INVESTIGATION OF MECHANICAL PROPERTIES OF FILAMENT WOUND UNIDIRECTIONAL BASALT FIBER REINFORCED POLYMERS FOR AUTOMOTIVE AND PRESSURE VESSEL APPLICATION

Eduard Kessler[1], Rainer Gadow[2], Patrick Weichand[2]

[1]NuCellSys GmbH, Kirchheim u. Teck, Germany
Neue Strasse 95, D-73230 Kirchheim u. Teck, Germany
Email: eduard.kessler@daimler.com, web page: http://www.nucellsys.com

[2]Institute for Manufacturing Technologies of Ceramic Components and Composites (IMTCCC),
University of Stuttgart, Germany
Allmandring 7B, D-70569 Stuttgart, Germany
Email: ifkb@ifkb.uni-stuttgart.de, web page: http://www.ifkb.uni-stuttgart.de

Keywords: Basalt Fiber Composite, Filament Winding, Mechanical Characterization, Polymer Composites, Pressure Vessels

ABSTRACT

Car manufacturers worldwide try to lower their fleet consumption and to fulfill new challenging environmental regulations. Some of the most promising candidates to lower CO_2 emissions are natural gas and fuel cell driven cars. For these purposes compressed natural gas (CNG) and hydrogen are stored in filament wound high pressure vessels. One of the main driving forces in current pressure vessel research and development is cost reduction. Major cost factor of pressure vessels is the fiber material, because of the use of high performance carbon fibers and the required wall thicknesses due to high pressure needed to store sufficient amount of CNG or hydrogen. So many researchers focus on new materials for filament winding of pressure vessels in order to lower manufacturing costs. During the last years basalt fibers came into focus of researchers and composite manufacturers as a cost competitive reinforcement material. Combining those two trends, investigations on mechanical properties of basalt fibers and unidirectional basalt fiber reinforced epoxy composites were performed and compared with state of the art fibers and polymer composites. The research included tensile testing of impregnated roving test specimens, tensile evaluation of unidirectional filament wound flat specimens, 3-point-bending tests and short beam shear tests. Unidirectional fiber composite specimens were manufactured by filament winding on a flat specimen winding tool with an epoxy matrix. Results show superior mechanical properties of basalt composites compared to E-glass-epoxy samples. Tensile strength and stiffness are between E-glass and S-glass-epoxy composites, but inferior compared to carbon-HT-composites. At present further investigations are conducted on tensile fatigue properties, Charpy impact properties and hoop tensile strength by split disk method for basalt fiber and hybrid-fiber polymers. Goal is a complete mechanical characterization of basalt fibers and basalt fiber polymer composites in order to build cost competitive pressure vessels made of basalt fibers or a basalt-/carbon fiber hybrid.

1 INTRODUCTION

In order to lower fleet consumption and reduce CO_2 emissions car manufacturers are looking for alternative drives. Promising candidates are natural gas and fuel cell driven cars. Therefor compressed natural gas (CNG) and hydrogen are stored in filament wound high pressure vessels. State of the art, so called type 4 pressure vessels consist of a polymeric liner and metallic bosses, reinforced with a carbon-fiber-epoxy composite filament winding [1]. Polymer matrix composites (PMC) offer great benefits regarding strength and stiffness, qualifying them as light weight alternative compared to classic engineering materials like metals. Main focus of current pressure vessel design is cost optimization to reach the challenging cost targets for alternative drive trains. Therefore different strategies are being conducted, e.g. optimization of current pressure vessel design via numerical simulation and optimization of winding patterns [2] or alternative manufacturing strategies, like braiding followed by RTM [3]. Somehow the research for different composite materials for pressure vessels was neglected. Hydrogen pressure vessels are manufactured with carbon fiber-epoxy composites, CNG pressure vessels sometimes also with glass or carbon-glass-hybrid composite.

Therefore in this work the authors focus on the investigation of alternative composite materials. In preliminary investigations reinforcing fibers with potential to replace the carbon fibers were scanned in a literature review and market analysis. According to different requirements like mechanical properties, density and cost, temperature and chemical resistance, fibers were selected for further investigation also with regard to a potential use as a hybrid fiber in combination with carbon fibers. As a result of these preliminary investigations basalt fibers were selected for further intensive research.

The basalt fiber came into focus of many researchers as a cost competitive reinforcing fiber during the last years. Research shows that it offers slightly higher mechanical properties and thermal stability than E-glass fibers at comparable reasonable prices [4]. As basalt fibers are a natural product, chemical composition and thus fiber properties vary with the mining region [5]. According to [6] high amounts of silicon oxide (SiO_2) and aluminum oxide (Al_2O_3) lead to better mechanical properties. In this work two commercially available basalt fibers were under investigation. Their chemical composition is shown in Table 1 [7] compared to the composition of an E-glass fiber [6]. According to that understanding similar tensile properties are expected for basalt fiber A and E-glass, slightly higher than for basalt fiber B.

Table 1: Chemical composition of investigated basalt fibers [7] and an E-glass fiber [6]

Element / Fiber	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO / Fe_2O_3
	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]
Basalt A	2,8	4,9	19,4	51,8	2,5	7,7	2,1	8,8
Basalt B	2,1	4,3	18,2	48,5	2,2	10, 7	1,8	12,2
E-glass	0,30	0,54	11,86	58,25	0,43	21,09	0,41	0,30

2 EXPERIMENTAL

2.1 Materials

Two commercially available basalt fibers were investigated in this work. Test specimens were manufactured via wet filament winding of continuous rovings. Depending on the experiments basalt test specimens were manufactured from rovings with different linear densities (480 tex, 1200 tex and 2400 tex). Basalt fibers have an averaged diameter of 17 µm and a density of about 2,65 g/cm³. These basalt fibers were compared to standard E-glass-, S-glass-, aramid-, HT carbon fibers, which are used for state of the art hydrogen pressure vessels and are labeled as Carbon A, and industry standard carbon fibers (Carbon B), which shall be tested as cost-effective carbon fiber alternative. Nominal properties of the fibers under investigation are shown in Table 2, as given by the fiber manufacturers.

Table 1: Fibers under investigation and their nominal properties (source: manufacturer data sheets)

Reinforcing Fiber	Linear density	Fiber diameter	Density	Tensile strength (manufacturer)	Tensile modulus (manufacturer)
	[tex]	[µm]	[g/cm³]	[MPa]	[GPa]
Basalt A	480, 1200, 2400	13-20	2,6	3400	90
Basalt B	1200	10-17	2,65	2900	90
E-Glass	2400	17	2,45	2400	80
S-Glass	1200	17	2,45	4060	92
Aramid	800	12	1,44	3600	120
Carbon A	1600	7	1,79	5000	245
Carbon B	3333	7,2	1,81	4137	242

Different epoxy resins were used for different test runs. For tensile tests of impregnated rovings a commercial epoxy resin (L with EPH161 hardener by R&G, Germany) was used as stabilizing matrix. It is a low viscosity cold-curing resin suitable for filament winding. For tensile tests of flat unidirectional composite specimens the epoxy-system Epicote LR285 with hardener LH 287 was used, which is a hot-curing low-viscosity system.

2.2 Composite Manufacturing

Composite test specimens were manufactured via wet filament winding at the ITCCC, Stuttgart, Germany. Flat unidirectional plates were wound on a square mandrel, as seen in Figure 1. After winding, corner supports are screwed outwards in order to pretension the fibers during curing. Afterwards stiffening plates are put on the wound fibers in order to create homogeneous composite plates with plain surfaces. A fiber volume content of 0,6 was aimed for. The specimens with the hot curing system LR 285/LH 287 epoxy matrix are put into an oven at 90 °C for 4 hours while rotating to increase the operation temperature up to about 110 °C. Afterwards the unidirectional plates are removed from the mandrel.

Figure 1: Filament winding of unidirectional plates – left: winding mandrel for flat composite plates; right: attachment of stiffening plates

Depending on the intended experiment, plates from 1 to 3 mm were manufactured. Required specimen geometries were cut out with diamond saw blades. Test specimens for tensile testing have the dimensions 250 x 15 x 1 mm. Thicker and wider specimens were tested as well, but reached the limitations of the 100 kN load cell, which was used during the preliminary tests. On each side 2 mm thick and 50 mm long (± 45°) glass-fiber-epoxy cap strips were bonded onto the specimens in order to ensure smooth load transmission and to prevent breaks caused by the fixture jaws, see Figure 2.

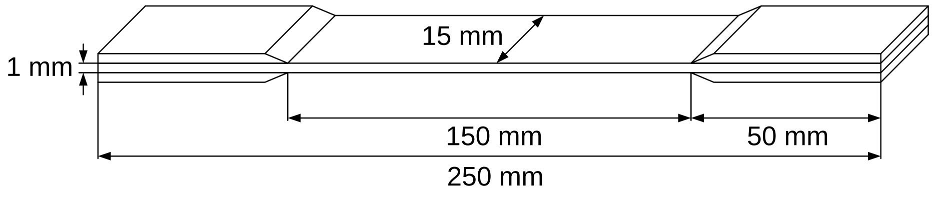

Figure 2: Dimensions of the tensile test specimens

Specimen quality was tested afterwards via reflecting microscopy. Fiber volume fraction was determined via optical measures and density determination via Archimedes' principle and showed good correlation. A fiber volume fraction of about 0,58 was determined for the tensile test specimens. Representative reflecting microscope pictures of polished sections of a basalt-epoxy and a carbon-epoxy test specimen are shown in Figure 3. Low porosity and a good fiber-matrix bonding can be observed for both specimens. For the basalt-epoxy specimen big differences in the diameter of the basalt fibers are visible. Possible reasons for these big differences could be a poor or worn-out spinning-nozzle or different haul-off speeds during manufacturing. For the carbon fibers a constant fiber diameter of 7 μm can be observed. Small matrix clusters are also visible between different layers.

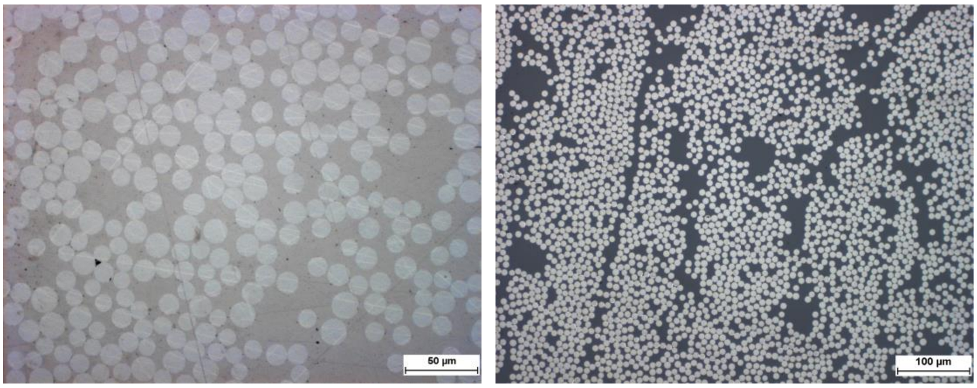

Figure 3: Reflecting microscope picture of a polished section of a basalt-epoxy test specimen (left) and a carbon-epoxy specimen (right)

2.3 Test methods

In order to provide information on fiber or rather roving properties, tensile tests with impregnated rovings were performed according to German standard DIN 65382 [8], which is close to ASTM D2343. Therefor fibers were impregnated on a manual winding device (Figure 4 left) with a cold curing epoxy matrix (epoxy L with EPH 161 hardener). Tensile tests were performed on a Zwick Z100 materials testing machine with a load cell of 5 kN at a speed of 1 mm/min. Displacement was measured with a mechanical displacement transducer. Test arrangement is shown in Figure 4 on the right. At least ten specimens of each material were tested in order to get enough valid results, which means breaking in the free section of the test specimens. This is an important factor, as the rovings are sensitive to breakage near the clamps, because of stress peaks in this region and only thin cardboard cap strips can be used as load transmission.

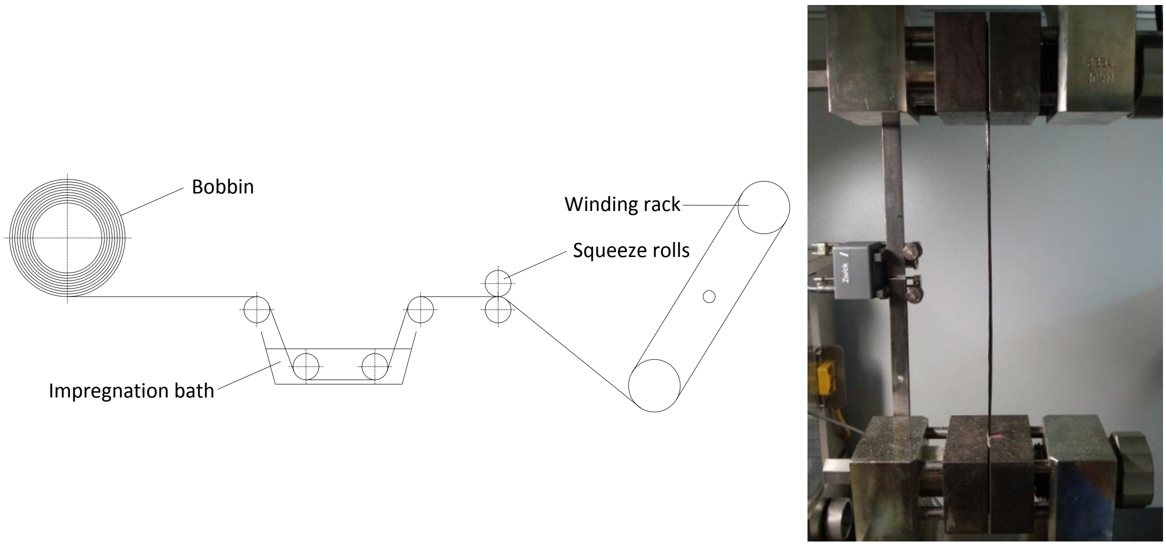

Figure 4: Left: Manual winding device to impregnate rovings according to German standard DIN 65382 [8]; right: tensile test of an impregnated roving in the testing machine

Tensile properties of polymer fiber composites at different temperatures were tested according to the international standard ISO 527-5 [9]. Tests were performed on a Zwick Z250 materials testing machine, capable of a maximum force of 250 kN, at a speed of 2 mm/min. Displacement was measured with a mechanical displacement transducer *multiXtens* directly on the test specimen.

Operating temperature for hydrogen pressure vessels varies between -40 °C and +85 °C. Therefore these temperature conditions had to be tested. Alongside tests at room temperature at 23 °C, tests were performed at -40 °C and +85 °C in a temperature chamber. Test specimens were preconditioned at the desired temperatures for two hours. Six specimens of each material were tested at each temperature, in order to get sufficient accuracy, even if some test runs fail. Experimental setup without temperature chamber is shown in Figure 5. Because of their high modulus and the explosive fracture tensile modulus of the carbon-epoxy-specimens was tested separately before testing the ultimate tensile strength. Test specimens were displaced until 0,3 %. Afterwards the displacement transducer was removed and specimens were tested until failure.

Figure 5: Tensile test of flat unidirectional polymer fiber composite test specimen without temperature chamber

3 RESULTS AND DISCUSSION

Results of tensile tests on impregnated rovings are shown in Figure 6. Basalt and E-glass fiber properties are close to each other. Basalt fiber A shows slightly higher tensile strength than basalt fiber B with similar modulus. Tensile strength corresponds with the assumption by [6] as mentioned before that tensile strength correlates with the content of aluminum and silicon oxide. Basalt fiber A was chosen for further investigation.

Basalt and glass fiber rovings are supplied with different linear densities. Yet higher linear densities are not produced directly but are accumulated of smaller rovings. For example the 1200 tex basalt roving consists of 2-3 smaller rovings, the 2400 tex roving of 4-6. Theoretically this can lead to twisting of the accumulated roving and therefore lower mechanical properties. In order to investigate this circumstance three different linear densities of basalt fiber A were investigated: 480 tex, 1200 tex and 2400 tex. As Figure 6 shows tensile strength is not being affected, yet tensile modulus decreases by 11,1 % for the 1200 tex and by 18,9 % for the 2400 tex rovings compared to 480 tex.

Furthermore a first step to investigate the influence of the silane sizing on the basalt fiber was taken. Before impregnation of the rovings the sizing on the fiber was removed via two modes. First, the sizing was removed via bathing the rovings in acetone for 24 hours (‘w/o sizing-1’ in Figure 6). Tensile strength and modulus decreased by approx. 8 %, so influence of the sizing on tensile properties of the roving is not a major factor. Yet further research should be carried out on the effect of sizing regarding the polymer composite, e.g. via composite tensile or interlaminar shear tests.

Secondly, the sizing was removed thermally in an oven at 450 °C and a dwell time of 2 hours ('w/o sizing-2' in Figure 6). Tensile strength decreased dramatically by 75 %, which is definitely a thermal and not a sizing factor. Similar results for thermal stress concerning sizing can be seen in [10], where the mechanical strength of thermally processed fabrics dropped by at least 80 %. This result is opposing to the general assumption of good thermal properties of the basalt fiber [11, 12] and will be motivation for further research in this field by the authors in the future.

Carbon industry standard fibers, as mentioned in Table 1 and later in the investigation of composites were tested as well, but are not shown in Figure 6. No valid result could be produced. On the one hand the 50k strand could hardly be impregnated reliably. On the other hand when this problem was handled, the specimens reached the 5 kN-limit of the available load cell for this experiment, because of the high linear density and tensile strength. This was also a problem for the carbon-HT 24k fibers which almost reached the 5 kN force limit.

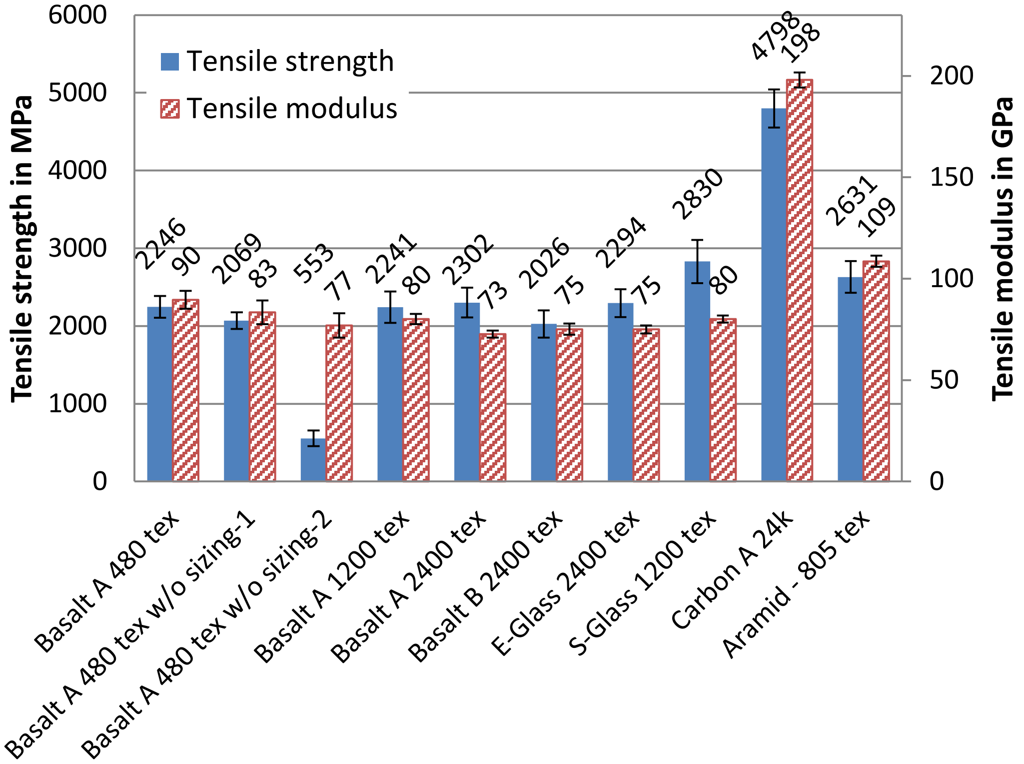

Figure 6: Tensile properties of impregnated roving specimens

Figure 7 shows a scanning electron micrograph (SEM) of the fractured surfaces of an impregnated basalt fiber roving after tensile testing (left) compared to the fractured surface of an impregnated glass fiber roving (right). Typical brittle glass like fracture pattern can be observed for both test specimens. Certain fiber pull out can be observed as well, but not very widespread. For the basalt fibers again different filament diameters can be observed.

Tensile tests of unidirectional filament wound composites were performed according to international standard ISO 527-5 [9] at three different temperatures: -40 °C, +23 °C and +85 °C, which are the limit operating temperatures for hydrogen pressure vessels. Results of those tests are shown in Figures 8 and 9. Noticeable for all composite materials is that tensile properties decrease with rising temperature and increase with decreasing temperature. While the roving properties were quite similar for the basalt and the E-glass fiber, the basalt composite has little higher tensile strength and tensile modulus than the E-glass composite. Basalt composite tensile strength is between E-glass and S-glass composite tensile strength at significantly lower prices than S-glass fiber composites. The temperature effect is much lower for the basalt-epoxy composite than for the other fiber reinforced composites.

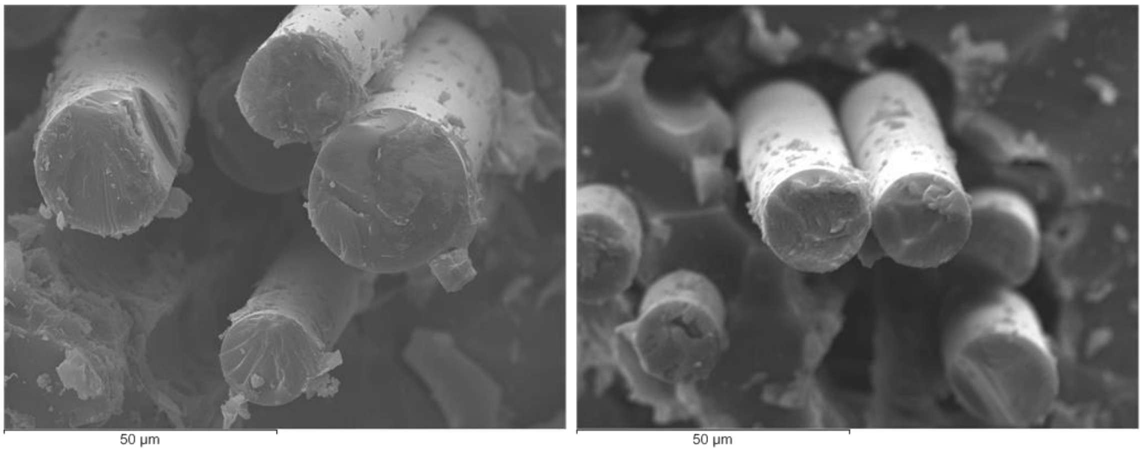

Figure 7: Scanning electron micrograph of fracture surfaces of impregnated basalt fiber roving (left) and glass fiber roving (right) after tensile test, both showing brittle glass fracture pattern

The aramid composite has low tensile properties compared to pure fiber properties. Although fibers with epoxy-compatible sizing were used, fiber-matrix bonding is more critical than for the other fibers. The tensile strength values for aramid composite at 85 °C are not valid, as all of the aramid composite specimens failed by separating of the cap strips of the specimens, which only happened very occasionally with the other materials. A two-component-epoxy glue was used for all specimens. Again it seems that bonding between aramid and epoxy is lower than for the other fibers, especially at high temperatures. The carbon B test specimens reach comparable modulus values to carbon A, but have about 15 % lower tensile strength. Considering the price this industry standard fiber seems to have competitive tensile properties to carbon HT fibers currently used for pressure vessels. However processing via filament winding of these rovings was more difficult than winding with carbon fibers A. The 50k roving is not as smooth and clean as the carbon A 24k roving. It is fuzzier and many filaments seem to break during fiber guidance. Many single filaments separated from the roving during winding and wound up on thread guides and rollers, which had to be cleaned after the winding process. According to the generated results S-glass composites don't seem to offer great benefits compared to the other composites under consideration of the designated purpose regarding tensile performance compared to carbon fibers or cost effectiveness compared to E-glass and basalt fibers.

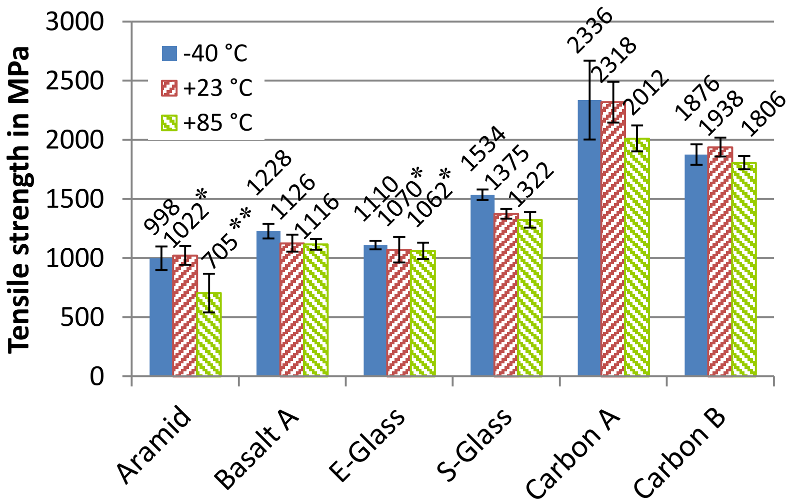

Figure 8: Tensile strength of different tested polymer fiber composites with epoxy matrix at -40 °C, +23 °C and +85 °C (* - test restarted at +23 °C after initial crack led to stop of testing machine; ** - invalid result, failure only by debonding of cap strips)

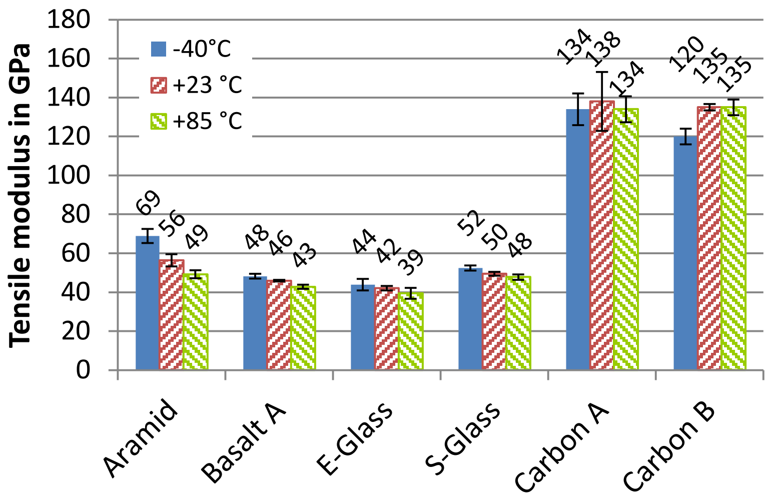

Figure 9: Tensile modulus of different tested polymer fiber composites with epoxy matrix at -40 °C, +23 °C and +85 °C

Aramid-, basalt- and glass fiber composites failed by fiber splitting (Figure 10), whereas carbon fiber composites failed more brittle by a mixture of preliminary fiber splitting and final fiber fracture (Figure 11). Fracture started at the weakest point of the specimen, which was at the free edge most of the time and spread into the rest of the test specimens. Fracture of several fiber bundles is visible in the stress-strain diagram as well. For the aramid composite at +23 °C and E-glass composite at +23 °C and +85 °C a first crack occurred quite early at about 60% of final strength. Although these test specimens weren’t fractured overall, the occurred single crack was enough for a drop in the stress-strain diagram to stop the test procedure (Figure 12). So these test specimens were tested again afterwards at +23 °C. This phenomenon didn’t occur at -40 °C, so this cold temperature has a strengthening influence on the composite, but especially on the epoxy matrix and the fiber matrix-interface as failure occurred as fiber splitting. In Figure 12 it can also be seen that the winding angle is not exactly 0°, but more like 1,5 to 2°,which is typical for the filament winding process.

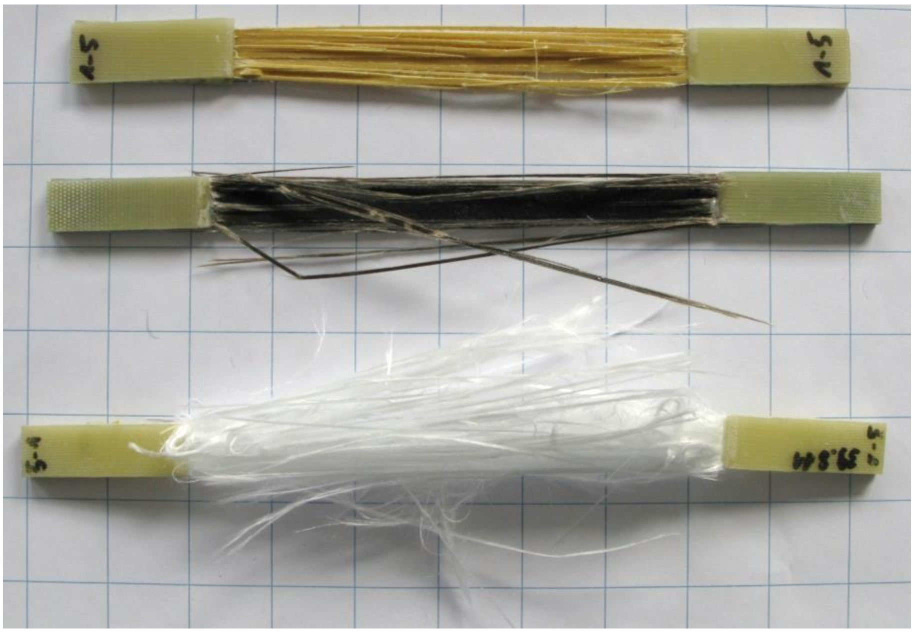

Figure 10: Failure of tensile test specimens aramid-, basalt-, and S-glass composite (from top to bottom) by fiber splitting at -40 °C

Figure 11: Brittle failure of carbon-epoxy test specimen by combined fiber splitting and final fiber fracture

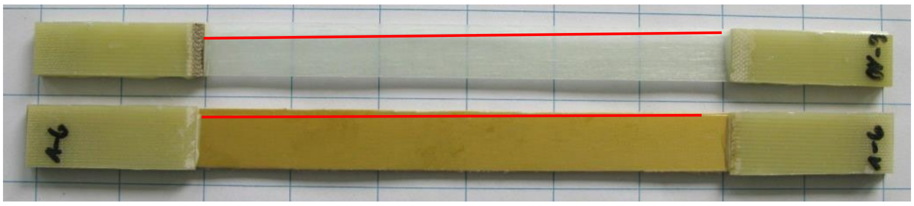

Figure 12: Single fracture in E-glass- and aramid-tensile test specimens at +23 °C, which led to stop of test apparatus; test specimens were tested again until final failure afterwards

Regarding the tensile properties of the basalt-epoxy composites, this material seems to be a reasonable alternative to glass-fiber composites. Because of the low price of the fiber in some applications it can be a reasonable alternative for carbon fibers as well. Regarding pressure vessels, in a next step hybrid-fiber composites, consisting of basalt and carbon fibers, will be investigated in order to reach a good compromise between cost and performance.

4 CONCLUSION AND PROSPECT

In conclusion it can be said that the mechanical tensile properties of polymer composites, reinforced with basalt fibers range between E-glass and S-glass composites, but at much more reasonable price than S-glass composites. Further research is needed in order to use basalt fibers as a reinforcing fiber for pressure vessels. A first thermal test presented in this work, showed weakness at high temperatures. Therefore this topic is under investigation right now.

Cost competitive industry standard carbon fibers (Carbon B in this work) show lower tensile strength than carbon HT fibers (Carbon A) currently used for pressure vessel manufacturing but at reasonable price. Further research is needed, if the 50k heavy tow can be wound the same manner, meaning comparable speed and fiber placement, as the HT carbon fiber.

In order to perform wide characterization on basalt fiber composites interlaminar shear strength and bending properties were measured as well. Those results will be shown in a following work.

Furthermore next steps in order to investigate the use of basalt fibers for pressure vessels have been taken. Research is performed on the tensile fatigue properties of the here investigated materials, as the fiber fatigue properties are an important parameter for the burst factors for pressure vessels. Furthermore hybrid composites with basalt and carbon fibers and glass and carbon fibers are being investigated. Test pressure vessels are wound with carbon, basalt, and glass fibers right now, burst and compared among each other. Hybrid vessels, wound with different layups of basalt and carbon fibers will also be investigated.

REFERENCES

[1] D. Mori and K. Hirose, Recent challenges of hydrogen storage technologies for fuel cell vehicles, *International Journal of Hydrogen Energy*, **34-10**, 2009, 2nd World Hydrogen Technologies Convention, pp. 4569-4574 (doi:10.1016/j.ijhydene.2008.07.115).

[2] P.F. Liu, J.K. Chu, S.J. Hou, P.Xu and J.Y. Zheng, Numerical simulation and optimal design for composite high-pressure hydrogen storage vessel: A review, *Renewable and Sustainable Energy Reviews*, **16**, 2012, pp. 1817-1827 (doi:10.1016/j.rser.2012.01.006).

[3] M. Lengersdorf, J.B. Multhoff, M. Linke, and T. Gries, Simulative design of overbraided pressure vessel for hydrogen storage, *Proceedings of the 19th International Conference on*

Composite Materials ICCM 2013 (Eds. S.V. Hoa, P. Hubert), Montreal, Canada, July 28-August 2, 2013, pp. 6499-6506.

[4] S.E. Artemenko, Polymer composite materials made from carbon, basalt and glass fibres. Structure and properties, *Fibre Chemistry*, **35**, 2003, pp. 226-229 (doi:10.1023/A:1026170209171).

[5] R.V. Subramanian and H.F. Austin, Silane coupling agents in basalt-reinforced polyester composites, *International Journal of Adhesion and Adhesives*, **1**, 1980, pp. 50-54 (doi:10.1016/0143-7496(80)90035-4).

[6] T. Deák and T. Czigány, Chemical composition and mechanical properties of basalt and glass fibers: A comparison, *Textile Research Journal*, **79**, 2009, pp. 645-651 (doi:10.1177/0040517508095597).

[7] R. Gadow and P. Weichand, Novel intermediate temperature ceramic composites, materials and processing for siloxane based basalt fiber composites, *Key Engineering Materials*, **611-612**, 2014, pp. 382-390 (doi:10.4028/www.scientific.net/KEM.611-612.382).

[8] DIN 65382:1988, Luft- und Raumfahrt – Verstärkungsfasern für Kunststoffe – Zugversuch an imprägnierten Garnprüfkörpern (German). *German Institute for Standardization, Berlin, Germany.*

[9] ISO 527-5:2009, Plastics – Determination of tensile properties – Part 5: Test conditions for unidirectional fibre-reinforced plastic composites, *International Organization for Standardization, Geneva, Switzerland.*

[10] R.J. Varley, W. Tian, K.H. Leong, A.Y. Leong, F. Fredo and M. Quaresimin, The effect of surface treatments on the mechanical properties of basalt-reinforced epoxy composites, *Polymer Composites*, **34,** 2013, pp. 320-329 (doi:10.1002/pc.22412).

[11] R. Parnas, M. Shaw and Q. Liu, *Basalt fiber reinforced polymer composites*, Technical Report NETCR 63, New England Transportation Consortium, 2007.

[12] V.P. Sergeev, Y.N. Chuvashov, O.V. Galushchak, I.G. Pervak, N.S. Fatikova, Basalt fibers – a reinforcing filler for composites, *Powder Metallurgy and metal ceramics*, **33**, Issue 9-10, 1994, pp. 555-557 (doi:10.1007/2FBF00559548).