A NEW TESTING SYSTEM TO DETERMINE THE FIBER-MATRIX ADHESION STRENGTH BY MEANS OF PULL-OUT TESTS

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ABSTRACT

In this article we discuss in detail the measurement of the fiber-matrix adhesion strength by means of a new testing system which has been developed as collaboration between the Leibniz-Institut für Polymerforschung (IPF) in Dresden, the Faserinstitut Bremen (FIBRE) and Textechno. The system determines the adhesion between fiber and matrix in terms of the local interfacial shear strength, the interfacial toughness and further parameters through a reproducible single-fiber pull-out test. In addition, an optical measurement of the contact angle between fiber and matrix is integrated in the system. The technique is suited for all kinds of fibers as well as all kind of thermoset and thermoplastic matrices with curing and melting temperatures up to 400°C. Our discussion includes hands-on examples on the application of the testing system for various fiber-matrix combinations.

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1. CHARACTERIZATION OF THE FIBER-MATRIX ADHESION

The mechanical properties of a fiber reinforced material, e.g. toughness and strength, are significantly determined by the interfacial properties between reinforcement fibers and matrix material. This is because the bonding between the two components is usually the first one to fail in a stress induced breakage of a composite part. Optimization of the fiber-matrix adhesion strength hence plays a central role in the development of new fibers, their sizing as well as matrix materials where it must be well adjusted to lead to an enhanced composite performance [1]. Beyond R&D purposes, the interfacial bonding is also a key quality parameter that needs to be monitored as production control.

2. MACROMECHANICAL VS. MICROMECHANICAL CHARACTERIZATION OF THE FIBER-MATRIX ADHESION

Macro- and micromechanical test methods have been employed to characterize the fiber-matrix adhesion. For macromechanical testing, most commonly composites with unidirectional aligned fibers are manufactured to perform a tensile test perpendicular to the fiber orientation (transverse tensile test) or an ILSS (interlaminar shear strength) test is performed. However, the maximum stress found in macroscopic tests is not only depending on the fiber-matrix adhesion, but also

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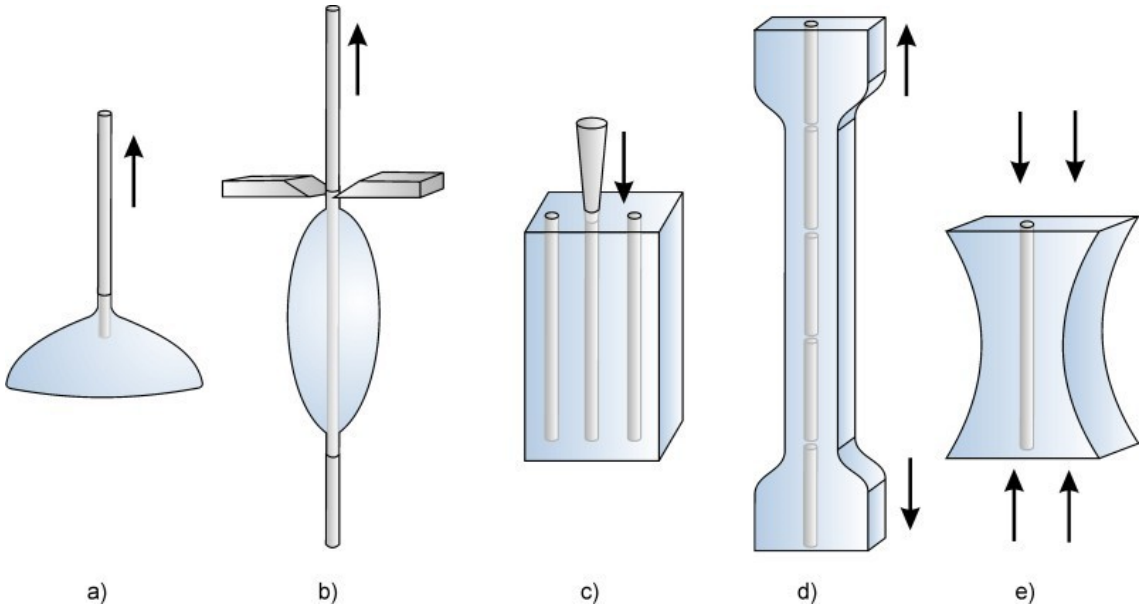

Figure 1. Micromechanical tests can be divided into two groups: 1) tests where an external load is applied directly to the fiber: pull-out (a), microbond (b) and push-out (c); and 2) tests where the load is applied to the matrix: fragmentation test (d) and Broutman test (e) [6].

influenced by additional factors: for instance the fiber content, orientation, length, diameter and fiber distribution homogeneity, the pore voids of the test specimens, and the mechanical properties of the fiber and the matrix. To achieve repeatable results for the fiber-matrix adhesion through macromechanical tests, it is hence necessary to keep tight control of the manufacturing process of the specimen, making it difficult to compare the results across laboratories.

In the case of micromechanical testing techniques, a fiber-matrix compound is usually created using just a single reinforcement fiber. Compared to the macromechanical testing, the factors listed above that influence the test result and originate from the manufacturing of the test specimen are excluded. Furthermore, suitable analysis techniques performed on the micromechanical test data allow to receive a direct measure of the adhesion strength alone.

3. MICROMECHANICAL TESTING TECHNIQUES

Various micromechanical testing techniques (c.f. Fig. 1) to characterize the fiber-matrix adhesion strength are discussed in the literature. An detailed overview of the different approaches is given in Ref. [2].

Among those techniques, the microbond and the pull-out test are probably most widely used [3] due to their experimental simplicity, well-defined test geometry and high reproducibility of experimental results. The fiber-matrix adhesion can relatively easily be characterized by these testing methods. Beyond the fiber-matrix adhesion strength, the initially measured data is influenced by the diameter and mechanical properties of the fiber and by the mechanical properties of the matrix. The mechanical properties of the matrix as well as of the fiber are determined separately and their influence can be removed from the data using appropriate analysis techniques as for instance demonstrated for the pull-out test in Refs. [4] and [5].

Figure 2. The FIMABOND embedding station of the FIMATEST system. The device is used to prepare the single-fiber composite samples for subsequent pull-out testing.

Finally, the pull-out test is distinguished from the other micromechanical test methods in the advantageous fact that it is applicable to reinforcement fibers which are relatively stiff but also to relatively soft fibers (e.g. Polypropylene fibers). This wide range of fibers can be tested in combination with ductile and brittle matrices that can be both thermoplastic and thermoset.

4. THE MICROMECHANICAL SINGLE-FIBER PULL-OUT TEST

When utilizing the pull-out test, the goal is to determine the interfacial interaction between fibers and matrices. Various test procedures to prepare the samples and perform the pull-out test have been developed by research institutes. However, since those implementations are not standardized, the measured values turn out to be hard to compare [6]. For the following discussion, we employ the FIMATEST system [7] that has been developed as a collaboration between Textechno, the Leibniz-Institut für Polymerforschung (IPF) and the Faserinstitut Bremen (FIBRE). At the time being, the FIMATEST is the only commercially available system to characterize the fiber-matrix adhesion strength by means of a pull-out test.

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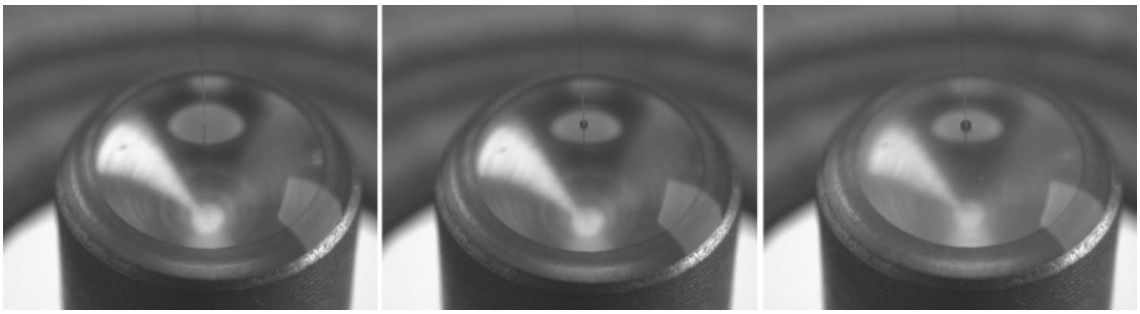

Figure 3. Process of embedding a glass fiber into epoxy resin with the FIMABOND. Left: fiber approaching the matrix. Center: contact between the fiber and the matrix surface and embedding. Right: curing of the epoxy resin.

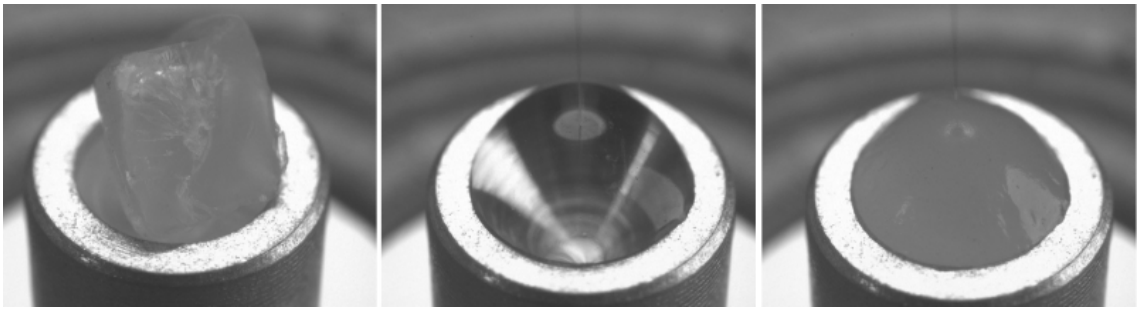

Figure 4. Process of embedding a glass fiber into PA 6. Left: flushing sample with inert gas. Center: melting of the matrix material and contact between the fiber and the matrix surface and embedding. Right: cooling and consolidation of the sample.

4.1 Sample Preparation for the Pull-Out Test

Fig. 2 shows the FIMABOND device of the FIMATEST system that is used to prepare the single-fiber composite samples. This is a partially automated embedding station, suitable for all kind of matrices such as thermoset, thermoplastic and inorganic matrices as well as all types of fibers. The embedding of the fiber into the matrix is the most critical point to gain reproducible results through the pull-out test. The fiber must be embedded exactly in the center of the matrix droplet perpendicular to the surface of the matrix to avoid additional undesired shear forces during the measurement.

Fig. 3 demonstrates an actual embedding process as performed with the system. First, the fiber is approached to the top of the matrix (Fig. 3, left) until contact is made. For typical fiber-epoxy systems a concave meniscus forms around the fiber (Fig. 3, center). The fiber is embedded to predefined depth into the matrix where typical embedding lengths range up to a few hundred microns. The embedding length is determined by the force that is necessary to fully debond the fiber from the matrix (F_{max} in Fig. 8) which should not exceed the tensile strength of the fiber, leading to fiber failure. Finally, the matrix is cured respectively consolidated (Fig. 3, right).

To process thermoplastics, the sample chamber can be flushed with inert gas, e.g. argon or nitrogen (Fig.4). After preparing the specimens, the sample is ready to pull out the fiber and to record the applied forces as a function of the displacement.

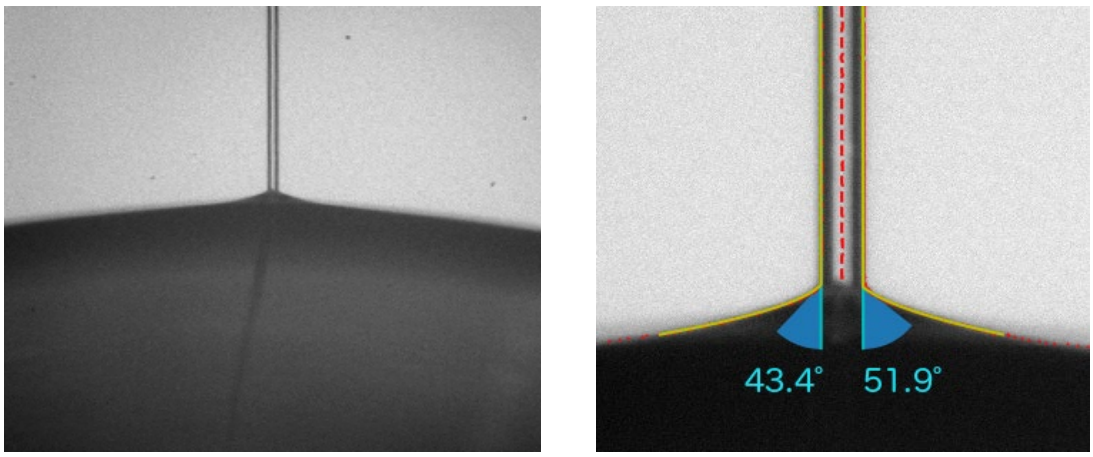

Figure 5. Observation of the meniscus forming between fiber and matrix during the embedding process as seen by the FIMABOND device – here, between a glass fiber and an epoxy resin. Left: the full image. Right: the automatic evaluation of the contact angle on both sides of the fiber.

Figure 6. Left: The single fiber linear-density and tensile tester FAVIMAT+. Right: The clamping mechanism to be installed in FAVIMAT+ to perform the pull-out test.

4.2 Contact Angle Measurement During Sample Preparation

The images shown in Figs. 3 and 4 are recorded during the embedding process with a camera under 45° with respect to the fiber axis and are used to tightly control the fiber placement. An additional camera system is monitoring the contact region under 90° angle to measure the contact angle between the matrix and the fiber. In this way, wettability and impregnation are additional topics that are addressed with the FIMATEST system. Notably, the setup enables the observation of contact angles under elevated temperatures and thus also on thermoplastic matrices up to 400 °C. A systematic study of contact angle information in combination with interfacial bonding properties

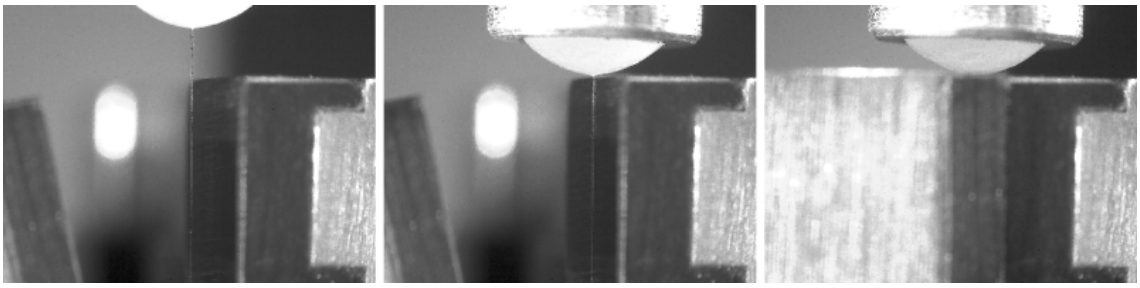

Figure 7. Process of adjusting the single-fiber composite sample in the clamping mechanism. The fiber is aligned parallel and at minimal distance to a fixed yaw. The opponent yaw closes and grips the fiber close to the matrix.

we leave to future studies. However, an exemplary meniscus recorded under 90° is shown in Fig. 5 (left) and the corresponding evaluation of the contact angles in Fig. 5 (right).

4.3 Performing the Pull-Out Test

We use the miniature tensile tester FAVIMAT+ [10] to perform the pull-out test (Fig. 6, left). This device is dedicated to single-fiber testing techniques and equipped with a high-resolution load cell (1 µN at 200 cN full range) and a travel resolution of 0.1 µm. The circumference of the embedded fiber must be known to fully evaluate the measured data. The circumference is determined – before embedding and pull-out test – using the vibration method (c.f. e.g. ASTM D 1577 or ISO 1973) which is integrated in the device as well. A special clamping mechanism (Fig. 6, right) is installed in FAVIMAT+ to hold the prepared single-fiber composite samples.
For the pull-out test, the sample is put upside-down in the direct clamping system of the pull-out device. To ensure a precise alignment of the fiber to the jaw faces and the matrix surface, a microscopic camera is integrated in the clamping mechanism. Using a lateral and a vertical movement of the clamps, the fiber is adjusted parallel to the yaws and with minimal distance between the jaws and the matrix (Fig. 7).

4.4 Evaluation of the Pull-Out Test Data

Fig. 8 shows a typical force displacement curve recorded during the pull-out test. The forces are applied to the fiber. At a critical force value, a crack is initiated where the fiber enters the matrix. This force in marked as F_d (debonding force) in Fig. 8 and is of special interest. From this point on the force continues to increase but at a smaller slope due to a superposition with additional frictional forces occurring between the debonded part of the fiber and the matrix. Here, the crack still propagates along the interface. At the maximum force F_{max} the fiber completely debonds from the matrix and the force drops rapidly to the remaining frictional force F_b followed by instable crack propagation. Since the embedded fiber is now fully debonded, the remaining force is only the friction between the fiber and the matrix. The actual embedding depth l_e is reached, when the applied force drops to zero – the fiber has been completely pulled out of the matrix.
After recording the force-displacement curve a next step is to evaluate it according to the scheme shown in Fig. 8, yielding the maximum (F_{max}), minimum (F_b) and debonding (F_d) force as well as the actual embedding length (l_e). Based on these measured values and the individual fiber diameters d_f, the following data reduction is used according to different methods that are extensively discussed in literature [4], [5], [8]. This is done automatically by the instrument

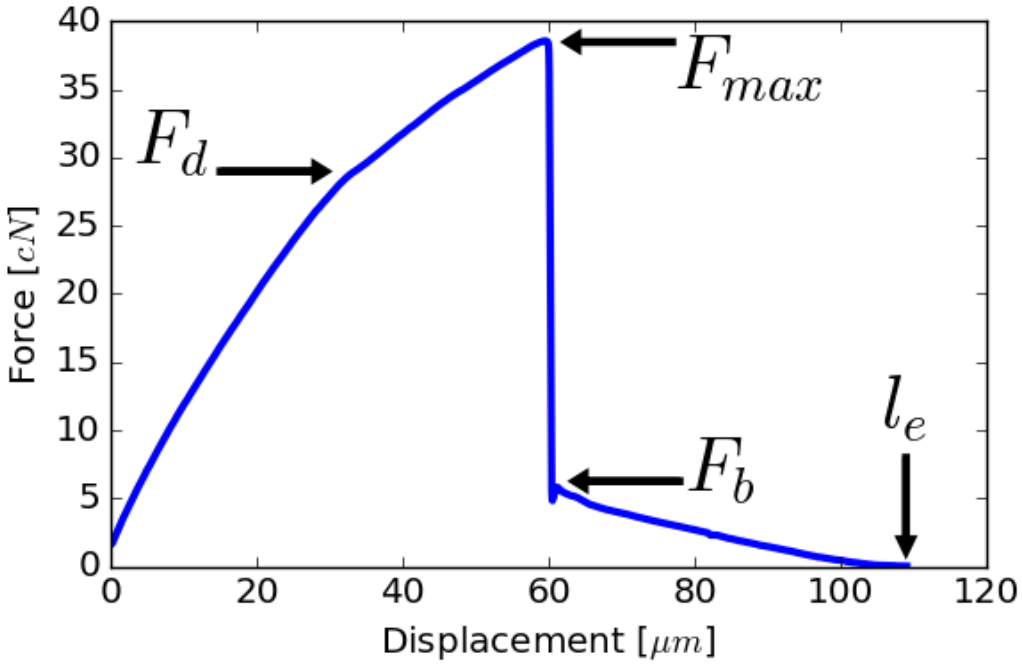

Figure 8. Force-displacement curve of a glass fiber in an epoxy resin.

software.

The apparent interfacial shear strength (τ_{app}) is the maximum force normalized on the wetted area of the fiber (Eq. 1). It is sufficient for a qualitative estimation, if different types of fiber-matrix adhesion strength are to be compared:

$$\boldsymbol{\tau_{app}} = \frac{\mathbf{F_{max}}}{\boldsymbol{\pi \cdot d_f \cdot l_e}} \quad . \tag{1}$$

Based on the strain-based method, the local interfacial shear strength (τ_d) is calculated (Eq. 2). Compared to the apparent interfacial shear strength, this excludes the influence of the friction between the fiber and the matrix and considers the specific geometry of the sample:

$$\boldsymbol{\tau_d} = \frac{\mathbf{F_d \cdot \beta}}{\mathbf{2 \cdot \pi \cdot r_f}} \cdot \mathbf{coth}(\boldsymbol{\beta \cdot l_e}) + \boldsymbol{\tau_T} \cdot \mathbf{tanh}\left(\frac{\boldsymbol{\beta \cdot l_e}}{\mathbf{2}}\right) \quad , \tag{2}$$

with β, the shear lag parameter as defined in Ref. [9] and τ_T, the thermal stress. The critical interfacial energy release rate (G_{ic}) – based on the energy-based method – allows to consider the bonding on its own as well. The energy release rate is calculated as a function of the crack length and takes the deformation of fiber and matrix during the pull-out into account (Eq. 3):

$$\begin{aligned} \boldsymbol{G_{ic}} = \frac{\mathbf{r_f}}{\mathbf{2}} \Bigg\{ & \boldsymbol{C_{33s} \cdot \bar{\sigma}^2} + \mathbf{2} \cdot \boldsymbol{D_{3s} \cdot \bar{\sigma} \cdot \Delta T} + \left(\frac{\boldsymbol{D_3}^2}{\boldsymbol{C_{33}}} + \frac{\boldsymbol{V_m \cdot (\alpha_T - \alpha_m)^2}}{\boldsymbol{V_f \cdot A_0}} \right) \cdot \boldsymbol{\Delta T^2} + \\ & \left[\frac{\boldsymbol{\sigma_0}}{\mathbf{2}} \cdot \left(\frac{\mathbf{1}}{\boldsymbol{E_A}} - \frac{\mathbf{1}}{\boldsymbol{E_m}} \right) + \boldsymbol{D_{3s} \cdot \Delta T} \right] \cdot \left[\left(\boldsymbol{\bar{\sigma}} + \frac{\boldsymbol{D_3 \cdot \Delta T}}{\boldsymbol{C_{33}}} \right) \cdot \boldsymbol{C_T'(a)} - \boldsymbol{k \cdot C_T(a)} \right] \Bigg\} \quad . \end{aligned} \tag{3}$$

As seen in the equations (2) and (3), parameters like the fiber and matrix tensile modulus ($E_{A,m}$), the coefficient of thermal expansion of the fiber and the matrix ($\alpha_{T,m}$) as well as the difference between reference stress-free temperature and the testing temperature ΔT are considered

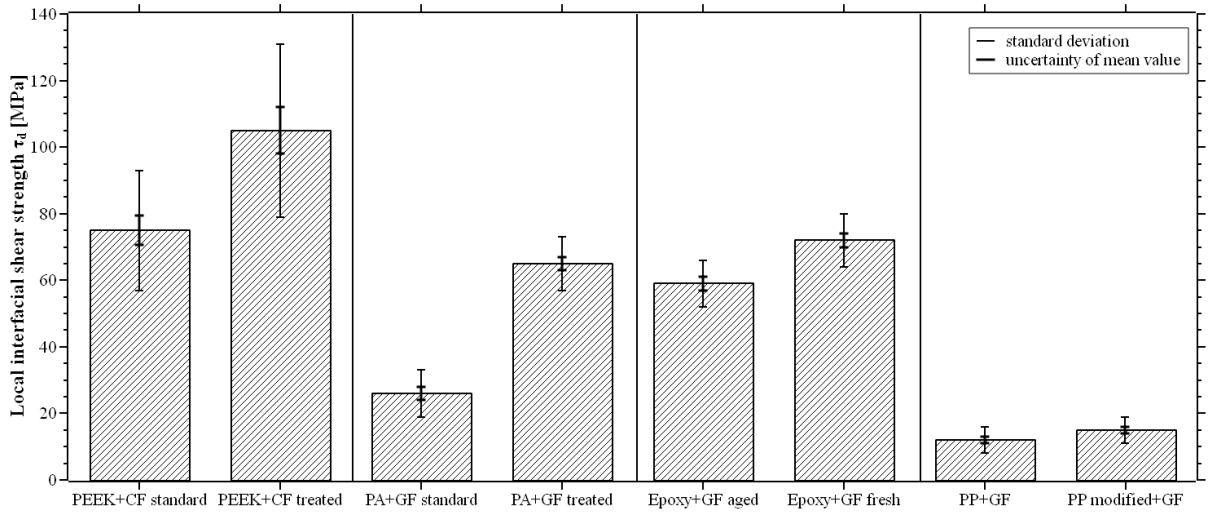

Figure 9. Local interfacial shear strength τ_d of standard and treated fibers in PEEK and PA, the effect of aging of the sizing of glass fibers (GF in Epoxy) as well as modification of polypropylene with maleic anhydride.

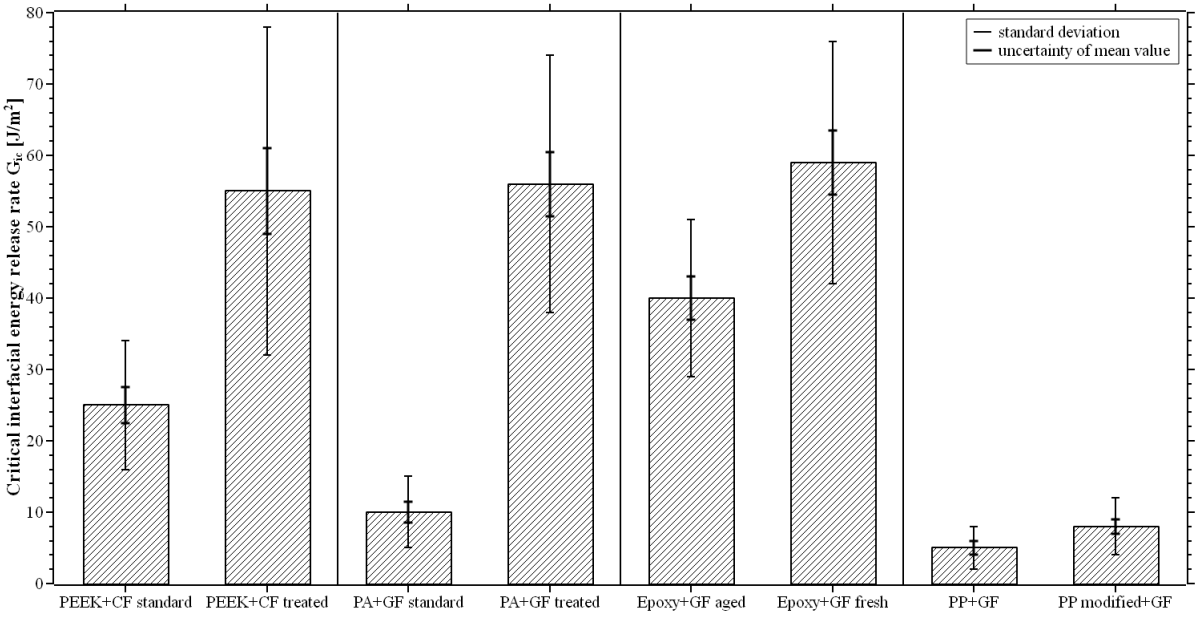

Figure 10. Critical interfacial energy release rate G_{ic} of the fiber-matrix combinations also shown in Fig.9.

parameters in the evaluation of the local interfacial shear strength and the critical energy release rate. A_0, C_{33}, C_{33s}, D_3, D_{3s} are constants that depend only on the fiber and matrix properties, $v_{f,m}$ are the fiber and matrix volume fractions. The cumulative stress transfer function is given by $C_T(a)$ and k is the frictional stress transfer rate. σ_0 is the net specimen stress whereas the actual tensile stress applied to the fiber enters through $\bar{\sigma}$. A detailed description of the parameters in given in Refs. [4] and [5].

After the debonding of the fiber from the matrix, the fiber will be completely pulled out. Thereby only friction, expressed by the interfacial frictional stress (τ_f), will occur (Eq. 4):

$$\boldsymbol{\tau_f} = \frac{\mathbf{F_b}}{\boldsymbol{\pi \cdot d_f \cdot l_e}} \quad , \qquad [4]$$

which is the final quantity evaluated by the analysis software.

5. SELECTED DATA FROM DIFFERENT FIBER-MATRIX COMBINATIONS

Using the testing procedure described in the sections above, we determine the local interfacial shear strength τ_d for several fiber-matrix combinations. Fig. 9 shows the results for standard and treated fibers of both carbon (CF) and glass (GF) embedded in different matrices – polyetheretherketone (PEEK), polyamide (PA) and an epoxy resin (Epoxy). Moreover, a glass fiber embedded in different modified polypropylene matrices is shown. For these examples, the kind of fiber treatment or modification to the matrix or fiber is not specified in detail.

We note that in all cases a significant improvement of the adhesion strength by treating the fibers or modifying the matrix could be detected. The well-known effect of the aging of sizing for epoxy-resins could be detected, too. Fig. 9 displays the local interfacial shear strength, whereas Fig. 10 shows the critical energy release rate for the same set of fiber-matrix combinations.

For some fiber-matrix combinations the differences in adhesion strength become more clearly visible in the energy-based model (Fig. 10) than by the evaluation through the strain-based model (Fig. 9). Again, it is noted that the adhesion strength increases significantly by the treatment of the fiber. Also, the use of different modified PPs leads to a significant difference in the results.

Another example for a glass fiber embedded in PP is given in Fig. 11. This study has been performed together with PHP Fibers GmbH with a focus on the amount of maleic anhydride masterbatch that is added to the PP fibers in hybrid tapes to optimize the adhesion to glass fibers in the consolidated composite. Starting without any maleic anhydride, both the strain-based (Fig. 11, top) and the energy based (Fig. 11, bottom) evaluation of the pull-out test show that the highest fiber-matrix adhesion strength is reached at 6 wt% fraction masterbatch in the PP. The data indicates, that at 10 wt% masterbatch the optimum amount of maleic anhydride has been exceeded.

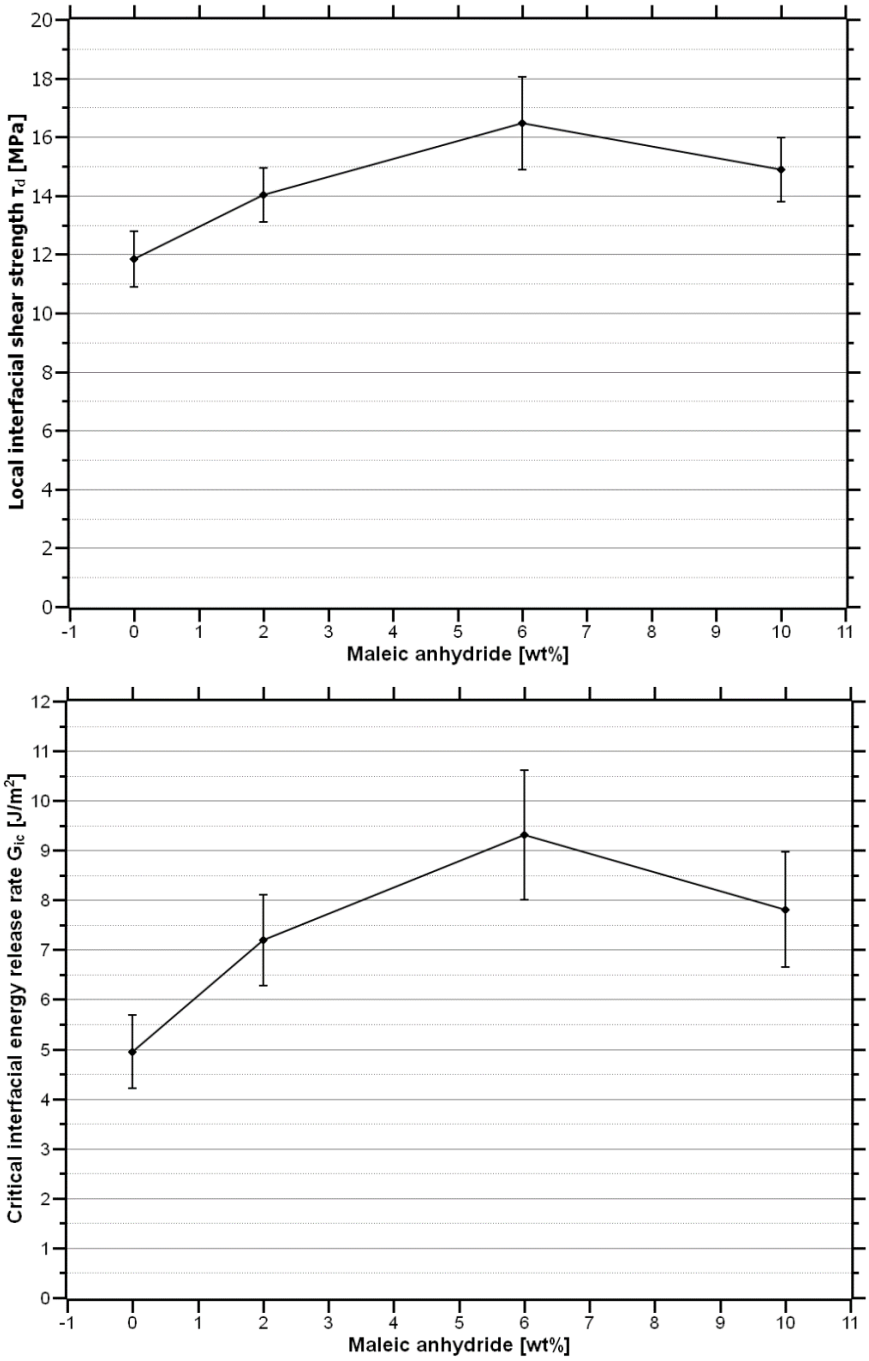

Figure 11. Fiber-matrix adhesion strength between GF and PP as a function of wt% maleic anhydride masterbatch in the PP. The error bars indicate the uncertainty of the mean value using 15 trials. Top: strain-based evaluation applied to the pull-out data. Bottom: the energy-based evaluation is used. In both cases the maximum adhesion is found at 6 wt% masterbatch.

6. CONCLUSIONS

We have used the micromechanical single-fiber pull-out implemented in Textechno's FIMATEST system to characterize the fiber-matrix adhesion strength for various fiber-matrix combinations. Mandatory for the test is a repeatable sample preparation which is performed here using the system's FIMABOND embedding station. In this way, it is possible to characterize the fiber-matrix adhesion strength in terms of the local and the apparent interfacial shear strength as well as the critical interfacial energy release rate (interfacial toughness). Differences in the fiber-matrix adhesion are usually due to the treatment of the fiber (e.g. sizing, plasma treatment) or the modification of the matrix material. We have demonstrated to trace such differences in the fiber-matrix adhesion on various kinds of combinations between fiber material and both thermoplastic as well as thermoset matrices.

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