Surface, interphase and tensile properties of unsized, sized and heat treated basalt fibres

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Surface, interphase and tensile properties of unsized, sized and heat treated basalt fibres

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Abstract. Recycling of fibre reinforced polymers is in the focus of several investigations. Chemical and thermal treatments of composites are the common ways to separate the reinforcing fibres from the polymer matrices. However, most sizings on glass and basalt fibre are not designed to resist high temperatures. Hence, a heat treatment might also lead to a sizing removal, a decrease of mechanical performance and deterioration in fibre-matrix adhesion. Different basalt fibres were investigated using surface analysis methods as well as single fibre tensile tests and single fibre pull-out tests in order to reveal the possible causes of these issues. Heat treatment in air reduced the fibre tensile strength in the same level like heat treatment in nitrogen atmosphere, but it influenced the wetting capability. Re-sizing by a coupling agent slightly increased the adhesion strength and reflected a decreased post-debonding friction.

1. Introduction

Recent investigations on the strength loss of heat treated basalt fibres were reported by [1] and [2]. Jenkins et al. compared thermal induced strength loss of sized E-glass and basalt fibres. Heat treatment beyond 300 °C led to significant drop of fibre strengths for both fibre types.

After treatment at 600 °C (25 min) the strength loss was about 80% for the basalt fibre sample. Jenkins et al. [1] pointed out that no correlation with the sizing degradation was found and assumed that the progressive oxidation of the fibre could affect the strength level of heat treated basalt fibres. Sabet et al. [2] observed the influence of the treatment temperature and duration on the tensile strength of basalt bundles. The authors determined a strength loss of about 20% after 5 to 15 min exposure at 300 °C. However, a 20 min exposure at 400 °C or 500 °C dropped the strength level drastically. The determined strength loss was about 65% and 89%, respectively. Sabet et al. [2] concluded that the strength loss was attributed to an amorphous-to-crystalline transformation, which is maximized at 450 °C. However, they pointed out that additional experimental studies are mandatory for the study of early crystallisation phenomena. In addition, based on their literature work, they refer to explanations for the basalt fibre degradation, e.g. the distortion of amorphous and local crystalline areas, the sizing burn-off or the corrosion/oxidation of iron.

Our previous studies indicate that the high temperature performance of basalt fibres preferably depends on their chemical composition. We investigated the single fibre tensile strength of unsized basalt fibres and could show that one of the basalt fibre compositions, in particular designated BAS11, remained the strength level whereas the other investigated composition, designated BAS12, showed a strength loss of more than 70% after 5 h heat treatment at a temperature of 600 °C. XPS results indicated that both fibre surfaces were slightly contaminated by carbon. However, considering

Thomason's rule of thumb for evaluating sizing coverage [3], the C/Si ratio of both fibre samples indicated unsized fibres. Therefore, a potential sizing burn-off is negligible. Interestingly, the XPS results reveal also that heat treated basalt fibres show a reduced presence of silica, whereas the calcium content was increased on the fibre surface. The iron content seemed to be not affected [4].

A formation of nano-layers caused by the heat treatment of basaltic glasses was already reported by Smedskjaer et al. [5]. The authors pointed out that the induced diffusion of divalent cations can influence properties like temperature stability as well as chemical durability. However, the impact on fibre-matrix adhesion due to thermal induced nano-layers has been less investigated.

In this study, first results of de-sizing and re-sizing experiments on basalt fibres were reported. Sized and unsized basalt fibres were heat treated in air and in nitrogen atmosphere. The initial tensile strength and the tensile strength after 0.5 h exposure at temperatures in the range of 250 to 600 °C were investigated by single fibre tensile tests. In addition, X-ray photoelectron spectroscopy (XPS), Atomic Force Microscopes (AFM) investigations, contact angle measurements as well as single fibre pull-out tests were carried out. Both initial sized and unsized fibres were investigated comparatively in order to evaluate the impact of the sizing-burn off on the mechanical performance and the surface properties, respectively

2. Experimental

Basalt fibre samples BAS11U and BAS11S were manufactured using an industrial scale pilot plant. The nominal diameter of the basalt fibres is 15 µm and the nominal yarn count is 100 tex. The unsized state is achieved by sizing only with water during the drawing process. BAS11U indicates the unsized sample, whereas the sized specimen is designated BAS11S. The sizing is compatible to EP resin and the amount is < 0.5%.

Unsized as well as sized fibres were heat treated. The heat treatment was managed by fibre storage in an oven (L5/11 Nabatherm) for 0.5 h or 1.0 h at temperatures up to 600 °C in air as well as nitrogen atmosphere. In addition, initially sized fibres were re-sized after the 0.5 h heat treatment at a temperature of 600 °C. Re-sized means the single fibres were dipped in an aqueous silane-surfactant solution. 3- glycidyloxypropyl-trimethoxysilane (GLYMO supplied by Evonik) was used. In addition, a nonionic surfactant was added in order to improve the wetting behaviour. Thus, surface tension of 27 mN/m was determined by Wilhelmy plate technique.

Single fibre tensile tests were conducted under air-conditioning (temperature 23°C, rel. humidity 50%) by using a Favigraph semi-automatic testing device (Textechno, Mönchengladbach, Germany) equipped with a 1 N load cell. The cross head velocity was 25 mm/min and the gauge length was 50 mm. The fineness of each selected fibre was determined by using the vibroscope method in accordance with ASTM D 1577. 50 single fibres were tested to calculate the mean values and standard deviations. A value of 2.8 g/cm³ is used as density for the evaluation of the tensile tests.

XPS was performed on Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK). XPS spectra were acquired with a pass energy of 160 eV using a Mono-Al KαX-ray source (hv = 1486.6 eV).

Advancing contact angles were measured with a Krüss K14 tensiometer (Krüss GmbH, Germany) using the Wilhelmy technique. Different liquids (water, ethylene glycol, hexadecane) were used in order to determine the surface energy (γ) according Owens-Wendt-Rabel-Kaelble (OWRK) approach.

Quasi-static single fibre pull-out (SFPO) tests were carried out. Therefore, single fibre model composites made of epoxy resin RIMR135/RIMH137 (Momentive) and treated basalt fibres were prepared by self-made sample preparation equipment and 15-20 force-displacement curves for each sample obtained. A characteristic force-displacement curve is shown in figure 1.

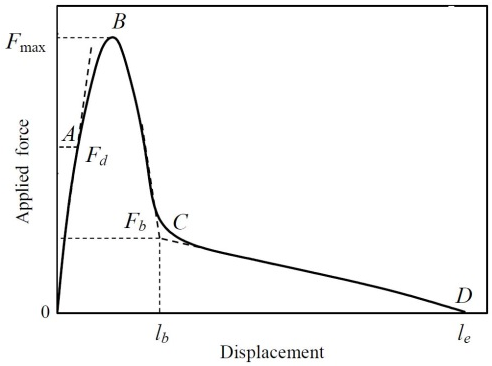


Figure 1. Typical force-displacement curve [6].

In order to get an interfacial shear stress value, the simple approach was applied using the maximum pull-out force, $F_{max.,}$ for the calculation of the apparent interfacial shear strength (apparent IFSS, τ_{app}): $\tau_{app} = F_{max} / (\pi d_f l_e)$, where d_f is the fibre diameter and l_e is the embedded fibre length [7].

3. Results

3.1. Strength-strain behaviour of BAS11 fibre after 5 h heat treatment at 500 °C in air

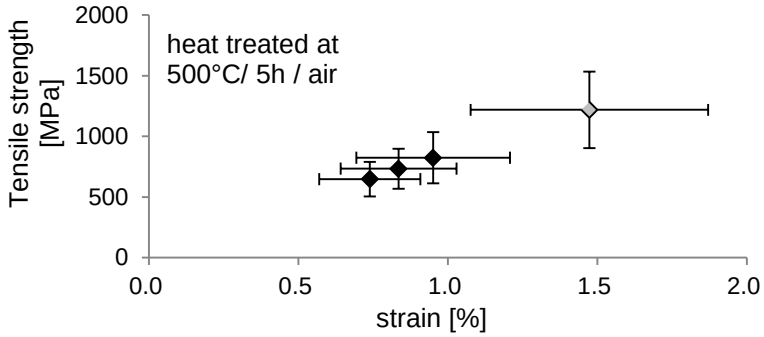


Figure 2. Tensile strength-strain behaviour of heat treated basalt fibre samples; (gray diamond indicates unsized BAS11 sample).

Figure 2 shows the strength-strain behaviour of different basalt fibre samples after a heat treatment at 500 °C for 5 h. The strength level of the unsized BAS11 fibre is advantageous compared to other investigated basalt fibre samples. As shown in [4] a moderate strength level remains after an enhanced heat treatment at a temperature of 500 °C or 600 °C. Thus, we continued experiments with this fibre type varying treatment time, temperatures and atmosphere. Figure 3 and 4 display the mechanical performance of sized BAS11 fibres. However, different samples were used in order to review the reproducibility.

3.2. Sizing burn-off

Figure 3a shows the single fibre tensile strength of sized fibre, BAS11S, after heat treatment at temperatures between 250 and 550 °C. A continuous strength loss with increasing temperatures is noticeable, especially if the fibres are treated at temperatures higher than 300 °C.

TGA/DTG-curve reveals mass loss at temperatures above 200 °C, preferable in the range of 200 to 370 °C in air as well as in nitrogen atmosphere. Thus, the sizing mostly seems to be removed up to a temperature of 450 °C. Considering the strength levels in Figure 3a, the strongest decrease in strength is obtained between 350 and 450 °C heat treatment.

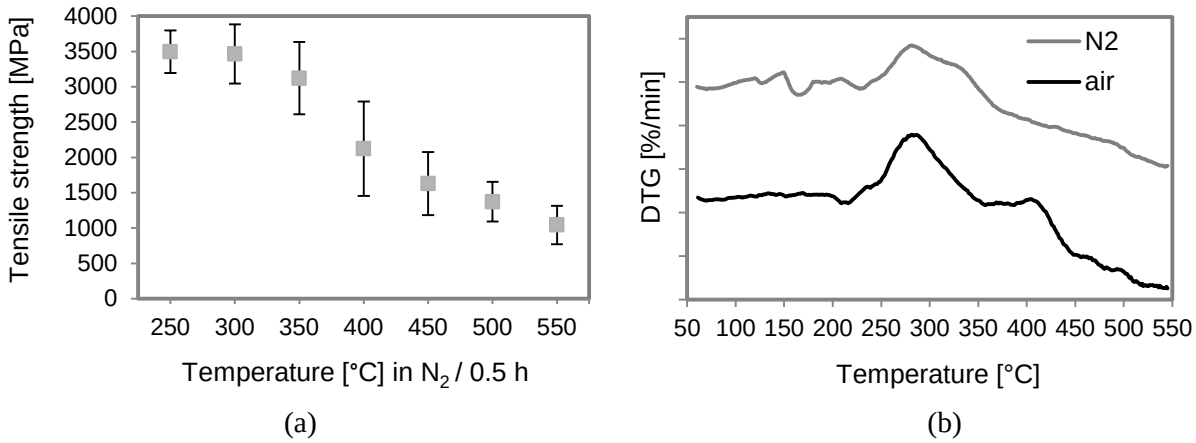


Figure 3. (a) Single fibre tensile strength of sized basalt fibres after 0.5 heat treatment in nitrogen atmosphere (b) TGA/DTG curves of sized basalt fibres.

3.3. Impact of temperature and atmosphere on the single fibre tensile strength

In spite of the advantageous chemical composition, the strength of BAS11S is decreased more than 55 % after treatment at elevated temperatures. Figure 4 compares the mechanical performance of BAS11U and BAS11S.

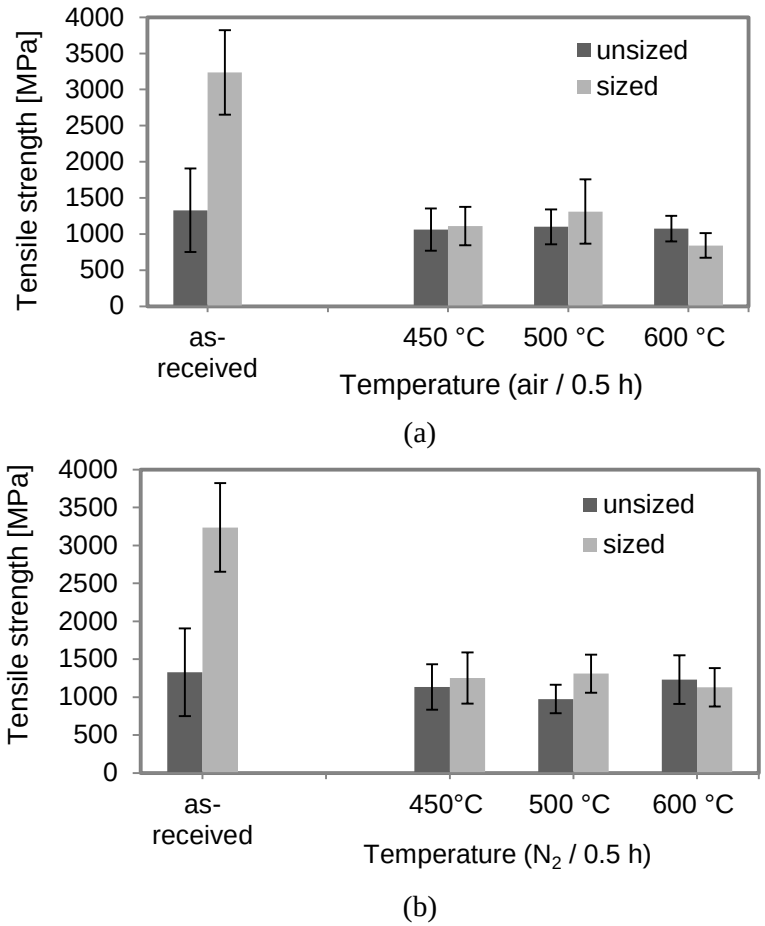
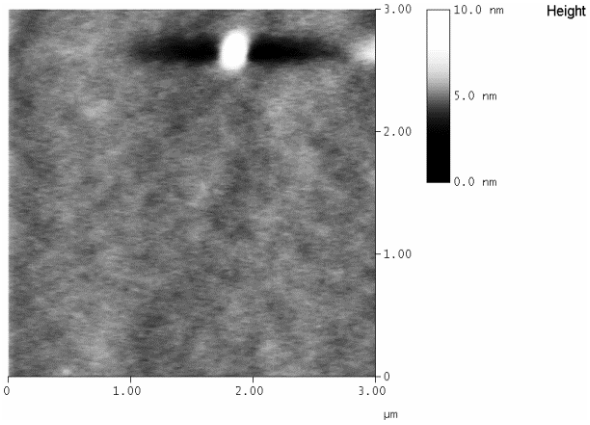


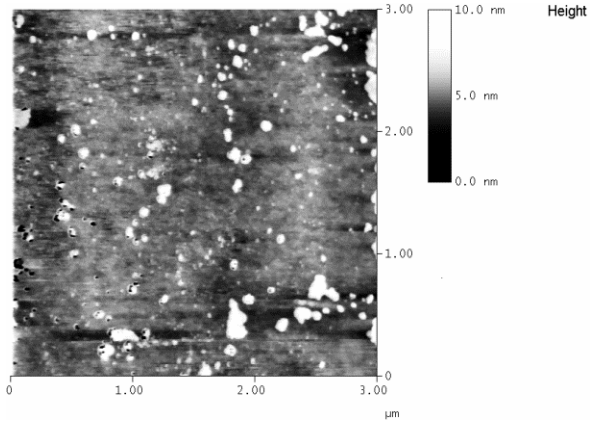
Figure 4. Single fibre tensile strength of unsized and sized basalt fibres after heat treatment in air (a) and in nitrogen atmosphere (b).

The unsized basalt fibre, BAS11U, shows a significantly reduced strength level compared to the sized as-received basalt fibre BAS11S. However, the strength of BAS11U remains independent of the treatment temperature. Heat treatments above 450 °C reduce the strength of BAS11S to the strength level of BAS11U. A significant impact by atmosphere was neither noticed for unsized nor for sized fibres. The results in figure 3a and 4b indicate that both samples taken from BAS11S show comparable strength values after 500-600 °C heat treatments. The remaining tensile strength is about 1000 -1400 MPa.

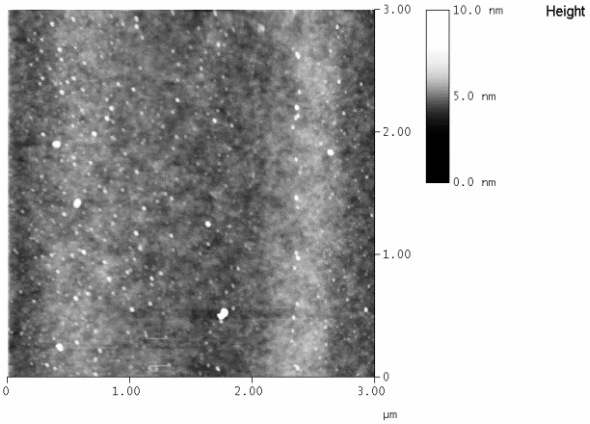
AFM topography images of the unsized basalt fibre BAS11U indicate a nanostructured surface (Figure 5d). The arithmetic surface roughness (R_a) is 0.37 nm. The surface of sized fibres is less rough due to the nanostructure is covered homogeneously by the sizing (Figure 5a). After 600 °C treatment the nanostructure is visible indicating a significant sizing removal.



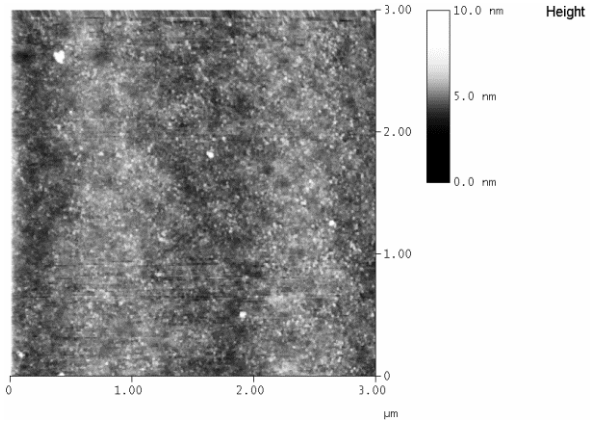
(a) BAS11S – as- received
R_a= 0.28nm



(b) BAS11S – heat treated 450 °C/0.5 h / ai
R_a = 0.56nm



(c) BAS11S – heat treated 600 °C/ 0.5 h/air
R_a=0.31nm



(d) unsized basalt fibre
R_a =0.37nm

Figure 5. Fibre surface and arithmetic surface roughness R_a of as-received (a), heat treated (b), (c) and unsized basalt fibres (d).

The chemical composition of the fibre surfaces was investigated by XPS. The amount of characteristic glass elements increased with the sizing removal. The surface composition of the unsized basalt fibre is shown as reference in table 1. In our previous work, we could show that the chemical composition of basalt fibres is changed after a heat treatment of 600 °C for 5 h [4]. Thus, we also analyzed the surface compositions of unsized basalt fibres after several heat treatments. The ratio

of [C] / [Si] indicates high contaminations on the heat treated surfaces. However, an increase of Ca within the surface layer is already noticeable after 0.5 h heat treatment at a temperature of 600 °C (table 1).

Table 2 shows the results of dynamic contact angle measurements and calculated surface energies of as-received and heat treated basalt fibres. Heat treatment in air changes the wettability. The measurement in water leads to a reduced contact angle. Furthermore, the polar-component of surface energy increased slightly.

Interfacial strength parameters of the BAS11S – as-received fibre and re-sized basalt fibres embedded in epoxy resin were determined by quasi-static single fibre pull-out tests. Re-sized fibres show a slightly increased adhesion strength compared to the sized as-received sample. The apparent IFSS were calculated for sized and re-sized fibres for sized fibres as τ_{app} = 35±4 MPa and for re-sized fibres τ_{app} (re-sized) = 45±8 MPa. Furthermore, we observed a decreased post-debonding friction in the case of the re-sized fibres.

Table 1. Surface composition in at %.

	Al2p	**Mg2s**	**Si2p**	**C1s**	**K2p**	**Ca2p**	**O1s**	**Fe2p**	**Na1s**	**Others**	**[C]/[Si]**
BAS11S			0.5	78.9			20.6				156
BAS11S 600°C/0.5h air	3.5	1.0	11.7	40.1		4.0	37.8	0.8	0.4		3.4
BAS11U	4.5	1.3	13.6	29.6	0.4	2.1	46.3	0.8	1.3	0.2	2.2
BAS11U 600°C/0.5h air	2.2	0.8	7.6	42.8		6.8	38.6	0.3	0.6	0.5	5.7
BAS11U 600°C/1.0h air	2.8	0.6	10.2	40.6		6.0	37.2	0.3	0.7	1.6	4.0
BAS11U 600°C/0.5h N2	3.0	0.8	9.0	37.1		7.9	40.3	0.8	0.4	0.6	4.1

Table 2. Contact angles and surface energies of basalt fibres.

	Contact angle [°] Advancing			**Surface energy [mN/m]**		
	Water	**Ethylene glycol**	**Hexadecane**	**total γ**	**polar γ^p**	**disperse γ^d**
BAS11U	65±6					
BAS11S as- received	71±5	31±3	31±4	**38**	13	25
BAS11S 450 °C/0.5/air	75±4					
BAS11S 600 °C/0.5/air	55±7	52±5	27±3	**42**	22	20
BAS11S - 600 °C/0.5/N2	73±4					

4. Discussion and Conclusions

Considering sustainable applications of basalt fibres, there is a lack of knowledge about the performance of heat treated basalt fibres. Thus, we continued heat treatment experiments and carried out first re-sizing trials.

The results substantiate that the strength level of heat treated basalt fibres is dropped significantly. However, the chemical composition as well as the sizing is able to influence the performance. We could show that the sizing burn-off led to a significant strength loss, but the maximum decrease of tensile strength took place at temperatures above 350 °C. However, TGA results indicated that until a temperature of 350 °C a high amount of sizing was already removed. The strength level of the as-received sized basalt fibre, BAS11S, remained almost the same after 0.5 h heat treatments at moderate temperatures. This confirms findings by Jenkins et al. [1] about a 300 °C threshold. Due to the high standard deviation of single fibre tensile tests we could not clearly verify an influence of the atmosphere on the fibre strengths. Here, further experiments and data treatment is necessary.

The AFM investigations of heat treated BAS11S indicated that the nanostructure of basalt fibres is still not unveiled after the heat treatment at 450 °C. Sizing remnants lead to an increase of surface roughness. The increase of surface roughness and the partial exposure of surface flaws accompanied by the possibility of superelevation of flaw depths both are discussable items for the drastic decrease in fibre strength after heat treatments above 300 °C. Interestingly, the strength loss after heat treatments above 450 °C is less significant neither for unsized nor sized basalt fibres.

The contact angle measurements indicate that the wetting properties are affected by the heat treatments. However, here also further investigations are necessary. Especially, XPS should be used to separate the influences of changed surface roughness and changed surface composition due to thermal induced cation diffusion.

The re-sizing experiments seem to be encouraging, but need to be extended and combined with tensile tests. The impact of the surfactant on the observed decrease in post-debonding friction cannot be excluded.

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