moisture absorption in a three-dimensional braided carbon/Kevlar/epoxy hybrid composite for orthopedic usage and its influence on mechanical performance, *Composites: Part A* **37**, 1480–1484.

[41] Liu, Q. , Shaw, M. T., Parnas, R. S. and McDonnell, A. (2006), Investigation of basalt fiber composite aging behavior for applications in transportation. *Polym Compos*, **27**: 475-483. DOI:10.1002/pc.20215.

[42] Scida D., Assarar M., Poilâne C., Ayad R. (2013). Influence of hygrothermal ageing on the damage mechanisms of flax-fibre reinforced epoxy composite. *Composites: Part B*, **48**, 51–58.

[43] H. Alamri, I.M. Low. (2012). Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites. *Materials and Design*, **42**, 214–222.

[44] Batista, N. L., Iha, K., & Botelho, E. C. (2013). Evaluation of weather influence on mechanical and viscoelastic properties of polyetherimide/carbon fiber composites. *Journal of Reinforced Plastics and Composites*, **32(12)**, 863–874. DOI:10.1177/0731684413482994.

[45] Mengting Li, Jun Wang, Weiqing Liu, Ruifeng Liang, Hota GangaRao, and Yang Li,. (2017). Combined Effects of Sustained Loads and Wet-Dry Cycles on Durability of Glass Fiber Reinforced Polymer Composites, *Advances in Materials Science and Engineering*, vol. 2017, Article ID 1532360. DOI:10.1155/2017/1532360.

[46] Kostopoulos V, Kelverkloglou P, Tsantzalis S. (2017). Models for combined diffusion and moduli degradation analysis of glass reinforced cyanate ester composites structures, *MOJ Poly Sci*., **1(2)**, 41–52. DOI:10.15406/mojps.2017.01.00007.

[47] Wang Mingchao, Zhang Zuoguang, Li Yubin, Li Min, & Sun Zhijie. (2008). Chemical Durability and Mechanical Properties of Alkali-proof Basalt Fiber and its Reinforced Epoxy Composites, *Journal of Reinforced Plastics and Composites*, **27(4)**, 393–407. DOI:10.1177/0731684407084119.

[48] Y. Li, B. Xue. (2016). Hydrothermal ageing mechanisms of unidirectional flax fabric reinforced epoxy composites, *Polymer Degradation and Stability*, **126**, 144-158.

[49] ASTM D570-98. (1998). Standard Test Method for Water Absorption of Plastics, ASTM International, West Conshohocken, PA, www.astm.org.

[50] ASTM D 5229/D 5229M – 92. (2004). Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite

Materials, *ASTM International*, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States.

[51] DIN EN ISO 62:2008-05, Plastics – Determination of water absorption.

[52] S. Kalachandra, R. P. Kusy, (1990). Comparison of water sorption by methacrylate and dimethacrylate monomers and their corresponding polymers, *Polymer*, Vol: 32, Issue: **13**, Page: 2428-2434.

[53] Dutta, Saikat Swapan. (2008) Water absorption and dielectric properties of Epoxy insulation, http://hdl.handle.net/11250/256588.

[54] K. T. Hassan. (2010). Study the Effect of Some Solutions on Epoxy Resin & Calculate Diffusion Coefficient of Solution. J. of university of anbar for pure science: Vol. 4: NO. 1.

[55] Comyn, J. (1995). Polymer Permeability. Chapman & Hall. 2-6 Boundary Row. London. DOl: 10.1007/978-94-009-4858-7.

[56] G. Z. Xiao, M. E. R. Shanahan. (1997). Swelling of DGEBA/DDA epoxy resin during hygrothermal ageing. *Polymer*, Vol: 39, Issue: **14**, Page: 3253-3260.

[57] Xiao, G. Z., Delamar, M. and Shanahan, M. (1997), Irreversible interactions between water and DGEBA/DDA epoxy resin during hygrothermal aging. *J. Appl. Polym. Sci.*, **65**, 449-458. DOI: 10.1002/(SICI)1097-4628(19970718)65:3<449::AID-APP4>3.0.CO;2-H.

[58] Flory, P. J. (1953). 0-8014-0134-8. Principles of Polymer Chemistry, Ithaca, New York: Cornell University Press.

[59] Davis, Joseph R. (2004). Tensile testing (2nd ed.). ASM International.

[60] Boniard, E., Pethrick, R.A. and Dalzel-Job, J. (1998). Studies of water permeation into fibre reinforced composite structures, *Plast. Rubber. Compos. Process. Appl.*, Vol. **27**, No. 4, pp. 206.

[61] "Basalt". USGS Volcano Hazards program – Glossary. USGS. 8 April 2015. Retrieved 27 July 2018.

[62] Meirovitch L. (1967). Analytical methods in vibration. London: Ccollier-MacMillan Ltd.

[63] A. KabirS, and V. Hoa, ICAF 2011 Structural Integrity: Influence of Efficiency and Green Imperatives, Montreal, Canada, 155 (2011).

[64] Bozkurt, Ö. Y. and Gökdemir, M. E. (2018), Effect of basalt fiber hybridization on the vibration-damping behavior of carbon fiber/epoxy composites. *Polym. Compos.*, **39**, E2274-E2282. DOI:10.1002/pc.24606.