CHEMICAL ENGINEERING TRANSACTIONS
VOL. 32, 2013
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791
DOI: 10.3303/CET1332273

Matrix/Fibre Boundary Layer in Fibre Reinforced Plastics: Characterization of the Adhesion

Anna-Katharina Saelhoff * , Chirstian Wilms, Moritz Warnecke, Davide Pico, Miron Sernecki, Gunnar Seide, Thomas Gries

Institut fuer Textiltechnik der RWTH Aachen University, Otto-Blumenthal-Straße 1, 52074 Aachen, Germany
Anna-Katharina.Saelhoff@ita.rwth-aachen.de

In order to successfully use the strength of carbon fibres in composite applications, the fibres must be embedded into matrix materials. Usually, thermoplastic or duroplastic polymers are used to hold the flexible fibres in a form in which they can be used, to guide mechanical stress into the fibres and to protect the fibres from the distortive influences of their environment, such as friction or misaligning stress. For the strength of the composite material, the fibre-matrix-adhesion is the crucial parameter to characterize the composite's quality and strength. Therefore, this paper shall present the need and the possibilities for different testing methods concerning fibre-matrix-adhesion.

1. Introduction: The need for a standard method to compare surface modification and the influence of sizing on carbon-fibre-matrix-adhesion

The strength of carbon fibre reinforced plastics is manly influenced by three factors: the carbon fibre's properties, the properties of the polymer matrix and the properties of the interface between the carbon fibre and the polymer matrix.
The first two factors can be tested and modified individually, while the properties of the interface between fibre and matrix are depending on the interaction between both systems.
The most relevant property of this interlayer between fibre and matrix is the so-called fibre-matrix-adhesion. A parameter which allows the quantification of the fibre-matrix-adhesion is the interlaminar shear strength. The interlaminar shear strength is the maximum force which can be transferred between fibre and matrix, addressing the fibre's direction. As this force is referring to the fibre's surface, the interlaminar shear strength is a shearing stress with the unit [N/mm^2].
Small values of the interlaminar shear strength signify that, when the fibre reinforced plastic is set under stress, filaments will debond from the matrix polymer and therefore cannot participate anymore in the force transmission process.
In the design and optimization of fibre reinforced plastics, the adaptation of the surface treatment processes in order to increase fibre-matrix-adhesion is crucial. The value for the interlaminar shear strength is important for having a benchmark parameter for evaluating improvements in surface activation processes.
After activation of the fibres' surface, a sizing is applied to the surface. The sizing provides protection to the fibres, especially when the fibres are further processed into textile structures on textile machines such as weaving looms, braiding machines etc. (Morgan, 2005). Ideally, the sizing also increases the interlaminar shear strength, but this effect is rather negligible compared to the effect of the surfaces activation process (Rensch, 1990).
Without any surface treatment, the carbon fibre surface is chemically nearly inert and the fibre-matrix-adhesion is poor (Geigl, 1979). Therefore, different methods for surface activation of carbon fibres have been developed. They can be categorized in two main groups: the oxidative and non-oxidative surface treatment (Wegener, 2011). As examples for non-oxidative surface treatment, surface whikerization or plasma deposition may be seen.

Please cite this article as: Saelhoff A.K., Wilms C., Warnecke M., Pico D., Sernecki M., Seide G., Gries T., 2013, Matrix/fiber boundary layer in fibre reinforced plastics: characterization of the adhesion, Chemical Engineering Transactions, 32, 1633-1638 DOI: 10.3303/CET1332273

In industrial processes where the possibility for in-line-activation is important for the time- and cost-efficient process, an electrolytic activation of the carbon fibre's surface is the most commonly used activation (He et al., 2010). The fibre is guided into a bath of electrolyte, while a tension is applied to the fibre. The fibre acts as a positively charged anode, while a negatively charged cathode is inserted into the electrolyte bath. In industrial processes, the electrolyte ammonium hydrogen carbonate (NH_4HCO_3) is the most commonly used, simply because after oxidation it is easy to wash away.

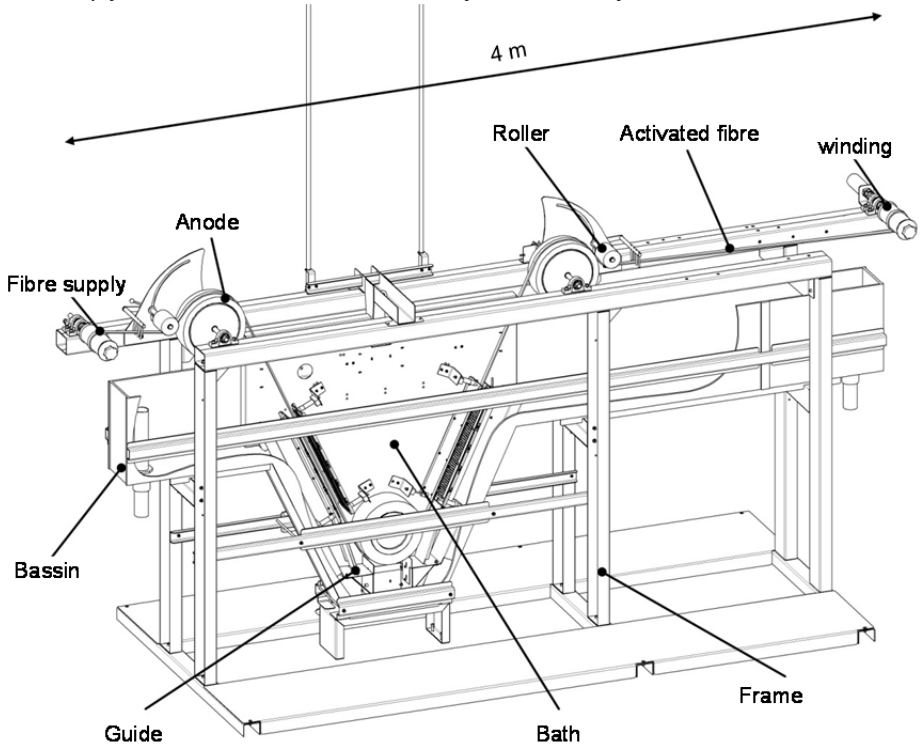

Figure 1: Surface activation for carbon fibres in laboratory scale.

The increase of the interlaminar shear strength through electrolytic activation is reached by a combination of different effects: functional oxygen groups will be implemented on the carbon fibres's surface. These functional oxygen groups can be seen as adhesion promoter between fire surface and matrix (Liubchev et al., 1992). According to the electrolyte either sour or basic oxygen groups such as COOH, COH, OH or C=O will be implemented (Jaeger and Hauke, 2010). Additionally, this surface activation increases already existing impurities such as corrugations or holes in the fibres' surface. This increases the interlaminar shear strength by an enhanced form fit between fibre and matrix (Park et al., 2010).
Anyway, even the conventionally used industrial process of surface activation of carbon fibres by electrolysis (see Figure 1) allows the variation of different parameters, such as amperage, concentration of the electrolyte and the duration of the treatment. Detailed investigation of this surface treatment results are necessary as commercial manufacturers of carbon fibres do not publish process parameters in order to protect the uniqueness of their products. Additionally, the results of all investigation on alternative ways to activate carbon fibre surfaces have to be compared and evaluated by a standard method.
Therefore, the results of examining the ILSS have to be reproducible and conclusion-drawing to the specific processes taking place at the interface between fibre and matrix.

2. Testing methods for determining the ILSS

In order to determine the interlaminar shear strength between fibre and matrix, different testing methods have been developed. In real samples, the interlaminar shear stress always occurs in a combination with other stresses, such as tensile stress, pressure and torsion. Nevertheless, the capacitance of fibre reinforced plastics depends significantly on the interlaminar shear strength.
In general, testing methods for the determination of the ILSS can be divided into two groups: direct and indirect testing methods (see Figure 2).

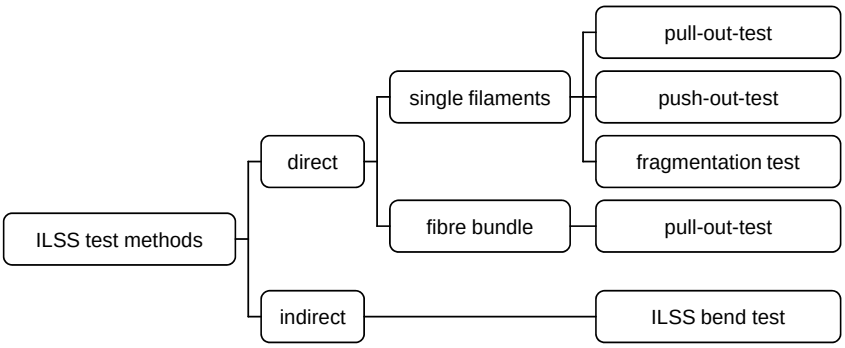

Figure 2: Overview about different test methods for the interlaminar shear strength (ILSS).

Indirect testing has certain drawbacks such as uncertainties in the final, calculated values. In contrast to this, during the direct testings, the test specimens are stressed in a way that the unidirectional stress allows a direct calculation of the ILSS. Still, local deviations from this unidirectional stress may occur also within the direct testing. Furthermore, fibre bundle pull-out-tests shall not be presented here as the use of more than one filament complicates the detailed investigation of processes which characterize the interface between the modified fibre surface and the polymer matrix.
For the direct testing of single filaments as it is covered in this paper, the pull-out-test, the push-out-test and the fragmentation test are available. With these methods, the interlaminar shear strength can be calculated directly by applying the tensile force which pulls the fibre to the cylindric interface between fibre and matrix:

$$\tau = \frac{F}{A} = \frac{F}{\pi \times d \times l} \tag{1}$$

In this formula τ represents the ILSS, F is the acting force and A is the contact area between fibre and matrix. This area can also be expressed by the diameter d and length l of the fibre. This is also demonstrated in Figure 3.
In a pull-out-test one single filament is embedded into a thin matrix block. During the examination, the fibre is pulled out of the resin block with a continuous force F until the fibre finally separates from the matrix. The interlaminar shear stress is calculated with the maximum force which is measured throughout the experiment (Bannister et al., 1995). By calculating the ILSS in this way, the assumption is taken that through the pullout test it come to shear stress only in the direction of the fibre. Closer investigations have shown that, at the interlayer of fibre and matrix, it also comes to normal stress.
A testing method where the ILSS can be calculated in the same way as in the single filament pull-out-test is the single filament push-out-test (Chandra and Ghonem, 2001). The main disadvantage is that the exact processes concerning the stress at the interlayer between fibre and matrix are not yet clear. As in the pull-out-test, the exact reason for the breakdown cannot be found out.

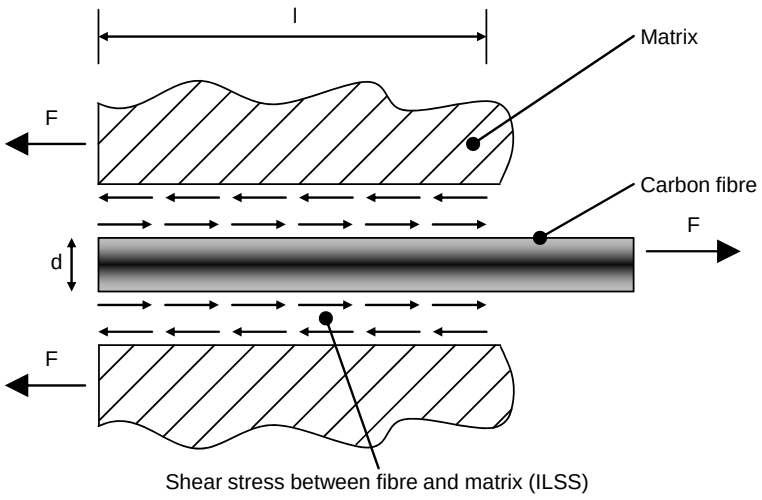

Figure 3: Interlaminar shear stress (ILSS) between fibre and matrix.

As a third and very suitable method for evaluating fibre-matrix-adhesion is the so-called single filament fragmentation test. A single filament is completely embedded into a long test specimen consisting of matrix resin. The specimen, well polished, is put under a microscope while the specimen is stretched. Because of the lengthening of the specimen, the incorporated filament will also be lengthened. Therefore, in the interface between matrix material and fibre surface, a constant shear stress is occurring. The specimen is stretched with a constant rate of elongation. Because of the increasing stretching, the tension in the filament is also increasing until it comes to the fraction of the filament (see Figure 4).
The carbon fibre is not necessarily breaking at the point of the highest stress but on parts of the fibre where there was a defect already before the fragmentation test. These defects will be statistically distributed on the fibre length. At the parts where the fibre cracked, the tension decreases down to zero at the fragmentation's ends.
Because of the increasing stretching, the number of fragmentations in the fibre increases until the saturation is reached. First fragmentations occur at a stretching of 2 % which is the region of fracture strain of carbon fibres, a steep increase follows and at about 3-4 % of the fracture strain, the number of fragmentations remains constant.
The mechanism behind this testing technology is that the shear stresses induce tensile stresses in the carbon fibre. If the tensile stress exceeds the strength of the carbon fibre, the fibre breaks into two parts. Once the fibre parts are too short that the shear stresses cannot induce high enough tensile stress into the fibre, it will not break again. The interlaminar shear strength can then be calculated using the following equation:

$$\tau = \frac{\sigma_z \times d}{2 \times l_c} \tag{2}$$

τ is again the ILSS, σ_z is the strength of the carbon fibre filament, as it was measured earlier, e. g. with a Favimat testing unit. d is, as in equation 1, the diameter of the fibre and l_c is the critical length of the broken fibre pieces. L can be derived from the mean length of the fibre pieces by multiplying with 4/3. This formula is derived in (Feih et al., 2004).

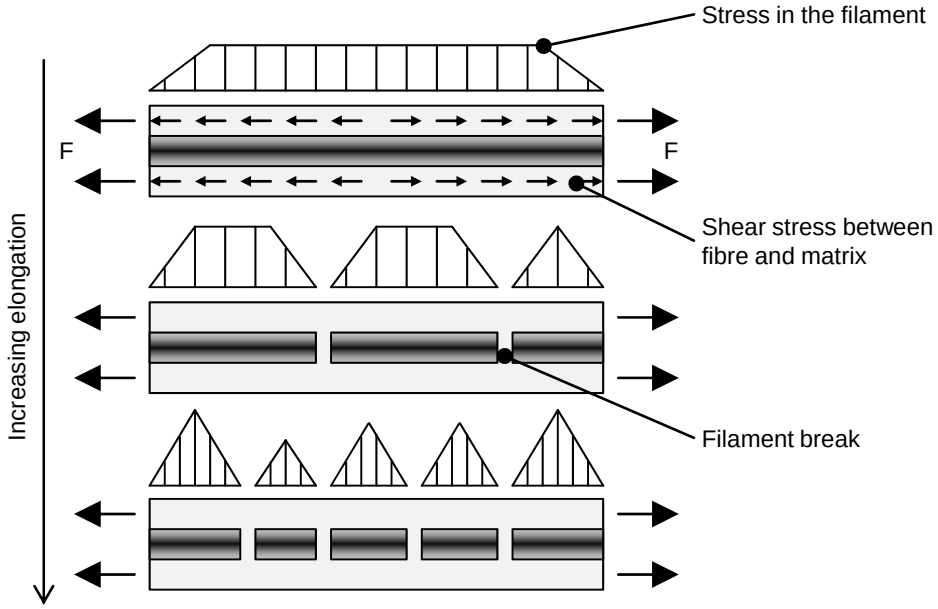

Figure 4: Development of the tension during the single filament fragmentation test.

3. Experimental results

To demonstrate that the fragmentation test method can prove the differences in ILSS of differently treated carbon fibres, the measurement results of commercially activated fibres with sizing are compared to carbon fibres which came directly out of the carbonisation oven without any further treatment.

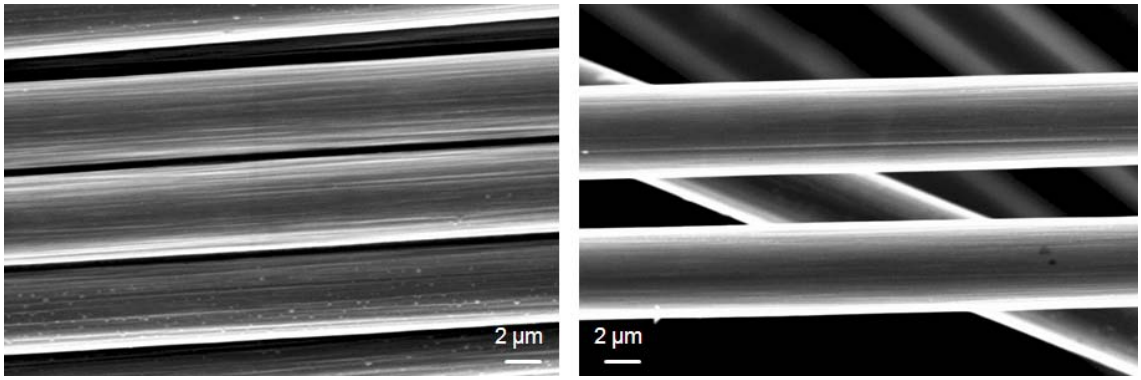

Figure 5: SEM images of untreated carbon fibres (left) and carbon fibres after surface activation and the application of sizing (right). Both images were taken at the accelerating voltage U=15 kV.

Already the scanning electron microscope (SEM) pictures taken from theses two fibre samples exhibit a clear difference in the surface quality (see Figure 5): the left image was taken on the fibre which received no further treatment, while the image on the right of Figure 5 was taken on the commercially treated carbon fibres with sizing applied. The difference which can be seen in the two images fits well to the observations already described in literature: the corrugations visible in the SEM picture of the non-treated fibres can be dedicated to the precursor spinning process and are conserved throughout the whole thermal transformation process from the polyacrylnitrile (PAN) precursor to the final carbon fibre. It is most likely that also the commercially treated fibre exhibited these corrugations, but they were smoothened by the chemical finishing treatment (Rensch, 1990).

Out of both fibre bundles single filaments are taken. The single filaments are embedded into 40 mm long form which is filled with the epoxy-based resin EPL-285, commercially available from Bacuplast Faserverbundtechnik GmbH, Remscheid, Germany. After the hardening of the resin, the specimens are polished so that the fibre is clearly visible under an optical microscope (enlargement factor 25). In this way, a good observation of the filament fragmentation is guaranteed.

The investigated specimens are mounted into an apparatus which was specially constructed for this purpose. The apparatus allows the application and measurement of tensile stress. The whole construction is implemented under an optical microscope. More than 20 microscope pictures throughout the whole specimen length are taken for each stress applied. Stepwise, the stress increases until the first filament fragmentation occurs. A second series of 20 pictures is taken for further stress increase and further fragmentations, and so on for the following stress values applied. An average of 15 different stresses are applied to the specimens.

The single microscope images for each stress applied are digitally stitched together. A macro, written for the open source program ImageJ, evaluates the sample's lengthening and the number of fragmentations.

Under consideration of the tensile strength of each fibre type and taking into account the Weibull statistic spread of these values, the interlaminar shear strength of the fibres investigated can be calculated according to equation (2).

Figure 6 shows the results of four measurements which were taken on the un-treated and commercially treated fibres. Even though the sample number investigated is not sufficient for statistical evidence, the clear tendency of values for the ILSS (a difference of about 50 %) shows that the interlaminar shear strength increases when a carbon fibre's surface is activated before embedding it into a matrix resin. As this result is in accordance with the expectation, it can be considered as a validation for the suitability of the single filament fragmentation test to investigate the interlaminar shear strength.

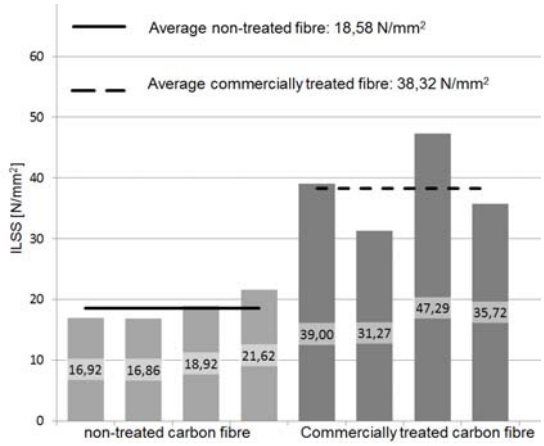

Figure 6: Results of the ILSS measurements on non-treated and commercially treated carbon fibres, carried out by using the single filament fragmentation test.

4. Conclusion

In this paper, the need for quantitatively investigating the quality of fibre-matrix-adhesion was illustrated and different methods to determine the interlaminar shear strength ILSS were presented. The single filament fragmentation test is considered to be the most suitable method in order to investigate processes at the fibre-matrix-interface as the reasons for breakdown can be understood by applying this test. First tests for trying out this method could show that the ILSS of carbon fibres with surfaces which were not activated show an approx. 50 % lower ILSS compared to fibres after surface activation and sizing application. By the first reasonable results, the single filament fragmentation test can be considered as a suitable method. Moreover, it cannot only be applied to investigate fibre-matrix-adhesion using carbon fibres, but also the fibre-matrix-adhesion of glass fibre composites.

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