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PhD dissertation

HOLLOW GLASS FIBER REINFORCED POLYMER COMPOSITES

THESIS BOOKLET

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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

The effective usage of the resources is an essential requirement in our developing word because the fossil energy stocks are finite. The resources could be used economically for example with light vehicles that uses less energy for movement, thus they produce much less pollutant.

Polymer composites are especially suitable for the construction of lightweight structures because of their anisotropic properties. When the magnitude and the direction of the typical load are known, utilizing the anisotropy, the material properties can be favorably designed. Thus, the use of composite materials is getting ever broader: e.g. the wing and the body of airplanes, wind turbines' blades, the control building of mother ships, sport equipment etc. are made out of fiber reinforced polymer composites. Composites typically consist of reinforcing fibers and the surrounding matrix, which have an excellent adhesion connection between them. The reinforcing fiber is quite thin (the diameter of it is only a few microns), and its' tensile strength is high. The most frequently used reinforcing fiber is glass fiber, carbon fiber and/or aramid fiber, but the usage of basalt-, flax-, hemp- and other thermoplastic artificial fibers is also increasing. Besides the development of the material of the reinforcing fibers several studies deal with the optimization of their shape. The matrix is a tough material, the principal tasks of it include the transfer of the loads to the fibers and to protect the fibers. The most frequently used matrix materials are polyester, epoxy and vinyl ester resins among the thermosetting polymers, polyamide and polypropylene among thermoplastic polymers.

The crash or failure of the composite materials, like every material, is achieved by preventing the evolution and propagation of cracks caused by the external environmental loads, mechanical, chemical or thermal stresses. The big advantage of the composite materials as compared to the materials with homogeneous internal structure is the slow cracking instead of sudden, catastrophic wrecking, and in most cases, the warning signs are visible for the naked eyes, so there is time for reducing or terminate the load. The failure of the composite begins with the evolution of the cracks in the matrix and some of them start to propagate. The propagation of the crack can be caused by cyclic or varying load and the degradation of polymers (e.g. aging caused by ultraviolet radiation). The crack propagates fast as long as it reaches a fiber, stops there and it can go further by going round or by breaking the fiber.

It would be very good, if the evolution of the cracks could be stopped without any external interference, so the failure of the structure could be stopped or at least delayed. In composites, for example the application of hollow reinforcing fibers could solve this problem. Hollow fibers ensure the possibility for simple status assessment or for self-repairing ability. Status assessment could be reached with the filling of the hollow fibers with ultraviolet (UV) fluorescent liquids, which would flow into the crack when the filled fiber breaks. After lightening the structure with a simple UV lamp, a fast and simple check of the structure could be executed and the status of the structure and the place of the crack could be determined.

Self-repairing effect could be reached imitating nature. After an injury, the bark immediately begins to cure and heal itself by the allocation of resin to the injured place, which defends the bark from the further injuries or rotting till the end of the healing. The human skin reacts with bleeding for a cut, and thus replaces the missing epidermis with scab. The analogy of composites reinforced by hollow fibers containing uncured resin in their hole is the same. In these composites some of the fibers contain resin component while other fibers contain the curing agent. As soon as a rupture evolves that breaks the filled fibers the components of the healing agents flow into the crack, there mix together and cure. Hereby the continuity of the structure is restored and the strength of the “repaired” section could reach the original level. This is the reaction of the material to the environment’s damaging effect. Materials that give an equivocal and fast response to the effects of the environment without any human interference are called intelligent materials. Hollow fiber reinforced composites are giving a equivocal and fast response to the appearing of the rupture by releasing liquid and filling the crack with the liquid stored by the hollow fibers , which cures there and thus the integrity of the broken halves is rebuilt.

The aim of my dissertation is the study of these intelligent materials, the study of the hollow fiber reinforced polymer matrix composites, the creation of hollow fiber reinforced composite and the investigation of the mechanism of the status assessment and self-repair.

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

By the review of the literature it was found that articles have appeared on the research of the hollow fibers since the beginning of the 1980s. According to some resources, some have dealt with such fibers already in the 1960s, but they stopped the production because of the high manufacturing costs and the low utilization. The utilization of the hollow fibers has always had two aims: to reach a better material property and later to create self-repairing composites from them.

Today the main limiting factor in the application of hollow fibers is the high manufacturing cost, so it is quite difficult to get such fibers. Different patents are describing production process for hollow fibers but the production of them is still more expensive than that of conventional solid fibers. Some researchers produced hollow glass fibers individually by heating and stretching thicker glass tubes. Fibers with different hollowness ratio were manufactured by this technique, so they could examine the mechanical properties of them. The mechanical properties of the fibers and thus the mechanical properties of the composites reinforced with them were affected by the fibers' outer diameter and the hollowness ratio. Although each researcher used glass fibers from the same material for the comparisons, the results were quite different due to the higher molecular orientation that is caused by the reduction of the wall thickness, which is the same for all materials.

There is not so much literature on the subject of hollow fiber reinforced self-repairing composites. There are some patents and some studies, however, the most articles were published in this field by the Department of Aerospace Engineering, University of Bristol, where I could prepare myself manually thick hollow glass fibers (75 μm outer, 50 μm inner diameter) during my two weeks professional trip. In the publications that are studying the self-repairing effect, they tried to damage the test specimens similarly then they examined the healing ratio as well as the status assessment function to visualize the damages. I have found such studies too, where the reinforcing hollow fibers of the composites were filled with premixed two-component healing agent and the damaging was executed before the curing of the repairing liquid.

In the hollow fiber reinforced self-repairing composites available in the literature the healing agent was stored in such hollow fibers that are much (>30 μm) thicker than the conventional solid glass fiber (~15 μm). The properties of the composites were weakened by the poor mechanical properties of the thick fibers resulting in several fault locations. The application of thin hollow fibers could be more effective that could ensure real reinforcing function as well as they could be filled with some indicator or healing liquid.

After reviewing the literature the goals of my dissertation were set as follows:

1. to analyze the hollow glass fibers available in the market, studying the geometrical, mechanical properties and refining their measurements, defining their chemical composition, and establishing the relationships between the properties.
2. to define the conditions affecting the filling the fibers, to determine the relationships between the filling speed and the affecting factors.

3. to map the mechanical properties of the fibers and to develop measurement method.
4. to work out a method to fill the hollow fibers before they are embedded into the composites in order to make it possible to apply the status assessment or self-repairing function in real structures.
5. to compare hollow and solid fiber reinforced composites by different mechanical examinations.
6. to fill the holes of the hollow fiber reinforced composites with indicator liquid, to examine the status assessment function of these plates.
7. to manufacture 0/90° directional hollow fabric reinforced composite plate, to fill the fibers with the two components of the healing agent subsequently, then to examine the healing ability under different conditions.
8. examination of self-repairing composites filled with one component healing agent.

3. Applied materials and experimental methods

3.1. Resins and their examination

Resins

During my measurements, I used resins of different types and properties; laminating and injecting resins. I chose the resin systems to cover a wide range of viscosity in order to examine the influencing effect of the viscosity. The properties of the chosen resins are collected in Table 1.

Resin component (A)	Viscosity of the resin component at 25°C [mPa·s]	Curing agent (B)	Viscosity of the curing agent at 25°C [mPa·s]	Mixing ratio A:B	Potlife [min]
Ipox MS90 A	660-790	Ipox MS90 B	10-30	100:33	570
Ciba LY 5082	1700-2200	Ciba HY 5083	10-25	100:23	100
Eporezit AH12	100-200	Eporezit T58	80-120	100:40	100
Polimal 1058	150-200	Butanox M50	20-25	100:1-100:4	5-20

Table 1. Resins and their nominal properties

Eporezit SZPM black and white coloring (Ipox), iron oxide pigment powder and Keystone Rhodamine B Base UV fluorescent dye were used to ensure the visibility of the resins.

Choosing the two-component healing agent, it important to find one that is neither sensitive to the mixing ratio nor to the imperfect mixing process. In case of partial polymerization the individual molecules are not connecting perfectly to each other, thus the mechanical properties are deteriorating, affecting the tensile, compression, bending properties and the energy absorbing ability. Regarding the above I chose Polimal 1058 injecting polyester resin and methyl ethyl ketone peroxide dissolved in dimethyl phthalate (Butanox M-50) as the curing agent.

Viscosity measurement

The dynamical viscosity tests of the liquids were carried out by a TA Instruments AR2000ex rotational rheometer. The ambient temperature of the measurement was 23°C, and the shearing speed was set after every 65 seconds between 0,01-10 1/s in 13 grades.

Contact angle measurement

The measurement of the contact angle was executed by a Ramé-Hart NRL C.A. 100 goniometer. The ambient temperature of the measurement was 23°C.

3.2. Fibers and their examination

Fibers

Zoltek Zrt gave the hollow and solid carbon fibers used for the preliminary experiments. The PAN based fibers were in roving packaging.

Hollow glass fibers were bought from R&G Faserverbundwerkstoffe GmbH in an atlas weaving fabric form. According to the datasheet the fibers are made from a mixture of alkali-free aluminum-borosilicates (patented manufacturing process), the areal weight of the fabric is 216 g/m^2. When there was a need for single roving, the fabric was separated. The roving of the hollow glass fabric has a twist of 150/m. Solid glass fibers were manufactured by 3b fiberglass, and they provided it in roving form. The fibers are made of E-glass and the linear density of the roving is 134 tex.

During my professional trip in Bristol I manufactured thick hollow glass fibers from glass tube preforms (Glass 8252) with the equipment developed by Bond *et.al.* The preform was fixed at the end of the tube and it was heated nearly to 1000°C in a tube furnace. The free end of the tube was pulled with a consistent speed. The fibers used in my dissertation are shown in Table 2.

Fiber type	Nominal outer diameter [μm]	Nominal inner diameter [μm]
R&G hollow glass fiber	10-13	5-8
3b Advantex 608 solid glass fiber	10	-
Manually manufactured hollow fibers (Bristol)	75	50
Zoltek carbon fiber	7	-
Zoltek hollow carbon fiber	22	11

Table 2. Used fibers

Chemical analysis of the fibers

The chemical composition of the surface of the fibers were examined by energy-dispersive X-ray spectroscopy, thus I could examine the composition of the sizing.

The accurate chemical composition of the fibers was determined with inductively coupled plasma optical emission spectrometry.

Determining the diameter and tensile strength of the fibers

The fiber diameter measurements were carried out by Olympus BX 51M optical microscope. The fiber tensile tests were carried out regarding to the EN ISO 5079 standard. The test specimens were torn by a Zwick Z005 universal tensile tester at 2 mm/min speed.

Fiber bending examinations

The bending properties of hollow and solid fibers were compared. The results are specified by the fiber diameter and the cross sectional area. The vertical deflection was measured of the free end of a 50 mm long fiber while the other end was fixed. This method includes lot of opportunity for the measurement errors thus the determining of the fiber bending moduli is inaccurate, so I improved this method.

Filling of the hollow fibers

Hollow fibers were filled with different resin components and curing agents, and the process of the sucking was examined horizontally. Different diameter hollow fibers were filled by the capillary action and the capillary length was examined as a function of the angle between the fiber and the vertical direction. The first position of the filling was vertical, then the fibers were turned when a balanced condition reached.

3.3. Composite plate examination

The mechanical properties of the composite plates reinforced with hollow and solid fibers were compared. The dry roving was wound for the suitable thickness, then they were impregnated by vacuum infusion technique.

The manufacturing of the composite plates reinforced with hollow and solid fibers

The row materials were 3b Advantex 608 solid glass fiber, hollow glass fiber turned over by R&G and ipox MS 90 epoxy resin system. The impregnation of the fibers was executed by vacuum infusion technique, the manufacturing of the same thickness plates carried out at the same phase in order to make the same conditions. For the status assessment tests Eporezit SZPM white dye was mixed into the matrix to increase the visibility of the indicator functions. For the self-repairing examinations two manufacturing methods were applied (hand layup, vacuum infusion).

Filling of the hollow glass fiber reinforced composites with liquids

The filling of the hollow fiber reinforced composite plates was carried out as follows: after drying the specimens' one end was put into a vacuum bag and a medium net was placed to both sides of the plate to avoid the closing of the holes. The other end of the specimen was placed into the liquid that would be filled.

Filling of the hollow glass fibers before building them into composites

I filled hollow glass fibers in order to facilitate the status assessment and the self-repairing for complex geometry products as well. Vacuum bagging technique was applied for the filling.

Composite examination methods

Determination of ash. The fiber content is determinable with the determination of the ash that I carried out according to EN ISO 3451 standard.

Tensile test. The tensile strength and Young's modulus were determined by tensile tests that were executed according to EN ISO 527 standard. The measurement was carried out by Zwick Z050 universal tensile tester at 2 mm/min speed.

Compression test. The compression strength and Young's modulus were determined by compression tests that were executed according to EN ISO 14126 standard. The measurement was carried out by Zwick Z050 universal tensile tester at 1 mm/min speed.

Three point bending test. The bending strength and Young's modulus were determined by three point bending tests that were executed according to ISO EN 14125 standard. The measurement was carried out by Zwick Z020 universal tensile tester at 2 mm/min speed.

Charpy dynamic bending impact test. The impact strength was determined by instrumented Charpy dynamic bending impact tests that were carried out by Ceast Resil Impact Junior and a DAS 8000 data collector according to EN ISO 179 standard. A 25 J hammer was used.

Falling weight impact testing. The falling weight impact tests were carried out by Ceast Fractovis falling weight impact test machine to damage the specimens.

Methods of the damaging and checking of the self-healing ratio

Specimens were cut out of filled and unfilled hollow glass fiber reinforced composites. The specimens were damaged by Ceast Fractovis falling weight impact test machine then the residual strength was measured by three point bending according to EN ISO 14125 standard. The speed of the bending was 2 mm/min.

Microscopy

The fracture surfaces and the cracks were examined by Olympus BX 51M optical microscope and JEOL JSM 6380LA scanning electron microscope after the self-repairing examinations, and the signs referring to the healing were searched. The specimens were embedded into resin and then the surfaces were prepared by Struers automatic polishing machine.

Finite element analysis

The finite element analyses were carried out by the aid of HyperWorks 12.0. The material models were set up on the basis of my measurements. According to the analysis type 2D (triangle and quadrangle) and 3D (tetrahedron and cube) elements were applied. The material models were linear and the analysis type was static.

4. Summary

My dissertation is about the development of the hollow fiber reinforced composites. Studying the literature I stated that the hollow fiber reinforced self-repairing composites have several advantages over the other self-repairing mechanism, besides the hollow fibers have the storing ability ensuring reinforcing function as well. I have studied the manufacturing method of the two most important reinforcing fibers (glass and carbon fiber) as well as the manufacturing possibilities of the hollow fibers. Furthermore I have studied the researches about the geometry of the hollow fibers and their application for self-repairing composites. The self-repairing and status assessment function were described, but the outer diameter of the thinnest hollow fiber found in the literature was 30 µm that is by far not so strong and thin as the conventional fibers (~15 µm). I have studied the influencing factor of the filling of the fibers and I have prepared an overview about the physical background of the filling.

In the experimental part I have examined the tensile strength of the hollow and solid glass fibers, and I found that the tensile strength is in inverse proportion to the fiber filling factor. I defined the bending stiffness of the fibers and it was shown that the bending stiffness of the hollow fibers is higher than that of the solid fibers due to the lower cross sectional mass and the higher mass/moment of inertia ratio. The fiber bending stiffness measurement methods found in the literature seemed inaccurate thus I have worked out a refined process. Previously the bending stiffness was defined by the vertical displacement of the fibers; however the new process I have established takes into account the horizontal displacement as well and the calculations to define the bending stiffness were set up. Thus the accuracy of the measurement was increased. I have examined the filling ability of the hollow fibers and it was shown that there is connection between the contact angle, the viscosity and the capillary action generated filling speed.

I have compared the mechanical and energy absorbing property of the composite plates reinforced with the same chemical composition hollow, solid and mixed fibers. It was shown that the strength and Young's modulus correlated to the mass is higher in case of hollow fiber reinforced composite than in case of solid fiber reinforcement. For tensile and compression tests the results normalized to the density shows hybrid effect in case of hybrid fiber reinforcement. The energy absorbing property was lower in case of the hollow fiber reinforced composites that could be increased by filling the fibers with a healing of indicator liquid. The energy absorbing property of the hollow fiber reinforced composites would also be higher if the wall thickness of the fibers were so small that they would splinter by a perpendicular hit. I have examined the micromechanical models of the hollow and solid fiber reinforced composites with finite element method. The calculations confirmed the advantages of the hollow fiber reinforcement.

I filled the holes of hollow fiber reinforced composites with indicator liquid, unsaturated polyester resin and its curing agent. Thus the status assessment function and the self-repairing ability were examined. Thanks to the indicator liquid the status checking can be quickly performed with a UV lamp, so the crack is definitely visible that has broken the hollow fibers. The filling of the fibers improved the bending and the energy absorbing properties. Test specimens manufactured with hand layup and vacuum infusion were damaged with falling weight impact test machine then the healing liquid was left to cure at 60 and 23°C for 12 and 120 hours. I have proved that the self-repairing is possible with the aid of the polyester resin filled hollow fibers at the temperature range where the hardening is possible. The cracks formed during the damaging were examined with scanning electron microscope, and I have proved that the polyester resin hardening in the crack restored the integrity of the structure thus the bending properties of the composites were improved.

I introduced the practical application of the materials developed by myself on the steering wheel of the BME Formula Racing Team race car. Hollow fibers were filled with indicator liquid before they were built into the composite and with these fibers I reinforced the critical places defined by finite element method. Micro cracks have evolved by fatigue tests that were invisible for the naked eyes, but under UV light the cracks could be clearly seen thanks to the indicator liquid. The status assessment function I developed, together with BME Formula Racing Team we applied for „Győr city’s special award for innovation” tender in the Formula Student Hungary competition and successfully we won the honourable mention in the international field.

5. New scientific results – Theses

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

1st thesis. I have developed a measurement process of the fibers' bending stiffness and worked out the corresponding evaluation method. The process described by Holden for the big deformation was refined with the measurement of the horizontal displacement of the fiber endpoint beside the vertical displacement. I demonstrated that the Ω parameter required for the calculation of the fiber modulus can be calculated which is more accurate than the previously applied reading from a curve. I introduced limiting functions that can filter out the inaccurate results caused by the measurement errors. Comparing the statistical methods I established that for the measurements' evaluation the most beneficial is the individual coordinates method [2, 9].

2nd thesis. I demonstrated with measurements and confirmed with finite element method the benefits of the hollow fiber reinforcement over the solid fibers: as a composite reinforcement assuming equal fiber volume contents 20% lighter structure can be reached (in case of 13 μm outer diameter, 8 μm inner diameter), with a 150% higher density specific stiffness normalized by the density and 22% higher specific modulus normalized by the density [2, 5, 7, 8].

3rd thesis. I have developed a new vacuum bagging technique to fill hollow fibers: on the one hand a two or more component healing agent's filling technique into the holes of hollow fiber reinforced composite plate was generated where the fibers could be filled from one side of the plate with different liquids, on the other hand a vacuum bagging technique was developed to make it possible to fill the fibers before embedding them into the composite structure in a long or a short fiber form.

a. During the filling of the hollow fiber reinforced composite plates I proved experimentally that thanks to the novel technique the amount of the two or more component healing agent can be controlled even in case of 100:5 weight ratio by separating the fibers. I could reach this mixing ratio inside the composite by filling the hollow fibers in more steps [3].

b. I determined that the amount of the fibers prefilled with different liquids before embedding them into a composite structure can be adjusted by the weight ratio, and with the right amount of filled fibers any shape and size of product can be made to become self-repairing. I proved that the liquid inside the fibers can fill the cracks on a real product (Formula Student racecar steering wheel) [9].

4th thesis. I demonstrated that the bending stiffness and the bending modulus of the hollow glass fiber (13 μm outer diameter, 8 μm inner diameter) reinforced epoxy matrix composites can be improved by filling the fibers with liquid polyester resin 3-15% depending on the applied manufacturing technique due to the incompressibility of the liquids. The impact resistance also improved thanks to the filling 28-250% that depends on the applied manufacturing technique (hand layup, vacuum infusion) which is affected by the damping effect of the friction between the liquid polyester resin and the fiber inner wall [3, 5].

5th thesis. I proved that self-repairing of the hollow glass fiber reinforced composites can be achieved not only with the matrix material but also with different polyester resin whose resin component and initiator are filled into different hollow fibers. With the partial damaging and then the three point bending of the hollow glass fiber reinforced composite specimens I demonstrated the healing ability of the bending strength and the bending stiffness is at least 20% compared to the damaged state [1, 3, 7].

6th thesis. Against the thick hollow fiber (outer diameter: $30<d_o<1150$ μm) reinforced self-repairing composites introduced in the international literature I proved that the status assessment and the self-repairing ability is possible in case of thin hollow fibers (13 μm outer diameter, 8 μm inner diameter) with smaller amount of indicator or healing liquid. The huge advantage of the thin fibers is the higher strength compared with thick fibers, so they are really reinforcing the composites [3, 9].

6. List of own publications

Publications in periodicals

[1] **Kling S**., Czigány T.: Analysis of applicability of the hollow carbon fibres for self-repairing composites. Materials Science Forum, 729, 246-251 (2013).

[2] **Kling S.**, Czigány T.: A comparative analysis of hollow and solid glass fibers. Textile Research Journal, 83, 1764-1772 (2013). **IF=1,332**

[3] **Kling S.**, Czigány T.: Damage detection and self-repair in hollow glass fiber fabric-reinforced epoxy composites via fiber filling. Composites Science and Technology, 99, 82-88 (2014). **IF_{2013}=3,633**

[4] **Kling S.**: Kompozit ülés tervezése és gyártása a BME Formula Student 2012-es versenyautójába. Műanyag és Gumi, 49, 453-458 (2012).

[5] **Kling S.**, Czigány T.: Üreges, tömör és hibrid szálakkal erősített kompozit lemezek mechanikai tulajdonságainak összehasonlítása. Műanyag és Gumi, 50, 222-226 (2013).

Conference proceedings and presentations

[6] **Kling S.**: Designing and manufacturing the steering wheel of the BME formula student race car. Gépészet 2010. 612-617 (2010).

[7] **Kling S.**, Czigány T.: Üreges üvegszálak vizsgálata, és öngyógyuló kompozitokhoz való használatának elemzése. Erősített Műanyagok 2012. Nemzetközi Balaton Konferencia, Proceeding p5 (2012).

[8] Czigány T., **Kling S.**: A comparative analysis of hollow and solid glass fiber reinforced composites. ECCM15 - 15th European Conference on Composite Materials, Proceeding p7 (2012).

[9] **Kling S.**: Üreges szálerősítésű kompozitok: a szálak mechanikai tulajdonságai, valamint öngyógyuló és állapotjelző kompozitokhoz való alkalmazása. Erősített Műanyagok 2014. Nemzetközi Balatoni Konferencia, Proceeding p14 (2014).

[10] **Kling S.**, Czigány T.: Üreges szénszálak alkalmazhatóságának elemzése öngyógyuló kompozitokhoz. VIII. Országos Anyagtudományi Konferencia, 2011. október 9-11., Balatonkenese, Magyarország (2011).