MŰEGYETEM 1782
**Budapest University of Technology and Economics**
**Faculty of Mechanical Engineering**
**Department of Polymer Engineering**

# Development of basalt fabric reinforced polymer composites

THESIS BOOKLET

Written by:
**Péter Tamás**
MSc Mechanical Engineer

Supervisor:
**Dr. Tibor Czigány**
Professor

to fulfill the requirements of the PhD degree

Budapest

**2013**

The referees' opinion and the minutes of the PhD examination can be inspected at the Dean's Office of the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics.

## 1. Introduction

Surrounding materials have a big influence on quality of our life. It can be declared that our century is the age of synthetic materials where our society and economic need newer and newer materials. Due to the decreasing quantity of fossil energy resources, the renewable energy types come into consideration and the development of connecting materials. Modern material science divides the engineering material into three groups: metals, ceramics and polymers. Combined systems of these materials are the composites which combine the beneficial properties of the components. Composites are structural materials in which there is good adhesion between the strong reinforcement and the tough matrix material. Using of composite materials such properties can be reached which without combination of components cannot. Widely used reinforcements for polymer composites are fiberglass, carbon fiber and aramid fiber and different kind of natural fibers. In the last two decades basalt fiber came into consideration as a potential reinforcement of composite materials. Basalt is a volcanic rock which can be found around the globe and it is an ideal raw material for fiber producing. Considering its mechanical properties and chemical composition it is similar to the glass fiber, but it can be used in wide temperature range without significant loss of the mechanical properties. Basalt fibers are biologically inert as well as environmentally friendly and can be used in aggressive environments. Due to these properties basalt fiber can be a good alternative instead of asbestos and fiberglass. Nowadays continuous basalt fibers are produced in the most volume in the Russian Federation, in Ukraine and in Israel but newer factories are built in China and the western countries. In some cases special requests arise against composites which can be complied with combination of advantageous properties. The easiest way to combine the different properties is the hybridization. At this moment a widely held combination of reinforcements is the glass/carbon fiber reinforced composites, because addition of the glass fiber can decrease the price and increase the toughness of composites with carbon fiber reinforcement. Due to similar chemical composition and mechanical properties glass fibers could be substituted with basalt fibers.

The aim of my research were the development and investigation of mono and hybrid composites by common mechanical and cyclic load tests. Besides of these I set target to discover and exploit the synergic effect in hybrid composites to extend the application field, especially the renewable energy industry (wind turbines and tidal).

## 2. Short overview of the related literature, goals of the thesis

The literature overview confirmed that in the last few decades the demand increased for continuous basalt fiber and basalt fiber reinforced composites in spite of basalt fiber came into consideration as a potential reinforcement in 1980. Nowadays using of continuous basalt fiber as a reinforcement is in experimental stage however at the same time a few such product can be found among traded goods. Many researcher deal with investigation of basalt fiber reinforced composites which indicate that basalt fiber is a very promising reinforcement.

On the basis of literature in aspect of application of fiber reinforced composites the most frequented energy type is the wind energy. Among the renewable energy types the wind energy develops the most dynamically. Efficiency of the moving parts of turbines can be improved by decreasing of mass for which purpose fiber reinforced composites afford an optimal solution. To increase the utilization of wind energy, wind turbines are installed far from the land in the sea with anchoring to the sea bed (off-shore system). Composites of wind turbine structures must resist different environmental effects (temperature, UV light, saltwater ageing especially at off-shore turbines) and impact, cyclic and fatigue loads. Some kind of reinforcement rarely can resist these environmental influences however combining each other by hybridization can comply with different requirements. In recent researches suitability of mono and hybrid composites with thermoset matrix are investigated where one of the reinforcement was carbon fiber and another was fiberglass. Using of glass fiber as reinforcement of off-shore wind turbines often problems can occur due to the salt water and UV irradiation sensitive mechanical properties of glass fiber and glass fiber reinforced composites. Due to chemical composition, basalt fiber can resist environmental influences much better than glass fiber, herby basalt fiber is more suitable as reinforcement of off-shore wind turbine blades.

Moreover, the scientific literature which deals with basalt fabric reinforced mono and hybrid composites is very inconsiderable and stressing as well as manufacturing principles are not composed. Nevertheless, due to the advantageous properties of basalt fabric, headway of research topic is predictable which deals with basalt fabric.

According to the above, the goals of this PhD thesis are the followings:

- to produce basalt, glass and carbon fiber reinforced composites with thermoset matrix material, investigation of mechanical properties and comparing each other, moreover to improve interlaminar shear strength by fillers.
- to investigate the effect of temperature on mechanical and physical properties of basalt fabric and basalt fabric reinforced mono and hybrid composites.
- to analyze the environmental influences, especially UV irradiation on mechanical properties basalt fabric and basalt fabric reinforced mono and hybrid composites.
- the investigation the changes of mechanical properties of the basalt fabric and basalt fabric reinforced mono and hybrid composites by concentration and immersion time of salt water medium.
- the investigation of electric conductivity and electromagnetic insulation ability of basalt fabric reinforced mono and hybrid composites.
- the analysis of behavior of basalt fabric reinforced mono and hybrid composites by cyclic tensile and flexural load with small cycle number and large deflection and to compose an equation to describe it.

# 3. Applied materials and experimental methods

## 3.1. Applied materials

***Matrix material***

In my research I used a laminating and a low viscosity epoxy resin as the matrix materials of the composites and hybrid composites. During the specimen production I have used the curing cycle, in case of the Ipox Chemicals MH3009 – MH3120, bisphenol-A based epoxy resin – amine hardener 4 hours at 60°C provided by the producers in a Heraeus UT20 oven. Mixing ratio of components was 100:20. Complete mixing was provided by a two-step mixing method. In the first step I mixed the components by an electric stirrer with 5000 rpm for 3 minutes after that I left the mixture in rest for 2 minutes and repeated the first step again.

***Reinforcements***

For my investigations I used glass, basalt and carbon rovings and fabrics with the same linear (3600 tex) and surface density (220 g/m$^2$) as well as same surface treatment (sizing for epoxy resin). Glass roving were supplied by Owens Corning, basalt roving by Kamenny Vek, carbon fiber by Zoltek, glass fabric by Saint-Gobain Vetrotex, basalt fabric by Basaltex and carbon fabric by SGL Group. According my preliminary experiments it can be declared that the mechanical properties of the used fabrics are the same in weft and in warp direction.

***Fillers***

In my experiments I used Bayer Baytubes BT C150HP multiwalled carbon nanotubes and XG Science Grade M graphene as nanosized reinforcement and milled basalt powder which were produced from Basaltex BAS 1500 basalt fiber by myself by using a ball miller.

## 3.2. Sample preparation

For preparation of composite specimens I used common hand layup technology independent from the structure of reinforcement. Voids and unnecessary resin were removed by rolling from the laminates. In every case laminates were made by stocking of six layer of reinforcements. According to the reinforcements prepared, composite laminates were designated (GFEP-glass fiber reinforced, BFEP-basalt fiber reinforced, CFEP-carbon fiber reinforced, GFCFEP-glass/carbon fiber reinforced, BFCFEP-basalt/carbon reinforced epoxy resin).

## 3.3. Applied experimental methods

All mechanical tests were performed at room temperature (25±3°C) and at a relative humidity of 40±5%.

**Tensile tests of monofilaments**

The geometrical properties of the used monofilaments were determined by an Olympus BX51 optical microscope and its software. Tensile testing of monofilaments were carried out by a ZWICK Z005 universal tensile tester according to JIS R 7601 Japanese standard.

**Tensile tests of rovings**

Tensile testing of rovings were carried out by a Zwick Z020 universal tensile tester according to MSZ EN ISO 9163 standard with video extensometer by multifilament tensile tests. Diameter of the mono and multifilament were determined by an Olympus BX-51A optical microscope.

**Tensile tests of fabrics**

Tensile tests of fabrics were carried out by a Zwick Z020 universal tensile tester according to MSZ EN ISO 13934-1:2000 standard equipped with a video extensometer by stripe tensile tests.

**Tensile tests**

Tensile tests were carried out by a Zwick Z020 universal tensile tester according to MSZ EN ISO 527-4:1999 standard equipped with a video extensometer.

**Flexural tests**

Three point bending tests were carried out by a Zwick Z020 universal tensile tester according to MSZ EN ISO 14125:1999.

**Interlaminar shear tests**

Static interlaminar shear strength (ILSS) tests were carried out by a Zwick Z020 universal tensile tester according to ASTM D3846-94 standard.

**Charpy dynamic impact tests**

Instrumented Charpy dynamic impact tests were performed on a Ceast Resil Impactor Junior with a DAS 8000 data collector device according to MSZ EN ISO 179 standard.

**SEN-T tests**

Quasi static fracture mechanics tests were carried out by a Zwick Z020 universal tensile tester according to ASTM E399 standard by investigation of single edge notched tensile (SEN-T) specimens.

**Acoustic emission (AE) tests**

Acoustic emission tests were performed on a 4 channel SENSOPHONE AED-40/12 acoustic emission machine equipped with a pieso electric microphone (type of A-11).

**Electric conductivity and electromagnetic shielding tests**

Electric conductivity tests were carried out by a Hewlett Packard High Resistance Meter 4339B multimeter with a three electrodes ring-shaped measuring head to determine surface and volume resistance according to MSZ EN ISO 1149-1 standard by DC. To determine the surface resistance multimeter was connected with the inner sphere and with the ring electrode, moreover to determine the volume resistance, the multimeter was connected with the inner sphere and with the secondary electrode. Electromagnetic shielding tests were carried out according to ASTM D4935 standard.

**Thermogravimetrical analysis**

Thermogravimetrical analysis was performed on a SETARAM Labsys TG DTA/DSC device in a temperature range of room temperature to 1200°C with 20°C/min heating rate under oxygen and inert atmosphere. The used volume flow of different atmospheres was 60 ml/min.

**Fourier-transformation infrared spectroscopy analysis (FT-IR)**

Fourier-transformation infrared spectroscopy analysis (FT-IR) was performed on a Perkin Elmer Spectrum 400 device in reflection mode. Light source of the equipment is a long-life IR light source in the range of 4000-650 cm-1 (2500-15385 nm) wave-length.

**Ultraviolet (UV) spectroscopy analysis**

Ultraviolet (UV) spectroscopy analysis was performed on a Hewlett Pakard 8452A device with diode string detector in absorption mode. The used equipment uses visible UV light source in range of 190-820 nm wave-length with 2 nm resolution.

**Microstructural analysis**

For scanning electron microscopy studies the fracture surfaces of the specimen were first sputtered with gold by a JEOL FC1200 fine coater device in argon atmosphere then pictures were taken of the surface by a JEOL 6380LVa scanning electron microscope.

# 4. New scientific results - Theses

Based on the results achieved in the framework of this PhD Thesis, the following theses have been deduced:

**1st thesis**

I proved the presence of positive hybrid effect at basalt/carbon and glass/carbon fabrics reinforced composites. The glass and basalt fabric Young's modulus was higher by 16±1%, flexural modulus by 9±1%, Charpy impact strength by 6±3% and critical stress intensity factor by 20±3% compared to the by hybrid rule of mixture calculated value. The increment of mechanical properties was caused by synergetic behavior of basalt and carbon fabrics [3-4, 7-13].

**2nd thesis**

I proved that the strength of basalt fabric begins decrease in the temperature range of 70-80°C. It is caused by thermo oxidative degradation which was confirmed by scanning electron micrographs. The initial degradation (70-80°C) was proved by the presence of oxygen by thermogravimetric analysis (TGA). Tensile strength of basalt fabric decreased continuously with increasing temperature. Quantity of the decrease was 19±2% at 100°C, 71±4% at 300°C and 98±2% at 500°C, which was revealed by stripe tensile tests. Extent of the degradation in inert atmosphere at 700°C was 66±5% lower than in oxygen atmosphere. It was caused by the bounded oxygen of the coupling agent [2, 15].

**3rd thesis**

I proved that the tensile strength of basalt fabric decreases in salt water medium with increasing solvent concentration (10, 20, 30, 38 w%) and immersion time (1, 2, 4 week) by stripe tensile tests. Reason of degradation is mainly the chemical reaction between salt water and iron, iron-oxide of basalt fiber, which was revealed by scanning electron micrographs and UV spectroscopy [14, 15].

**4th thesis**

I confirmed that the volume resistance, electric strength and electromagnetic shielding ability of carbon fiber reinforced composites with epoxy resin matrix can be increased by the addition of basalt fabric where carbon fiber provides electromagnetic shielding due to stable electric current and basalt fiber fulfils the electric insulation due to defense of stable electric current. Due to addition of basalt fabric, surface resistance of carbon fabric reinforcement increased by 14±2% and volume resistance increased by 5±1% [15].

**5th thesis**

I proved that milled basalt powder is usable to improve the interlaminar shear strength of basalt fabric reinforced composite with epoxy resin matrix. The optimal basalt powder (average particle size: 1.72±0.30 μm) content was 1 w%. At this basalt powder content the interlaminar shear strength increased by 18±2% compared to the composite with nanosized fillers. Same carbon nanotube content effected 29±2% decrease, same graphene content caused 49±4% decrease in interlaminar shear strength. The reason of this phenomenon was agglomeration of nano particles which behaves as stress concentration [1, 2, 15].

**6th thesis**

I created an equation (T1) to describe the damage of glass, basalt and carbon fiber reinforced mono and hybrid composites with epoxi resin matrix by low cyclic tensile and bending load. Adaptation of my equation can be defined by an asymptotic modulus which characterizes the hybrid composites:

$$E_\infty = E_o + \sum_{k=1}^{N} E_k g_\infty \left( \frac{t_{ok}}{\tau_k} \right) \tag{T1}$$

where $E_0$, $E_k$ are modulus parameters, $g$ is a time factor, $t_{0k}$, $\tau_k$ are time constants. I proved that the mechanical properties of basalt fabric reinforced mono and hybrid composites decreases by cycle number. The decrease was caused by fiber-matrix debonding. Tensile strength of basalt fabric reinforced composite decreased by 8±1% and carbon/basalt reinforced decreased by 9±1% at 10th cycle [14].

## 5. List of own publications

*Publications in periodicals*

[1] Czigány T., Deák T., **Tamás P.**: Discontinuous basalt and glass fiber reinforced PP composites from textile prefabricates: effects of interfacial modification on the mechanical performance. Composite Interfaces, 15, 697–707 (2008) **IF=0.69**

[2] Deák T., Czigány T., **Tamás P.**, Németh Cs.: Enhancement of interfacial properties of basalt fiber reinforced nylon 6 matrix composites with silane coupling agents. Express Polymer Letters, 4, 590-598 (2010) **IF=1.575**

[3] **Tamás P.**, Czigány T.: Investigation of mechanical properties and crack propagation behaviour of hybrid composites with epoxy resin matrix. Materials Science Forum 729, 284-289 (2013)

[4] Tábi T., **Tamás P.**, Kovács J.G.: Chopped basalt fibres: A new perspective in reinforcing poly(lactic acid) to produce injection moulded engineering composites from renewable and natural resources. Express Polymer Letters, 7, 107-119 (2013) **IF=2.294**

[5] Tábi T., Égerházi A., **Tamás P.**, Czigány T., Kovács J.G.: Investigation of injection moulded poly(lactic acid) reinforced with long basalt fibres. Composites Part A, (submitted) **IF=2.744**

[6] **Tamás P.**: Mágneses tulajdonságú polimerek fejlesztése és tulajdonságainak elemzése. Műanyagipari Szemle, 2, 79-84 (2009)

[7] **Tamás P.**, Czigány T.: Üveg/szén és bazalt/szén hibridszálas epoxigyanta mátrixú unidirekcionális kompozitok összehasonlítása. Műanyag és Gumi, 47, 187-191 (2010)

*Conference proceedings and presentations*

[8] Czigány T., Deák T., **Tamás P.**: Investigation of mineral fiber reinforced polypropylene matrix composites. 13th European Conference on Composite Materials, 2-5. June 2008., Stockholm, Sweden

[9] **Tamás P.**, Czigány T.: Static and dynamical behavior of mineral fiber reinforced composites with polypropylene matrix. 6. Nemzetközi Gépészeti Konferencia, 29-30. May 2008., Budapest, Hungary

[10] **Tamás P.**, Czigány T.: Polimer mátrixú hibridkompozitok. Erősített Műanyagok 2010 Nemzetközi Balaton Konferencia, 18-20. May 2010., Keszthely, Hungary

[11] Czigány T., **Tamás P**.: Comparison of the mechanical properties and the damage progression of basalt, glass and carbon fiber reinforced composites with epoxy resin matrix. 5th Asia-Europe Symposium on Processing and Properties of Reinforced Polymers, 29. May - 1. June 2011., Dresden, Germany

[12] **Tamás P**.: Characterization of mono-- and hybrid composites by the investigation of the mechanical properties of basalt, glass and carbon fiber reinforced composites. ISSP 2011 International Summer School on Polymers, 22-26. August 2011., Szmolensz, Slovakia

[13] **Tamás P**., Czigány T.: Epoxigyanta mátrixú hibridkompozitok mechanikai tulajdonságainak és repedésterjedésének vizsgálata. VIII. Országos Anyagtudományi Konferencia, 9-11. October 2011., Balatonkenese, Hungary

[14] **Tamás P**.: Development of basalt fabric reinforced hybrid composites for wind turbine blades. Sao Carlos Advanced School on Materials Science & Engineering, 25-31. March 2012., Sao Carlos, Brazil

[15] **Tamás P**., Czigány T.: Basalt fiber - a promising reinforcement for wind turbine blades. 6th Asia-Europe Symposium on Processing and Properties of Reinforced Polymers, 2-6. June 2013., Wuhan, China