TAILORING AND EVALUATING FIBRES AND COMPOSITE INTERPHASES: CURRENT APPROACHES

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1 ABSTRACT

Driven by the composite applying industries, in particular automotive, wind energy or mechanical engineering, the demand on new fibre surface as well as interphase concepts for advanced material developments and customized fibre properties increase. Likewise, a better comprehension of sizings, and first and foremost the access to “sizing knowledge” is required. Effective surface treatment of reinforcement fibres is a key task in order to achieve improved composite properties. Thereby, fibre sizings are considered as powerful “tools” to tailor interphases in fibre reinforced composites, protect the filaments during the fibre drawing process and enable efficiently post-processing. However, fibre sizings, its anticipating independencies on the composite performance are still poorly understood, and thereby its potential seems to be still far from being exhausted.

Fundamental studies of surfaces, new methods to quantify the interfaces as well as interphase properties are significant issues to push sizing development and initiate new interphase concepts. In this work, surface sensitive methods, single fibre and composite tests, and their expected outcome for the fibre development as well as interphase design were discussed. Furthermore, recent work on carbon nanotubes-enriched interphases is presented.

1 INTRODUCTION

Glass Fibres (GF): Quo Vadis? Developments in the field of GF are boosted by environmental and performance issues. The basic GF processing and the GF themselves have changed only by refinements since its commercialization more than 80 years ago [1]. Due to the rapid growth of the composite market, in particular with regard to the increasing amounts of wind farms, burning questions are adequate composite recycling strategies and the recovery of fibre properties of recycled fibres, e.g. by sizings containing nanomaterial and/or new interphase concepts.

In general, sizings consist of various components, predominantly organic compounds, e.g. film formers, coupling agents and surfactants. Some “sizing formulations” were disclosed in literature [2]. Moreover, extensive remarks might be found in patent literature. In 2015, a review of size formulation patents [3] was published, and supports the recent trend of making sizing knowledge available.

Fundamental knowledge in terms of the molecular and microstructure of interfaces as well interphases is reflected comprehensively by Ishida [4]. Indeed the interdiffusion and formation of interpenetrating polymer networks (IPN) have been described many times, and is generally accepted. It is also well known that the interphases of glass fibre reinforced composites contain covalently bonded, chemisorbed, and physisorbed polysiloxanes [5–7]. According the current stage of knowledge, a gradient in the degree and the density of crosslinking exists. In close vicinity to the fibre surface the silane coupling agent is strongly crosslinked. Numerous studies substantiate that the coupling agent is crucial for the fibre-matrix adhesion. Less known is that the coupling agent also affects the fibre and yarn properties. Without going into detail, the capability of healing surface flaws is mentioned at this point and reported in [8–11]. However, based on our experiences, it must be mentioned that glass fibres sized only with organosilanes may show high adhesion strength, but often the processing properties are disadvantageous. Effects like electro static charging, enhanced filament breakage (fuzz), or deficient thread stiffness may occur. Therefore, aqueous polymeric dispersions like epoxy (EP), polypropylene (PP), polyamide (PA), polyurethane (PU) dispersions or other auxiliaries...
are commonly included in fibre sizings. For instance, PU is interesting because of the wide range of film properties adjustable by the molecular structure, an advantageous issue considering the development of fibre sizings. A reasonable compromise between highest adhesion strength and best possible processing behaviour is striven for. Thereby, the processability should be considered from both the perspective of textile processing as well as the composite consolidation process. Indeed, issues like the wettability by the matrix resin, the reactivity of the sizing as well as the resulting interphase morphology may be decisive for the composite performance. As early as 2001, Thomason and Adzima [12] pointed out that the sizing formulation itself is one of the major technological challenges of glass fibre production requiring an ingenious balance of key issues like profitability, processibility and performance. The highly empirical procedure of sizing development demands making trade-offs, but may end up in considerable complex formulations. Therefore, a better understanding of fundamentals as well as cost effective sizing raw materials and suitable screening methods for fibre-matrix interaction are mentioned as main objectives [12].

More than 20 years later, these ambitions are more than ever demanded. Particularly regarding carbon fibre sizings, the role of film formers to the interphase performance is reconsidered. In contrast to glass fibre sizings, the addition of silane coupling agents does not significantly improve the fibre-matrix adhesion. Thus, searching for suitable alternative sizing raw materials improving the adhesion, strength, and modifying the fibre surface by, e.g. grafting molecules to the surface or even plasma treatments are recently subject of many studies [13–16]. Current approaches point out, that the adhesion challenges can be tackled by both fibre surface modification and matrix modification. Thus, novel matrix polymers are pursued occupying not alone a high compatibility to the reinforcing fibres but also facing a higher cost-efficiency of the composite manufacturing [17].

Moreover, nowadays, the interphase approaches have been more and more focused on both the improvement of the mechanical performance of composites as well as the implementation of additional functions to create multifunctional composites. The notion “interphase engineering” has been arisen in the last years. New properties, starting with sensory, adaptive, self-healing through to damping, are pursued to create “smart” interphases responsive to stimuli. In fact, further functions, e.g. with regard to thermoconductivity, the temperature management or the electromagnetic shielding, localized in the interphase are forecasted by Karger–Kocsis et al. [18]. Intensive research has been under way in the fields of nanofillers, nanocomposites and nanostructuring technologies. Likewise, researchers at Leibniz-Institut für Polymerforschung Dresden e. V (IPF) has been working in the fields of composites, interphases and surfaces for many years, and is extensively following the approach of multifunctional interphases [19–25]. Implementing a percolated carbon nanotube (CNT) network into composite interphases allows the detection of mechanical stress-strain behaviour by monitoring electrical response. The change in electrical resistance gives a quantitative parameter for the deformation as well as the early stage damage formation in highly strained regions of the interphase [26]. Besides the incorporation of CNTs into the interphase by sizings and/or coatings, recently we followed up a more non-conventional route, the surface treatment by chemical vapor deposition (CVD) in order to initiate hierarchical CNT architectures [27].

In this proceeding paper, we will discuss the current state of our work and present several examples in terms of fibre surfaces, fibre sizings and its impact on composite properties.

2 EXPERIMENTAL

IPF glass fibre pilot plant operating with molten glass marbles allows the manufacturing of continuous glass fibres as well as hybrid yarns made of both continuous commingled polymer and glass filaments, and offers the opportunity to modify fibre surfaces immediately within the fibre drawing process. The potential of single sizing components is shown by the application of model sizings and subsequent composite tests, e.g. transverse tensile test or compression shear test.

Moreover, quasi-static single fibre pull-out (SFPO) tests were carried out using IPF pull-out test equipment. Therefore, single fibre model composites were prepared by self-made reliable sample
preparation equipment and 15-20 force-displacement curves for each sample were performed. A characteristic force-displacement curve is shown in Figure 1. In order to get an interfacial shear stress value, the simple approach was applied using the maximum pull-out force, \( F_{\text{max}} \), for the calculation of the apparent interfacial shear strength (apparent IFSS, \( \tau_{\text{app}} \)):
\[
\tau_{\text{app}} = \frac{F_{\text{max}}}{\pi d_l I_e}
\]
where \( d_f \) is the fibre diameter and \( I_e \) is the embedded fibre length.

Further interfacial parameters, e.g. the local interfacial shear strength (\( \tau_d \)) and the critical interfacial energy release rate (\( G_{\text{IC}} \)), may be additionally be calculated using the stress- and energy-based approach described in [28].

![Figure 1](image)

**Figure 1.** Single fibre pull-out test: Typical force-displacement curve

The investigation of the fibre surface before and after the pull-out test, e.g by SEM is recommended to support the understanding of the obtained data.

Electrokinetics was applied for studying the adsorption of fibre sizing components. The streaming potential measurements were carried out using the electrokinetic analyser (A. Paar GmbH/ Graz/Austria). Thereby, a cylindrical cell developed for fibrous samples was used. The setup of the measurements as well as the data treatment is described comprehensively in [29]. According to Jacobasch [30], it is possible to characterise the surface groups of the outermost surface layer of fibres. Hence, the resulting surface properties of differently sized fibres can be investigated.

The isoelectric point (IEP=\( \text{pH}_{\text{IEP}} \)) and the plateau value in zeta-potential (\( \zeta_{\text{max}} \)) determined from the zeta-potential vs. pH plot describe the characteristics of the outermost surface.

### 3 RESULTS AND DISCUSSION

#### 3.1 Modifying the matrix

Fibre matrix adhesion of carbon fibre and PP matrix was investigated by single fibre pull-out test (SFPO). The carbon fibre (CF) surface is PP-functionalized by grafting, and investigated in unmodified PP and PP modified with 2 wt% maleic anhydride grafted PP (PPgMAH), respectively. It should be noted that no additional sizing was applied.

The force-displacement curves reveal clearly that the interfacial interaction is significantly improved due to the matrix modification (Figure 2). Both the apparent interfacial shear strength and the local interfacial shear strength indicate the significance of maleic anhydride (MAH) matrix modifier (Table 1). Considering the impact of the surface functionalisation, the oxidized carbon fibre surface seems to be less efficient.
Table 1. Interfacial parameters of CF/PP model composites

<table>
<thead>
<tr>
<th>Unsized carbon fibre</th>
<th>Matrix</th>
<th>$\tau_{\text{app}}$ [MPa]</th>
<th>$\tau_d$ [MPa]</th>
<th>$G_{\text{ic}}$ [J/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>modified with PP-compatible functional groups</td>
<td>Unmodified PP</td>
<td>4.4±1.5</td>
<td>5.3±1.9</td>
<td>0.9±0.5</td>
</tr>
<tr>
<td></td>
<td>PPGMAH</td>
<td>14.9±4.5</td>
<td>16.1±4.4</td>
<td>7.1±3.6</td>
</tr>
<tr>
<td>oxidized</td>
<td>PPGMAH</td>
<td>10.3±3.8</td>
<td>12.5±3.9</td>
<td>4.3±2.3</td>
</tr>
</tbody>
</table>

Figure 2. Force-displacement curves of carbon fibre with PP-compatible functional groups (unsized) in: (a) PP and (b) PPGMAH matrix

In addition, the work of Wiegand and Mäder [26] substantiates the impact of matrix grafting and sizing formulations. Several sizing components are investigated in both maleic anhydride grafted polypropylene (PPgMAH) and pure PP matrix. For this purpose, online commingled GF/PP yarns were spun and manufactured to unidirectional GF/PP composites having fibre volume content of 50% were made. The transverse tensile strength values of the GF/PPgMAH composites were significantly higher compared to the ones made of pure PP matrix. For instance, a simple sizing composed of PPGMAH film former and aminopropyltriethoxysilane (APS) results in a strength value either of about 18 MPa or about 7.5 MPa depending on MAH matrix modifier was used or not. In any case the included APS can form covalent bonds with the glass fibre surface, and additionally react with the functional group of the film former. It is assumed that the film former may crystallize via physical entanglements with the molecular chains of the PP matrix. In this way the interphase is formed, and an effective stress transfer from the matrix into the fibre is possible. The enhanced transverse tensile strength is probably due to the increased possibilities of chemical bonding. Interestingly, a transverse tensile strength of about 8 MPa is achieved independent on the issue if the MAH was implemented by the film former or by the matrix polymer.

3.2 Modifying the fibre surface by sizing components

Bellmann and co-workers [29] silanized glass fibres as well as glass fibres sized with a mixture of silane and lubricant were investigated by several methods. The surface of the APS treated glass fibre shows strong basic properties with an isoelectric point (IEP= pH|ζ=0) of about pH_{IEP}= 10. Interestingly, the elektrokinetic properties changed remarkably due to the additional use of a cationic surfactant, particularly an oleytrimethyl-ammoniumchlorid. The IEP changed to about pH_{IEP}= 6. The authors revealed that the resulting fibre surface properties after sizing processes are strongly dependent on the interplay of the individual sizing components used. Competitive adsorption reactions are responsible for that. Investigations of differently sized wafer surfaces by atomic force microscopy (AFM) show that the cationic lubricant is able to hamper the film forming process, and lead obviously in a more
insular surface structure. The amine functionality of both the APS and the cationic surfactant compete for adsorption positions on the solid surface.

Finally, the streaming potential measurements reveal that the surface functionality of glass fibres is adjustable due to the concentration and/or ratio of sizing components used within the sizing formulation. In the presence of the cationic surfactant, higher amounts of APS are necessary to obtain basic surface properties.

Beside the lubricants, the film formers may affect the resulting surface properties. Figure 3 shows the zeta-potential as a function of the pH for differently sized glass fibres. A positive (basic) surface will be expected due to the usage of APS as sizing ingredient. However, the APS/PP treated fibres revealed a surface which is covered by negative (acidic) functional groups. The IEP is about pH= 3.6 and can be explained by the acidic groups of the maleic anhydride modified film former dispersion.

In further studies, we investigated the influence of modified water-based PU dispersions on the performance of GF/epoxy resin (EP) composites. Therefore, continuous E-glass fibres were sized by a formulation composed of 2.7 wt% PU film former, 0.5 wt% coupling agents, in particular a 1:1 mixture of APS and glycidyloxypropyltriethoxysilane (GPS) was used, and 0.4 wt% surfactants. The polyurethanurea dispersion used for the fibre sizing was supplied by Bayer Material Science, and varied in formation components, the chain termination level and the content of COOH-groups [31]. Table 2 presents the transverse tensile strength of selected composite samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>Polyester used</th>
<th>NCO [%]</th>
<th>Chain termination level [%]</th>
<th>Proportion of COOH [% by wt.]</th>
<th>Transverse tensile strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>2.17</td>
<td>18</td>
<td>0</td>
<td>37±2</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>2.72</td>
<td>28</td>
<td>0.83</td>
<td>49±2</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>3.34</td>
<td>28</td>
<td>1.34</td>
<td>56±3</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>2.42</td>
<td>18</td>
<td>0.73</td>
<td>40±3</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>1.84</td>
<td>28</td>
<td>0</td>
<td>40±2</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>1.95</td>
<td>28</td>
<td>1.31</td>
<td>56±2</td>
</tr>
</tbody>
</table>

A*: polyester polyol formed from adipic acid, hexane-1,6-diol and neopentyl glycol, B**: polyester formed from adipic acid, isophthalic acid and hexane-1,6-diol
The tensile strength values indicate that the molecular structure of dispersions may affect the interphase properties. The fibre-matrix adhesion can be influenced by specific formation components of the polyurethane. Thereby, higher chain termination level and an increase in -COOH groups seem to be advantageous. It is assumed that the free acid groups of the PU dispersion might initiate epoxy ring opening reactions, and enhancing the performance due to the formation of covalent bonds between the sized fibre surface and the polymer matrix [31].

3.3 Modifying the fibre surface by CVD treatments

Beside the fibre surface modification due to sizing application during the fiberizing process, we followed up a more non-conventional route, the surface treatment by CVD on basalt fibre surfaces without catalysts, in order to initiate hierarchical CNT architectures [27]. CVD experiments were carried out on unsized, sized, and NaOH-treated basalt fibres, and the resulting fibre surfaces were investigated by SEM, AFM and XPS. It was found that growth temperatures of 700 °C as well as 800 °C may induce CNT growth, but depending on the basalt fibre surface, the growth process was differently affected. It was demonstrated that a corrosion shell, formed due to a NaOH treatment, is able to support CNT networks (Figure 4). However, our investigations do not expose distinctively the mechanisms by which unsized basalt fibres sometimes induce vertically aligned CNT carpets, isotropically arranged CNTs or no CNT growth. The XPS results suggest surficial iron is not crucial for the CNT growth. Currently, it is assumed that the nano-roughness of surfaces could be a critical parameter for CNT growth.

![Figure 4 SEM image of the surface of a NaOH and subsequent CVD treated basalt fibre.](image)
The corrosion shell formed due to a NaOH treatment at a temperature of 80 °C induces CNT growth.

As mentioned, previous CVD experiments create hitherto no uniform CNT coatings on basalt fibre surfaces. However, electrical conductivity can be induced by the treatment. Recent work of Hao et al. [32] observed a thin pyrolytic carbon coating due to the CVD and revealed that initial insulating basalt fibre changes into an electrical conductive one. First model composites were prepared to demonstrate the potential for sensing applications.

The capability to stimulate CNT growth is a very exciting feature which could open totally new application fields for basalt fibres if the mechanism behind it is more understood. If successful, the multifunctional interphase approach could also reveal recycling strategies and contribute to upgrading the properties of recycled basalt fibres or, rather, the properties of 2nd-life composites.
4 CONCLUSION

In summary, the examples disclose the multitude possibilities to approach the interphase challenge. The individual components, in particular matrix polymers, sizing formulation and fibre surface, are offering - each one considered separately - a huge number of levers for advancements and of course further potential due to combining those ones. Characterisation techniques and/or novel methodologies, which support the decision-making and preselection of suitable approaches, will be required.

The single fibre pull-out test is a micromechanical testing method, which allows some closer look into fibre-matrix interactions, but it should be kept in mind that the test is a simplification, and not always expedient or feasible. Issues like fibre content, orientation and distribution, but also the size and distribution of pores and/or further specific effects due to the composite processing are more or less neglected. Nevertheless, the SFPO test allows comprehensive studies and first interphase remarks can be passed facilitating the development of composites, especially if novel materials with still limited availability are investigated.

Gaining deeper insights in fibre-matrix interactions takes the application, preferably combination, of various techniques. Thereby, surface sensitive methods including electrokinetics, wetting measurements, XPS, AFM provide specific information valuable for prospective surface and interphase “engineering” approaches. The CNT growth onto basalt fibre surfaces initiated by CVD treatments is not fully understood at this time. The role of surface chemistry, surface roughness as well as surface defects on the formation of hierarchical interphases must be studied in further work.

REFERENCES


