Interfacial interactions in carbon fiber reinforced polymer composites: surface characterization, chemistry and adhesion

Ph.D. Thesis

by

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Chapter 1

Introduction

Polymers, combined with other polymers, fillers or reinforcing fibers are used in increasing quantities in all fields of application. These materials contain the second component in quantities comparable to that of the matrix. Their growth rate exceeds those of commodity polymers and traditional structural materials like metals, wood or concrete. Arbitrarily they can be divided into three main categories: polymer blends, particulate filled polymers, and fiber-reinforced composites. All three offers some advantages compared to simple one-component polymers. Blends possess increased impact resistance, tailored properties, price advantage. Particulate filled polymers are stiffer, have good dimensional stability, improved processability, specific properties and price. Fiber reinforced polymers offer very high stiffness and strength, which are comparable to the same properties of steel at much lower weight, high heat deflection temperature and dimensional stability and chemical resistance (see Table 1.1).

Blends, filled polymers and composites usually posses heterogeneous, two phase structure. The properties of such heterogeneous polymer systems depend on four factors: component properties, composition, structure and interfacial interactions. Component properties may vary in a wide range: the stiffness of the second component changes from a few pascals to hundred gigapascals as we proceed from elastomers trough liquid crystalline polymers to fillers and fibers. Composition may also cover a wide range from 5 wt% in nanocomposites to 80 vol% in advanced composites. The structure of these heterogeneous systems can be very complicated, e.g. two boundary structures can form in three-component PP/CaCO$_3$/elastomer composites, which result in very different properties. The components maybe distributed separately in the PP matrix in a stiffness of 1.1 GPa, while the elastomer can embed the filler yielding a material of 0.5 GPa stiffness. Interaction of the components is also very important, it may determine the micromechanical deformation processes taking place during deformation and thus the macroscopic properties of the material.

The effect of the last two factors is especially important in fiber reinforced polymers. Because of the very different properties of the fiber and the matrix (Table 1.2), their function and role is also dissimilar in the composite: the fibers carry the load, while the matrix distributes it among the fibers. However, this simple principle works only if some conditions are fulfilled: the fibers must be oriented in the direction of the load (structure) and the adhesion between the two components must be sufficient to make possible the transfer of stress (interfacial interaction). The first is achieved by the appropriate design of the composite; the compressive strength of composites is usually rather poor. The necessary adhesion strength is usually reached by the chemical coupling of the components, the creation of covalent bonds. However, the surface of the fiber must be modified and coupling agents must be used to reach this goal, since the surface of the fiber is chemically inactive. This thesis focuses attention mainly on the second question, on the surface properties of the fibers, on their characterization and on the modification of interactions.
**Table 1.1** Advantages offered by modified polymers, specific properties

<table>
<thead>
<tr>
<th>System</th>
<th>Modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Impact strength (kJ/m²)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>3.15</td>
<td>55.0</td>
<td>25&lt;sup&gt;a&lt;/sup&gt;</td>
<td>appliances, ruler</td>
</tr>
<tr>
<td>HIPS</td>
<td>2.65</td>
<td>38.0</td>
<td>450&lt;sup&gt;a&lt;/sup&gt;</td>
<td>instruments</td>
</tr>
<tr>
<td>PP</td>
<td>1.40</td>
<td>32.4</td>
<td>1.73&lt;sup&gt;b&lt;/sup&gt;</td>
<td>utensils</td>
</tr>
<tr>
<td>PP/talc</td>
<td>4.82</td>
<td>33.8</td>
<td>1.77&lt;sup&gt;b&lt;/sup&gt;</td>
<td>automotive</td>
</tr>
<tr>
<td>Steel</td>
<td>20.7</td>
<td>69.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epoxy/CF</td>
<td>13.8</td>
<td>137.9</td>
<td></td>
<td>space and air</td>
</tr>
</tbody>
</table>

<sup>a</sup> unnotched  
<sup>b</sup> notched

**Table 1.2** Comparison of the properties of reinforcing fibers and some polymers

<table>
<thead>
<tr>
<th>Component</th>
<th>Stiffness (GPa)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>1.5</td>
<td>33</td>
</tr>
<tr>
<td>Polyamide</td>
<td>2.3</td>
<td>65</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>3.1</td>
<td>72</td>
</tr>
<tr>
<td>Glass fiber</td>
<td>70</td>
<td>2600</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>210</td>
<td>3400</td>
</tr>
</tbody>
</table>

Carbon fibers have excellent properties, they offer the best performance of all reinforcing fibers. They are mostly prepared from pitch or poly(acrylonitrile) precursors. PAN based carbon fibers usually possess better properties than those prepared from pitch. Moreover, such fibers are produced also in Hungary by Zoltek, a fact that in part initiated this research. First the organic fiber is prepared and oriented then it is subjected to heat treatment. In the oxidation step cyclization takes place and the majority of heteroatoms is eliminated from the polymer. Oxidation is followed by carbonization when the final structure of the fiber forms. Besides carbon atoms the fibers contain only a few percent of other atoms, mainly nitrogen. The crystalline structure of the carbon fiber is oriented parallel to its length, which leads to the very high stiffness and strength characteristic for these fibers. Although the fiber itself is very strong, its interaction with any polymer matrix is poor, because of the lack of functional groups on its surface.
In order to increase the chemical activity of the fiber surface and make chemical coupling possible, the fibers are activated by a separate technological step. Active groups are usually created on the surface by oxidation, which can be carried out according to several techniques. Although the fiber surface can be oxidized in gas phase, or in solution by different acids, electrochemical oxidation is applied the most often in industrial practice. Various electrolytes are used for this purpose and the other conditions of oxidation (time, concentration, potential) also may vary in a wide range. All of these conditions influence the type and concentration of chemical groups forming on the surface of the fibers, however, the exact relationship between oxidation technology and surface chemistry is not known yet.

Although electrochemical oxidation of the fibers increases their surface activity, they cannot be used for the preparation of composites in that form. For handling purposes they must be covered by a sizing, and coupling agents must be added in order to bond the fiber chemically to the matrix. The sizing material usually contains the same or similar polymer as the matrix and some further additives, surfactants and lubricants that help the high-speed production and handling of the fibers are also added. The coupling agent used must be selected according to the chemical character of the matrix, but the type and concentration of the functional groups formed on the fiber surface in the oxidation process must be also taken into account. The composition of the sizing material is usually proprietary, a closely guarded secret of the companies producing the fibers. These proprietary treatments may perform well in certain matrix/fiber combinations, but fail completely in others. Further knowledge about the coupling reactions and the factors influencing the strength of adhesion may help the development of more efficient composites with improved properties.

It is clear from the above paragraphs that further information is needed about the processes and factors influencing interfacial interactions in carbon fiber reinforced composites. As a consequence the main goal of this thesis was to carry out detailed studies on certain aspects of this problem. PAN based carbon fibers were oxidized electrochemically under a wide range of conditions and the chemical composition of the fibers was studied by various methods. Attempts were made for the determination of the correlation between the oxidation process and the type, as well as number of active groups formed on the surface. In a further step various coupling agents were used to bond the fiber chemically to different matrix polymers. Interfacial adhesion was determined and related to surface chemistry. The correlation between the structure and properties of short fiber reinforced thermoplastic composites are discussed in the final section of the thesis. The topic of the individual chapters is introduced somewhat more in detail in the following paragraphs.

The chemical composition of the inactive surface of the fiber was changed by an electrochemical oxidation process used also in industry. Five different electrolytes were applied; the conditions of oxidation varied in a wide range. In Chapter 2 we selected 20 fibers among the 160 prepared and studied the effect of electrochemical oxidation on the chemical composition of their surface. The type and concentration of functional groups were determined by diffuse reflectance infrared spectroscopy (DRIFT); conclusions were drawn from the results about the chemical reactions taking
place on the fiber surface during oxidation. We tried to find quantitative correlation among the parameters of oxidation, surface chemistry and interfacial shear stress (IFSS), which characterizes the adhesion of the components. This latter quantity was determined in epoxy resin microcomposites, since this polymer is often used as the matrix of carbon fiber reinforced composites.

In Chapter 3 we focused our attention on the more detailed investigation of fibers oxidized in sulfuric acid and sodium hydroxide. The fibers were characterized by DRIFT, but the electrochemical activity of their surface was also determined by cyclic voltammetry (CV). We looked for correlation between oxidation parameters and the electrochemical activity of the fiber. The intensity of oxidation transitions detected by cyclic voltammetry was compared to interfacial adhesion and to the concentration of active groups developed on the fiber surface during oxidation. Good correlation was found among these quantities for fibers oxidized in sulfuric acid, but contradictory results were obtained in sodium hydroxide. NaOH seemed to adsorb on the surface of the fiber and interfere with matrix/fiber adhesion. Chapter 4 focuses attention on this phenomenon; a detailed study was carried out in order to check the possible adsorption of the electrolyte and its effect on adhesion. Oxidized fibers were soaked in distilled water for different periods of time and both the solution and the fiber were characterized by various methods. We measured the pH of the solution, its sodium ion concentration, the electrochemical activity of the fiber by CV and IFSS in an epoxy matrix. We found close correlation among the amount of adsorbed NaOH, the electrochemical activity of the fiber and IFSS. The results called attention to an important phenomenon, which must be considered also during the large-scale production of carbon fibers.

Fibers must be coated by various compounds, sized, before they can be introduced into composites. Chapter 5 of this thesis deals with the modification of the carbon fiber with various potential coupling agents. The compounds were selected by using the knowledge obtained in previous studies, which revealed the chemical composition of the fiber surface. We assumed that the most active groups of the fiber are carboxylic and hydroxyl groups and we hoped that the selected coupling agents would react with them, create covalent bonds and increase interfacial adhesion in an epoxy resin. First we determined the adsorption of the coupling agents on the surface of the fiber and the chemical structure, as well as composition of the interphase formed. We found that the reactions, the amount of bonded coupling agent and the structure of the layer formed on the surface, depend very much on the chemical structure of the compound. Some coupling agents polymerize on the surface of the fiber. Interfacial adhesion depend both on the amount of the coupling agent bonded to the fiber surface, but also on its structure. Relatively strong adhesion can be achieved by the application of an epoxy silane coupling agent.

In the last decade, considerable attempt was made to use thermoplastic matrices for fiber reinforced composites due to their advantageous properties (high impact resistance, low sensitivity to water, faster processing, etc.). As a consequence, we studied the coupling of carbon fibers also to polycarbonate matrix. The results of this study are presented in Chapter 6. Model experiments were carried out in an extruder in order to determine possible chemical reactions of the polymer with the
coupling agent. The effect of these reactions on the adhesion of the fiber and the matrix polymer was determined by the measurement of interfacial shear stress. The largest increase of IFSS was achieved with the epoxy silane again. However, the experiments proved that the extent of reaction depends also on the molecular weight of the polymer and the conditions, especially the temperature, of the coupling reaction. Only limited reinforcement can be achieved in polycarbonate because of the very limited concentration of active groups available in this polymer.

Besides interfacial interactions, the structure of the composite also considerably influences its properties. This effect is especially pronounced in short fiber reinforced composites, where the fibers assume a three-dimensional arrangement. Structure-property correlations of short carbon fiber reinforced polyamide composites are studied in Chapter 7 of the thesis. Injection molded specimens containing various amounts of carbon fiber were produced under a wide range of processing conditions. The average length and length distribution as well as orientation and orientation distribution of the fibers were determined in the specimens. We studied the effect of processing parameters on the structure and properties of the composites, with special attention to mechanical properties generally, and fracture resistance particularly.

The final section of the thesis summarizes the most important conclusions of the study. The large number of experimental results obtained supplied useful information and led to several important conclusions, which can be used during the production and use of fiber reinforced composites. Nevertheless, several questions remained open in the various parts of the study, their explanation needs further experiments.
Chapter 2

Electrochemical oxidation of carbon fibers; surface chemistry and adhesion

2.1. Introduction

Interfacial interactions play a crucial role in the performance of all fiber reinforced composites. Good adhesion is absolutely necessary to transfer load from the matrix to the fiber. On the other hand, the optimum strength of the adhesion is a much debated question, since weak adhesion leads to debonding, while very strong interaction to a brittle composite. Nevertheless, the importance of interfacial interaction is shown by the numerous studies carried out to determine its mechanism and even more by the large number of attempts to modify it by surface treatment [1-4]. The study of interfacial interactions is further complicated by the fact that in composites an interphase forms spontaneously even in the absence of surface treatment. However, some treatment is always used in continuous fiber reinforced composites [1,5], which invariably leads to the formation of an interphase of very complex structure [6-8]. The thickness and properties of this interphase have a crucial impact on composite properties.

Interfacial interactions are extensively studied also in carbon fiber reinforced epoxy composites. Spectroscopic techniques, like XPS or SIMS are frequently used for the identification of the functional groups on the surface of the fiber [9]. Surface characteristics are studied by inverse gas chromatography showing the important role of acid base interactions in fiber/resin adhesion [10]. This property is usually measured by single fiber tests, frequently by fragmentation [11,12]. The surface of carbon fibers is modified by various techniques, but epoxy or amino compounds are used the most often [13]. These compounds are supposed to react with the acid or hydroxyl groups at the surface. However, a considerable number of studies are carried out with commercial fibers having an unknown proprietary treatment [14]. This might be efficient in a given resin/fiber system, but fail completely in another. Such contradictions can be explained by the fact that the properties of the matrix and the interphase change from one system to the other and all components of an epoxy resin adsorb differently on the surface of the fiber [15,16].

The functional groups necessary to couple the fiber to the matrix are usually formed in an oxidation process resulting in a wide variety of reactive sites, among others carboxyl, phenolic hydroxyl, quinone type carbonyl, lactone, carboxylic acid anhydride, cyclic peroxide, etc. [17]. The oxidation of the fiber can be carried out under dry conditions in air or oxygen [18], but most often oxidizing solutions are used [5,17,19-25]. In industrial practice electrochemical oxidation is used for functionalisation. The type and amount of the functional groups formed depend on the type of the electrolyte, its concentration, treatment time, and voltage [19,20]. The strength and surface area of the fiber are said to remain constant in this treatment [26], but surface activity increases considerably shown by a significant improvement of interfacial shear stress [27]. The proper selection of the
conditions of electrochemical oxidation is essential for achieving optimum composite properties.

In the first stage of the study a PAN based carbon fiber was subjected to electrochemical oxidation under a wide variety of conditions. The aim of the work was the determination of the effect of electrolyte type and oxidation conditions on the chemical changes occurring on the surface of the fiber. An attempt was made to establish correlation between surface chemistry and interfacial interaction in an epoxy matrix.

### 2.2. Experimental

**Table 2.1** *Interfacial shear stress measured in an epoxy matrix on carbon fibers oxidized under different conditions*

<table>
<thead>
<tr>
<th>Electrolyte Type</th>
<th>Concentration (wt%)</th>
<th>Voltage (V)</th>
<th>IFSS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>-</td>
<td>-</td>
<td>17.3 ± 2.8</td>
</tr>
<tr>
<td>(NH₄)₂CO₃</td>
<td>20</td>
<td>0.5</td>
<td>18.8 ± 2.5</td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>20</td>
<td>0.5</td>
<td>17.1 ± 2.1</td>
</tr>
<tr>
<td>HNO₃</td>
<td>3</td>
<td>0.5</td>
<td>23.1 ± 4.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>29.3 ± 8.6</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.5</td>
<td>36.0 ± 14.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>25.8 ± 8.8</td>
</tr>
<tr>
<td>NaOH</td>
<td>3</td>
<td>5.0</td>
<td>23.7 ± 5.7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>23.8 ± 4.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>25.7 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.5</td>
<td>37.7 ± 8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>32.6 ± 7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>29.0 ± 3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>27.5 ± 5.9</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>3</td>
<td>5.0</td>
<td>29.0 ± 4.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>25.6 ± 5.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>30.1 ± 4.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.5</td>
<td>20.6 ± 7.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>23.0 ± 3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>27.8 ± 3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>36.0 ± 9.6</td>
</tr>
</tbody>
</table>
The untreated PAN based carbon fiber (Panex 33) used in the experiments was supplied by Zoltek Co., Hungary. The diameter of the fiber was 7 µm and its modulus 250 GPa. The fiber was subjected to electrochemical oxidation under different conditions. Sodium hydroxide, ammonium hydrogen carbonate, ammonium carbonate, sulphuric acid and nitric acid were used as electrolytes in concentrations of 2, 5, 10 and 20 wt%. The potential of oxidation changed in the range of 0.5 and 5.0 V (0.5, 1, 2 and 5 V). The oxidation was carried out in a continuous process, the time of the treatment was changed by the linear rate of the fiber passing through the electrolyte. Two rates, 20 and 30 cm/min, were used in the experiments. The oxidized fibers were washed with distilled water also in a continuous process. Altogether 160 combinations of conditions were employed in the study.

The epoxy matrix used consisted of 100 phr epoxy resin (Eporezit E 064), 25 phr isophoron diamine hardener (Polypox IPD) and 15 phr reactive extender (Eporezit AH-24). All components were supplied by P+M Ltd., Hungary. Curing was carried out in two steps, first at 25 °C for 1.5 hours, followed by the second step at 100 °C for 2 hours.

The characteristics of 21 selected samples were determined in this preliminary study. Experimental conditions, i.e. electrolyte, concentration, potential, are listed in Table 2.1. The effect of oxidation on fiber strength was determined for all five electrolytes. The surface chemistry of the fibers was analyzed by Fourier transform infrared spectroscopy (Mattson Galaxy 3020, Unicam) in diffuse reflectance mode (DRIFT). The fibers were cut to small pieces, milled and diluted with KBr powder in a ratio of 9.6/750 mg. The spectra were taken in 256 scans between 4000 and 400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). The interfacial shear stress (IFSS) was determined by fragmentation. Five parallel measurements were carried out and the number of fragments, as well as their length were measured under a light microscope after reaching the maximum number of fragments. IFSS was calculated by the Kelly-Tyson equation [28]. The fracture surface of the microcomposites after fragmentation was studied by scanning electron microscopy (SEM, JEOL JSM-5600 LV).

2.3. Results

Since a wide range of oxidation conditions were used in the study, first the effect of treatment on fiber strength was determined and is discussed in the paper. This is followed by a detailed analysis of surface chemistry, then the results obtained on interfacial adhesion are presented. The correlation of surface chemistry and interfacial adhesion is discussed in a separate section.

2.3.1. Fiber strength

Although literature data indicate that the strength and specific surface area of carbon fibers do not change during electrochemical oxidation [26], measurements were carried out to check this statement. FTIR analysis of the fibers indicated that some of the electrolytes had a very strong effect on the type and number of functional groups on the surface (NaOH, H\(_2\)SO\(_4\)), while others did not influence surface chemistry at all [e.g.
(NH₄)₂CO₃. Table 2.2 presents the effect of electrolyte type on the strength of the fibers oxidized in 20 wt% solution at 0.5 V. The measurements were done with various gauge lengths. Although some differences can be observed among the fibers oxidized in various electrolytes, the effect is relatively small. The largest differences can be observed at 10 mm gauge length, but even these are within the limits of the standard deviation of the measurement. We may conclude from these results that under the conditions used in our experiments, the electrochemical oxidation of carbon fibers does not influence their strength. As a consequence, we assumed that fiber strength is the same also under the other conditions. Thus the strength at the critical length was calculated by interpolation and this value was introduced into the Kelly-Tyson equation in order to calculate IFSS.

### Table 2.2 Effect of electrolyte type used in the oxidation process on the strength of carbon fibers; oxidation at 20 wt% concentration and 0.5 V

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Fiber strength (GPa) at gauge length (mm)</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>4.29 ± 0.67</td>
<td>4.24 ± 0.70</td>
<td>3.80 ± 0.59</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>4.03 ± 0.67</td>
<td>3.70 ± 0.61</td>
<td>3.66 ± 0.63</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>4.08 ± 0.54</td>
<td>4.01 ± 0.46</td>
<td>3.71 ± 0.57</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>4.00 ± 0.71</td>
<td>3.97 ± 0.66</td>
<td>3.72 ± 0.46</td>
<td></td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>4.02 ± 0.85</td>
<td>3.75 ± 0.39</td>
<td>3.69 ± 0.61</td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂CO₃</td>
<td>4.20 ± 0.59</td>
<td>4.17 ± 0.50</td>
<td>3.78 ± 0.72</td>
<td></td>
</tr>
</tbody>
</table>

2.3.2. Surface chemistry

The study of the chemical composition of carbon fibers by FTIR is difficult because of two reasons. First, the absorption of the fiber is very intense, while the concentration of the different functional groups on its surface is relatively low. As a consequence, the signal/noise ratio is often not sufficiently high even if the sample is scanned many times. Preliminary experiments revealed that this ratio improves with increasing number of scans up to 256, but does not change afterwards. The other difficulty is caused by the fact that the diameter of the fiber falls in the analytical wavelength range of infrared light, which may lead to strong interference at low wavenumbers. Thus the technique of sample preparation has a strong influence on the quality of the IR spectra, and because of the very low concentration of functional groups, the results must be treated with the utmost care during evaluation.

The FTIR spectrum of the neat, untreated carbon fiber reveals the presence of different functional groups (Fig. 2.1, Spectrum 1), confirming that the surface of carbon (even diamond) oxidizes in air [29]. According to Ref. 29 the surface of oxidized carbon black contains phenolic hydroxide and carboxyl groups, quinone functions, lactones and C-H bonds. The peaks of Spectrum 1 in Fig. 2.1 are broad and most of them overlap each other. The strong absorption band appearing at around 3500 cm⁻¹ (A) may be attributed to phenolic OH groups and/or water adsorbed on the surface of the fiber. The adsorption of water seems to be supported by the vibration at 1633 cm⁻¹ (B), although
quinoidal carbonyl groups, which are also expected to be present on the fiber surface [29], absorb in the same wavelength range [30]. The vibration between 1816 and 1680 cm\(^{-1}\) (C) results from the superposition of several C=O absorptions. The carboxyl group absorbs in the range of 1700-1680 cm\(^{-1}\) [30]; obviously it is not the main component of carbonyls forming on the surface of the neat carbon fiber. The position of the maximum of the C=O vibration at 1730 cm\(^{-1}\) indicates that ester groups and/or δ- or larger lactones, which absorb in the same range as open-chain esters [30], dominate the spectrum. The electrochemical oxidation of the carbon fiber changes its IR spectrum, but the characteristic absorptions of the neat fiber can be recognized also in the spectra of the oxidized samples. However, as an effect of oxidation the vibration of some new functional groups appear in the spectrum, which superimpose on those of the neat fiber (Spectra 2 and 3, Fig. 2.1).

In order to facilitate evaluation difference spectra were generated by subtracting the spectrum of the neat fiber from those of the treated ones. The effect of electrochemical oxidation is shown in Fig. 2.2, where the difference spectra of fibers oxidized in the various

**Figure 2.1** DRIFT spectra of carbon fibers subjected to different treatments: 1) neat, oxidised in electrolytes of 20 wt% at 5 V: 2) HNO\(_3\), 3) H\(_2\)SO\(_4\)
electrolytes at 20 wt% and 0.5 V are compared to each other. Both the shape and the intensity of the various absorption bands change considerably from one electrolyte to the other.

The surface chemistry of the original carbon fiber practically does not change when it is oxidized in ammonium carbonate solution of 20 wt% concentration at 0.5 V (Fig. 2.2, Spectrum 1). Under the same conditions, oxidation in ammonium hydrogen carbonate results in a more significant chemical modification of the fiber surface (Fig. 2.2, Spectrum 2). The difference spectrum indicates the formation of several functional groups. The most intense, sharp absorption band at 1384 cm\(^{-1}\) (A) may be assigned to nitrate ion (NO\(_3^-\)) or nitrile oxide (N\(\rightarrow\)O), which form in the reaction of the neat carbon fiber with the electrolyte. Alexander and Jones [31] claim that mainly amide groups form in ammonium hydrogen carbonate according to the reaction of Scheme 2.1 [32]:

**Figure 2.2** Effect of electrolyte type on the difference spectra of carbon fibers oxidised in solutions of 20 wt% at 0.5 V; 1) (NH\(_4\))\(_2\)CO\(_3\), 2) NH\(_4\)HCO\(_3\), 3) HNO\(_3\), 4) NaOH, 5) H\(_2\)SO\(_4\)**
This assumption seems to be supported by the appearance of broad absorption bands around 1640 cm\(^{-1}\) (B; C=O str.) and 1400 cm\(^{-1}\) (C; C-N str.). However, carboxylate ions absorb also in the same frequency ranges (\(\nu_{as}\) and \(\nu_s\) stretching vibrations of CO\(_2^-\)) [30], therefore their presence cannot be excluded either. As a consequence, the exact composition of the fiber surface cannot be determined solely on the basis of FTIR spectroscopy.

The oxidation of carbon fiber in nitric acid, either in solution [33, 34] or in an electrochemical process [35], leads to the formation of different functional groups. Under the conditions applied in this work oxidation results in the appearance of a sharp absorption band at 1384 cm\(^{-1}\) (Fig. 2.2, Spectrum 3, A). As mentioned above, this vibration can be assigned to nitrate ion or nitrile oxide. The intensity of this absorption band increases with increasing electrolyte concentration and voltage. At low concentration and low voltage (3 %, 0.5 V), two other absorption bands can be observed at 3500 and 1640 cm\(^{-1}\), respectively, in the difference spectrum. The first can be assigned to hydroxyl groups, while the second either to quinones or to organic nitrites (C-ONO) [36, 37].

The fibers oxidized in NaOH reveal broad absorption bands of varying intensities (Fig. 2.2, Spectrum 4). The formation of sodium phenoxides is indicated by the vibrations appearing at 1050 and 570 cm\(^{-1}\) in the spectrum of a fiber oxidized at low concentration and voltage (3 wt%, 0.5 V). Such groups may form in the reaction presented in Scheme 2.2 [32]:

According to Sellitti, et al. [33] the treatment of oxidized carbon fiber with sodium hydroxide solution results in the transformation of carboxyl groups to carboxylates and in the hydrolysis of esters. The appearance of absorption bands at around 1600 (B) and 1400 cm\(^{-1}\) (C) seems to confirm the formation of carboxylic acid salts. However, sodium hydrogen carbonate has a very similar spectrum with a characteristic vibration at 1300 cm\(^{-1}\) [38,39], which can be clearly distinguished also in Spectrum 4 (D). Attention must be called here to the fact that at 1338 cm\(^{-1}\) a sharp peak (E) accompanied by a wide shoulder at 1450 cm\(^{-1}\) is superimposed onto the broad band of –COO\(^{-}\) stretching.
vibration in each spectrum recorded on fibers oxidized in NaOH. These absorptions may result from NaOH bonded to the fiber surface [39]; the assumption is supported by the fact that the intensity of this vibration becomes stronger with increasing electrolyte concentration, but does not change much with potential.

Compared to the neat fiber, the largest changes were observed in the difference spectra recorded on fibers oxidized in sulphuric acid solutions (Fig. 2.2, Spectrum 5). The frequency and intensity of the various absorption bands depend on the concentration of the electrolyte (Fig. 2.3). At 3 (Spectrum 1) and 5 (Spectrum 2) wt% characteristic absorption bands are located at 1401 and 1130 cm$^{-1}$. These bands can be assigned to the $\nu_{as}$ and $\nu_s$ stretching vibrations of the SO$_2$ group of covalent sulphonates (R-SO$_2$-OR’) and sulphates (R-O-SO$_2$-O-R’) [30]. At higher sulphuric acid concentrations (10 wt%, Spectrum 3 and 20 wt%, Spectrum 4) sulphonic acid (R-SO$_2$-OH) is also formed on the surface indicated by the bands appearing at 1200 cm$^{-1}$ (D), 1100-1000 cm$^{-1}$ (E) and 900-800 cm$^{-1}$ (F). These groups may form in the reactions shown in Schemes 2.3 and 2.4 [32,40]:

![Figure 2.3 Effect of electrolyte concentration on the difference spectra of carbon fibers oxidised in H$_2$SO$_4$ at 5 V; 1) 3, 2) 5, 3) 10, 4) 20 wt%](image)
The reactions of aromatic acids may also lead to the formation of sulphonic acid [32,40]. Moreover, peroxidisulphuric acid (HO₃S-O-O-SO₃H) is also formed in the electrolysis of sulphuric acid, which can further react through radical decomposition [41].

Figure 2.4 Dependence of integrated absorption of carbon fibers in the range of 1838-1550 cm⁻¹ on electrolyte concentration. Oxidation: H₂SO₄, 5 V
Besides the functional groups containing sulphur a further absorption band (B) appears at 1630 cm⁻¹ in the spectrum of fibers oxidized in H₂SO₄. This band is assigned to quinoidal carbonyl groups, which may form in reactions catalyzed by sulphuric acid (Scheme 2.5 [40]):

\[
\begin{align*}
  &\text{C} &\text{O} &\text{OH} \\
  + &\text{HO} &\text{C} &\text{O} &\text{OH} \quad \text{- H₂O} \\
  &\text{HO} &\text{O} &\text{O} &\text{OH}
\end{align*}
\]

Scheme 2.5

The intensity of all characteristic groups (SO₂, -OH and quinoidal C=O) of the fiber oxidized in H₂SO₄ increases with increasing electrolyte concentration (Fig. 2.4). At 20 wt% H₂SO₄ concentration the potential of the oxidation practically does not influence the shape of the spectra. All functional groups discussed above appear in them with varying intensity.

2.3.3. Interfacial adhesion

![Figure 2.5](image.png)

**Figure 2.5** Correlation between electrolyte concentration and interfacial adhesion (IFSS) measured in an epoxy matrix. Oxidation: 5 V, electrolyte: (○) H₂SO₄, (□) NaOH
The fragmentation experiments revealed considerable differences in the behaviour of the fibers oxidized under varying conditions. The interaction between the fiber and the epoxy matrix characterized by IFSS changes in a wide range depending on the type and concentration of the electrolyte, as well as on the voltage used. The IFSS values determined under the various conditions are also listed in Table 2.1. The average standard deviation of IFSS is around 20 %, which corresponds to the values published in the literature before [42-44]. Oxidation in ammonium carbonate and ammonium hydrogen carbonate solutions of 20 wt% at 0.5 V leads only to an insignificant increase of IFSS. Under the same conditions the effect of sulphuric acid is also moderate, while oxidation in nitric acid and sodium hydroxide results in enhanced IFSS values indicating strong interfacial interaction.

At low potential (0.5 V) oxidation in HNO₃ leads to an increase of IFSS with increasing concentration and increasing potential has the same effect at low electrolyte concentration (3 wt%). At high concentration and high potential IFSS decreases somewhat. This result emphasizes the importance of optimization, appropriate oxidation conditions must be used in order to achieve maximum efficiency.

The effect of electrolyte concentration on fiber/epoxy interaction is presented in Figure 2.5 for sodium hydroxide and sulphuric acid. The increase of IFSS is non-linear, the strength of interaction approaches a limiting value as a function of concentration. The existence of the tendency shown in Fig. 2.5 may be questioned because of the large standard deviation of the determination of IFSS (see Table 2.1). As a consequence, variance analysis was carried out to check the effect of electrolyte concentration on the interaction.
interfacial adhesion. The influence of both NaOH and H$_2$SO$_4$ proved to be significant at the 99.9 % level, thus we must accept the tendencies presented in Fig. 2.5. The effect of potential used for oxidation in electrolyte solutions of 20 wt% is shown in Fig. 2.6 for the same chemicals. While IFSS increases with increasing voltage in sulphuric acid, an inverse relationship is observed for sodium hydroxide. The use of the latter electrolyte at a concentration of 20 wt% and at 0.5 V resulted in the highest IFSS value among all the oxidizing media and conditions studied.

Figure 2.7  *SEM micrograph taken from the fracture surface after the fragmentation test of a CF/epoxy microcomposite prepared with the neat fiber*

Figure 2.8  *SEM micrograph taken from the fracture surface after the fragmentation test of a CF/epoxy microcomposite. Oxidation: H$_2$SO$_4$, 20 wt%, 5 V*
The effect of oxidation conditions on fiber/matrix adhesion is demonstrated well also by the SEM micrographs taken from the fracture surface of the microcomposites after the fragmentation test. Weak adhesion results in long fiber fragments pulled out of the polymer matrix (Fig. 2.7), while an increase in interfacial adhesion leads to a significant shortening of the fragments (Fig. 2.8).

2.4. Discussion

Electrochemical oxidation results in the formation of a wide variety of functional groups on the surface of carbon fibers. Their composition and amount depend on the type and concentration of the electrolyte, as well as on the potential used. In most cases the infrared spectra of the fibers are very complex, the absorption bands are often broad and overlap each other. Moreover, the intensity of the vibrations is weak, with the exception of those recorded on the fibers oxidized in sulphuric acid. Although these factors considerably complicated the quantitative evaluation of the spectra, a thorough analysis of the results revealed strong correlations between the chemical composition of the fiber surface and the strength of fiber/matrix interaction.

![Graph showing relationship between IFSS and A1403 cm^-1]  

**Figure 2.9** Relationship between the intensity of infrared absorption (1403 cm\(^{-1}\)) of fibers oxidised in H\(_2\)SO\(_4\) and their interfacial interaction with an epoxy resin.
Compared to the neat fiber, oxidation carried out in ammonium carbonate solutions does not result in a significant change either in the chemical composition of the fiber surface or in interfacial adhesion. Oxidation in ammonium hydrogen carbonate and in nitric acid leads to the formation of $\text{NO}_3^-$ or $\text{N}\rightarrow\text{O}$ groups on the surface. In the case of nitric acid, the appearance of these groups was accompanied by an increase in fiber/matrix adhesion, while oxidation in ammonium hydrogen carbonate resulted only in a very moderate improvement of IFSS. Also carboxylate ions and amide groups form in this electrolyte, which indicates that several chemical reactions take place during oxidation.

These results prove that fiber/matrix interaction is determined by the entire surface chemistry and not by single functional groups. The FTIR spectra of carbon fibers oxidized in sodium hydroxide and in sulphuric acid yield absorption bands at around 1630 and 1400 cm$^{-1}$, which were assigned to different functionalities. In the case of sulphuric acid, the measured IFSS values do not correlate at all with the integral absorption intensity of the peak at 1630 cm$^{-1}$ (Fig. 2.3, B). This suggests that quinoidal functional groups basically do not improve the strength of interaction between the fiber and the matrix. $\text{SO}_2$ groups seem to enhance interfacial adhesion as shown by Fig. 2.9, where IFSS is plotted against the intensity of the vibration appearing at around 1400 cm$^{-1}$. This band (Fig. 2.3, C) is assigned to the asymmetric $\text{SO}_2$ stretching vibration of sulphonates and sulphates [30].

![Figure 2.10](image)

**Figure 2.10** Correlation between the integral infrared absorption in the range of 1550 - 1150 cm$^{-1}$ of fibers oxidised in NaOH and their interfacial interaction with epoxy
Although the intensity of the broad bands related to the vibration of the -COO⁻ groups is relatively weak for the fiber oxidized in sodium hydroxide, a good correlation exists between IFSS and the absorption area integrated in the range of 1550-1150 cm⁻¹ (Fig. 2.2, Spectrum 4). The correlation presented in Fig. 2.10 indicates that interfacial interaction improves with increasing concentration of carboxylate ions on the fiber surface. However, the concentration of carboxyl groups is not the only factor influencing the behaviour of the fiber oxidized in NaOH. As it was shown in Figure 2.6, increasing potential of oxidation resulted in a decrease of IFSS. In order to obtain an insight into this phenomenon, IFSS values were plotted as a function of the intensity of the peak detected at 1338 cm⁻¹ (Fig. 2.2, Spectrum 4, E) in Fig. 2.11. This adsorption band can be assigned to sodium hydroxide bonded to the fiber surface. From the close inverse correlation we can conclude that the beneficial effect of increasing carboxylate ion concentration is gradually counteracted by the increase in the amount of NaOH adhering to the fiber from the electrolyte.

![Figure 2.11](image)

**Figure 2.11** Decrease of IFSS with increasing amount of NaOH bonded to the fiber surface

### 2.5. Conclusion

The oxidation of carbon fibers in different electrolytes under varying conditions resulted in considerable changes of surface chemistry, as well as fiber/epoxy interaction. Different functional groups are detected in the spectrum of the neat fiber and the groups forming in the oxidation process superimpose on them. The chemical composition of the surface of oxidized fibers is very complex in most cases, since several functional groups...
can form in each electrolyte. Surface chemistry is determined by the electrolyte, as well as by the other conditions of the process. The type of the functional groups which form during oxidation depends on the type of the electrolyte, while their number changes both with electrolyte concentration and voltage. Close correlation was found between surface chemistry and the strength of interfacial adhesion. The experiments revealed that improper oxidation conditions lead to poor adhesion. The strength of interaction is determined by the entire chemistry of the surface, and not by the concentration of a single functional group. The combination of infrared spectroscopy and fragmentation experiments proved to be useful for the characterization and optimization of the oxidation process.

2.6. References

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Chapter 3

Characterization of carbon fibers by cyclic voltammetry

3.1. Introduction

As mentioned previously, the advantageous properties of carbon fiber (CF) reinforced composites can be fully exploited only if the adhesion of the matrix and the fiber is sufficiently strong. Good interaction of the components is usually achieved by surface treatment, by their chemical coupling [1-4]. However, the surface of PAN based carbon fibers is rather inactive after production, and the number of functional groups is very low on the surface. In order to increase the surface activity of the fibers, they are subjected to an oxidation process. This can be carried out by various techniques in the gas phase or in liquids, but electrochemical oxidation is used the most often in industrial practice [5,6]. In process uses various electrolytes under the most diverse conditions. Beside the type of the electrolyte, its pH, the polarization potential, the duration of the treatment and the morphology of the surface also influence the chemical structure of the final product [7]. H₂SO₄ and NaOH are used the most often as electrolytes for the oxidation of carbon fibers.

As a result of the treatment, various functional groups form on the fiber surface and their type and number depends very much on the factors mentioned above. Extensive studies have been carried out in order to determine the surface composition of oxidized fibers. Depending on the technique used, as well as on oxidation conditions, various functional groups were detected on the fiber surface including carboxyl, phenolic hydroxyl, quinone type carbonyl, lactone, carboxylic acid anhydride, cyclic peroxide, etc. [8]. XPS is frequently used for the determination of the chemical composition of CF surface [8-12], but FTIR, microscopy and other techniques are also applied [13]. Unfortunately these investigations seldom yield a quantitative correlation between the surface composition of the fiber and interfacial adhesion in the composite. One of the techniques, which might be suitable for the characterization of carbon fibers is cyclic voltammetry (CV) [14-20]. With this technique, a larger surface area can be characterized than with XPS or microscopy, thus reflecting better the overall performance of the fiber. Background and peak currents supply information about the surface quality of the fiber and the intensity of the electrochemical processes taking place on it, while the peak potential depends on the character of the reaction [16-19]. Phenolic hydroxyl, quinone type carbonyl, and lactone groups were detected also with this technique on the fiber surface [21,22].

In Chapter 2, we analyzed the effect of electrochemical oxidation on the surface composition of carbon fibers and on fiber/matrix interaction. The chemical composition of the surface was characterized by diffuse reflectance infrared spectroscopy (DRIFT), while interfacial interaction by fragmentation. Close correlation was found between chemistry and adhesion for fibers oxidized in several electrolytes. However, analysis of the fibers by FTIR is rather difficult because of technical reasons, thus a new technique was looked for. The goal of this study was to characterize electrochemically oxidized carbon fibers by
cyclic voltammetry and compare the results to those obtained by IR spectroscopy, as well as by fragmentation tests.

### 3.2. Experimental

The characteristics of the fiber used in the study as well as the conditions of electrochemical oxidation were described in the previous chapter and they were also published in Ref. 23. The same matrix was used also for the study of interfacial adhesion. The characteristics of 21 selected samples were determined in our earlier study, of which only those oxidized in H₂SO₄ and NaOH are discussed in this chapter. As described there the surface chemistry of the fibers was analyzed by Fourier transform infrared spectroscopy (Mattson Galaxy 3020, Unicam) in diffuse reflectance mode (DRIFT). The interfacial shear stress (IFSS) was determined by fragmentation, the details of which can be also found in Chapter 2. IFSS was calculated by the Kelly-Tyson equation [24].

In cyclic voltammetry a bundle of fibers was used as working electrode and current vs potential correlations (CV traces) were recorded with 100 mV/s scan rate. In our experiments a platinum plate was used as counter electrode. The measurements were done in 1 M KNO₃ electrolyte and 2·10⁻³ M K₃[Fe(CN)₆] was used as electroactive probe. Saturated calomel electrode was used as reference.

### 3.3. Results

The results are discussed in three sections. The most important results related to the surface chemistry of the fibers is summarized first, then the results of the cyclic voltammetric measurements are presented in the next section. This is followed by the discussion of the relation between surface properties and adhesion.

#### 3.3.1. Surface chemistry

As mentioned in the previous chapter, the study of the chemical composition of carbon fibers by FTIR is difficult because of the intense absorption of the fiber, on the one hand, and the similarity in the diameter of the fiber and the wavelength range of infrared light. Nevertheless, careful sample preparation and measurements yield spectra, which reveal the chemical composition of the fiber surface. In order to facilitate evaluation, difference spectra were generated by subtracting the spectrum of the neat fiber from those of the treated ones. The difference spectra of fibers oxidized in H₂SO₄ and NaOH at 20 wt% and 0.5 V are compared to each other in Fig. 3.1. Both the shape and the intensity of the various absorption bands differ considerably in the two cases.
The fibers oxidized in NaOH revealed broad absorption bands of varying intensities (Fig. 3.1, Spectrum 1). The formation of sodium phenoxides is indicated by the vibrations appearing at 960 (A) and 570 (not shown in the figure) cm\(^{-1}\) in the spectrum of fibers oxidized at low concentrations and voltages. According to Sellitti et al. [13] the treatment of oxidized carbon fiber with sodium hydroxide solution results in the transformation of carboxyl groups to carboxylates and in the hydrolysis of esters. The absorption bands at around 1600 (B) as well as 1460 cm\(^{-1}\) (C) strongly supports this statement, but sodium hydrogen carbonate has a very similar spectrum with a characteristic broad band at 1300 cm\(^{-1}\) [25,26], which can be clearly distinguished also in Spectrum 1 (D). It must be noted here, that at 1338 cm\(^{-1}\) (E) a sharp peak superimposes onto the broad band of -COO\(^-\) stretching vibration in each spectrum obtained on fibers oxidized in NaOH. This absorption may result from NaOH adhering to the fiber surface. This explanation is confirmed by the increasing intensity of this vibration as electrolyte concentration increases; however, it depends much less on oxidation potential. The dependence of the intensity of two characteristic absorption bands is plotted against the concentration of the electrolyte used for oxidation in Fig. 3.2. Both the number of -COO\(^-\) groups and the amount

**Figure 3.1** Drift difference spectra of carbon fibers oxidized in 20 wt% solution of 1) NaOH, 2) H₂SO₄
of adsorbed sodium hydroxide increase with the concentration of NaOH. The former was shown to improve interfacial shear stress, while the second considerably deteriorated it [23].

![Graph showing the dependence of the number carboxylic groups (○) and the amount of adsorbed NaOH (□) on the concentration of the electrolyte used for oxidation (Potential: 5 V)](image)

**Figure 3.2** Dependence of the number carboxylic groups (○) and the amount of adsorbed NaOH (□) on the concentration of the electrolyte used for oxidation (Potential: 5 V)

Compared to the neat fiber, large changes were observed in the difference spectra recorded on fibers oxidized in sulfuric acid solutions (Fig. 3.1, Spectrum 2). The frequency and intensity of the absorption bands increase with increasing concentration of the electrolyte. Various sulfur containing groups form on the surface of the fiber. Sulfonates (R-SO₂-OR') and sulfates (R-O-SO₂-OR') absorb at 1401 (F) and 1130 (G) cm⁻¹. The presence of sulfonic acid (R-SO₂-OH) is indicated by the bands at 1200 (H), 1100-1000 (I) and 900-800 (J) cm⁻¹, but also peroxidisulfuric acid (HO₃S-O-O-SO₃H) may form during electrolysis in H₂SO₄ [27]. Besides the functional groups containing sulfur, the quinoidal carbonyl groups can also be detected on the surface of the fiber at 1630 (K) cm⁻¹. The formation of this group is catalyzed by sulfuric acid. The number of all groups (sulfuric and non-sulfuric) increases on the surface with increasing electrolyte concentration, as it was shown earlier in Chapter 2.

### 3.3.2. Cyclic voltammetry

The cyclic voltammograms of three fibers are compared to each other in Fig. 3.3. The electrochemical activity of the neat fiber is relatively weak. Slightly increased activity is observed on the fiber oxidized in NaOH, while the current measured on the fiber treated
in H₂SO₄ is even larger. In the measurement configuration used in this study, the following electrochemical process takes place on the surface of the fiber

\[ [\text{Fe(CN)}₆]^{3-} + e^- \rightarrow [\text{Fe(CN)}₆]^{4-} \]

The similarity of the peak potentials indicates that other electrochemical processes are absent in the scanned potential range [14]. Several characteristic quantities may be derived from the voltammograms. As mentioned above, the peak potential is determined by the electrochemical reaction, which takes place on the surface of the electrode. The background current indicates the “contamination” of the surface, i.e. the amount of reaction products formed during oxidation, while the cathodic peak current \( I_p \) depends on the intensity of the reaction. This latter quantity is used the most often in practice and it can be expressed quantitatively as [28]

\[ I_p = k n^{3/2} A D_s^{1/2} v^{1/2} C \quad 3.1 \]

where \( k \) is a constant, \( n \) the number of electrons involved in the oxidation/reduction process, \( A \) is the surface area of the electrode, \( D_s \) the diffusion coefficient of the probe molecule in the solution, \( v \) scan rate and \( C \) the concentration of the solution. In our case all parameters of Eq. 3.1 are kept constant, thus the changes observed in Fig. 3.1 must be caused by the quality of the surface, the type and number of active groups formed on it in the oxidation process.

**Figure 3.3** Comparison of the cyclic voltammograms of the neat ——— and oxidized fibers: NaOH -----, H₂SO₄ …….; (5 V, 20 wt%)
Characterization of carbon fibers by cyclic voltammetry

Fig. 3.4 presents the effect of electrolyte concentration on the voltammograms measured on fibers oxidized in H₂SO₄ at 5 V potential. Both peak current and peak potential increase continuously with increasing electrolyte concentration. This is in complete agreement with the results of DRIFT measurements showing that the number of all functional groups increases on the surface as a function of this variable. Below 5 V the potential used in the oxidation process does not influence either the shape of the voltammograms or the value of the characteristic quantities derived from them. However, at 5 V oxidizing potential, both the peak potential and the peak current are larger than in the other cases, which can be explained by the fact that the limiting potential of graphite electrodes in sulfuric acid is around 1.7 V [29]. Below this value, electrochemical process practically does not take place on the electrode.

The fibers oxidized in NaOH show a completely different behavior. Neither the oxidizing potential nor the concentration of the electrolyte influences significantly the voltammograms. The CV traces recorded as a function of oxidizing potential at 20 wt% electrolyte concentration are presented in Fig. 3.5. The peak potentials of the fibers oxidized at 0.5 and 5.0 V seem to differ somewhat from those of the others. Moreover, the background current measured on the fiber treated at 0.5 V is also somewhat larger than in the other cases. However, far reaching conclusions cannot be drawn from these small changes.

The quantitative evaluation of the characteristic values derived from the CV traces completely corroborates the conclusions drawn from the above presented qualitative analysis of the voltammograms. Peak current is plotted against the potential of oxidation in Fig. 3.6 for both electrolytes. Low peak currents and very small changes can be observed in the case of fibers oxidized in NaOH. For the fibers oxidized in sulfuric acid, Iₚ remains more or less constant at low potentials, but it increases more drastically at 5 V as it was mentioned in one of the previous paragraphs. Obviously, the intensity of electrochemical reactions is very low in NaOH, but also in H₂SO₄ below 5 V oxidization potential.

A somewhat different picture is obtained if peak current is plotted against the concentration of the electrolyte (Fig. 3.7). Although the peak currents measured on fibers oxidized in NaOH remain constant at a low value, again, the effect of H₂SO₄ concentration is more significant. Iₚ increases continuously as a function of electrolyte concentration and reaches the relatively high value of 14 mA at 20 wt%. As mentioned before, these observation are in agreement both with those made during the qualitative evaluation of the voltammograms, but also with the results of the FTIR measurements.

The results may be explained by the increase in the active surface of the carbon fiber as an effect of electrochemical oxidation in H₂SO₄. Apparently, the reduction and oxidation of the [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻ ions, respectively, take place only at certain active places of the electrode. The number of active places obviously increases when the fiber is oxidized in sulfuric acid. On the other hand, NaOH was shown to adsorb onto the surface of the fiber. This seems to block the electrochemical processes in spite of the fact that the number of carboxylate groups also increases on the fiber surface with increasing electrolyte concentration (see Fig. 3.2). Due to the adsorption of NaOH neither the background nor the peak current changes above 5 wt% electrolyte concentration.
Figure 3.4  Effect of electrolyte concentration on the CV traces of carbon fibers oxidized at 5 V potential in H₂SO₄; neat ——, 3 wt% -----, 10 wt% ……, 20 wt% ——

Figure 3.5  Cyclic voltammograms of carbon fibers oxidized in NaOH of 20 wt% concentration at various potentials; neat ——, 0.5 V -----, 2 V ……, 5 V ——
Figure 3.6  Dependence of peak current on the potential of oxidation at 20 wt% electrolyte concentration; (○) NaOH, (□) H₂SO₄.

Figure 3.7  Effect of electrolyte concentration on the peak current of CV traces recorded on oxidized carbon fibers. Oxidation potential: 5 V. (○) NaOH, (□) H₂SO₄.
3.3.3. Interfacial adhesion

Earlier, very close correlation was shown to exist between the number of certain functional groups and interfacial adhesion characterized by IFSS [23]. The results of cyclic voltammetry seem to be in agreement with those of DRIFT measurements at least for fibers oxidized in H$_2$SO$_4$. The correlation of IFSS and peak current is presented in Fig. 3.8. An excellent correlation exists between the two quantities, especially if we take into account the large standard deviation of both techniques. Obviously, peak current depends on the number of functional groups, which form on the fiber surface during oxidation, and these latter play an important role in interfacial adhesion. In this case cyclic voltammetry is an excellent tool for the characterization of carbon fibers treated by electrochemical oxidation. The relationship between the chemical composition of the surface and the electrochemical activity of the fibers is further corroborated by Fig. 3.9. Peak current is plotted against the intensity of infrared absorption detected in the range of 1838-1550 cm$^{-1}$. This absorption band was assigned to the vibration of quinoidal carbonyl groups [23]. A very good correlation is obtained between the two quantities sufficiently proving our above presented tentative explanation.

**Figure 3.8** Correlation of interfacial adhesion (IFSS) and peak current ($I_p$) for fibers oxidized in H$_2$SO$_4$
Fibers oxidized in NaOH behave in a completely different way. The relationship of IFSS and the peak current derived from the CV traces is presented in Fig. 3.10. The correlation is much looser than the one presented in the previous figure and with increasing peak current IFSS seems to decrease drastically. Earlier, the decrease of IFSS with changing oxidation parameters was explained by the adsorption of NaOH, a close correlation was observed between the intensity of IR absorption assigned to this compound and IFSS [23]. Obviously peak current increases slightly with this amount, but the NaOH layer hinders chemical reactions, or generally interaction at the fiber surface. In such cases CV measurements are less useful for the characterization of carbon fibers, than in cases when the composition of the fiber surface changes by chemical reactions.

3.4. Discussion

Apparently close correlations exist among the chemical composition of the fiber surface (DRIFT), its electrochemical activity (CV) and interfacial adhesion (IFSS) in the studied epoxy composites. However, several groups studied the effect of surface treatment on matrix/fiber interaction before and some of them reached different conclusions. In an extensive study Drzal et al. [4, 30-32] proved that the surface treatment of fibers improve interfacial adhesion in a two-part mechanism. First,
treatments remove a weak outer fiber layer initially present on the surface then chemical groups are added which increase interaction with the fiber. The treated fibers were exposed to the effect of heat and hydrogen, which removed most of the surface oxygen. Interfacial adhesion decreased, but exceeded significantly the one achieved with the untreated fiber proving that the removal of the weak layer is more important in the improvement of interfacial interaction than chemical bonding. Their results shed a different light onto the observations presented in this paper.

On the other hand, the fibers investigated in the above mentioned study were subjected only to a single, unspecified treatment [4, 30-32]. In this and in the previous chapter clear, quantitative correlations were established among the conditions of electrolytic oxidation, chemical composition of the fiber surface and IFSS [23]. The changes in the quality of the fiber surface induced both positive (H₂SO₄) and negative (NaOH) changes in interfacial adhesion. The correlations were strongly supported by independent CV measurements. If the removal of the weak surface layer of the fiber were the only or dominating mechanism in the determination of interfacial adhesion, such correlations would not exist. Moreover, instead of continuous functions, stepwise changes would be expected, since the weak layer is either removed or remains on the surface.

![Figure 3.10](image_url)

**Figure 3.10** Correlation of interfacial adhesion and the electrochemical activity of carbon fibers oxidized in NaOH

Although the quantitative correlations presented in this and in the previous chapter unambiguously prove the effect of surface chemistry on interfacial adhesion, further experiments must be carried out to resolve contradictions and verify tentative explanations.
Characterization of carbon fibers by cyclic voltammetry

Similar heat treatment as used by Drzal et al. [4] may reveal the existence and role of the weak layer also in the present case. The mechanism of the removal of this layer has not been determined yet and the role of chemical reactions may change from one composite to the other, as indicated by the same authors [4]. The presence of the adsorbed NaOH layer must be proved by direct measurements and CV must be carried out also without electroactive probe molecules to check the existence of active functional groups on the fiber surface. The results of the experiments designed to answer at least a part of these questions are reported in the next chapter.

3.5. Conclusions

Carbon fibers were oxidized in two electrolytes at different electrolyte concentrations and potentials. The chemical composition of the fiber surface changed considerably in both cases. The oxidation in H₂SO₄ resulted in the formation of considerable number of sulfur containing groups, but also quinoidal compounds were detected on the surface. The concentration of all functional groups increased with increasing electrolyte concentration at 5 V, but did not change as a function of oxidation potential in 20 wt% solutions below this value. Carboxylic functional groups formed on the fiber surface in NaOH, but some adsorbed NaOH also remained on the surface after oxidation. Cyclic voltammograms reflected the various changes differently. Peak potentials did not change significantly, while peak currents depended on the type of the treatment. Good correlation was found among peak current, the chemical composition of the fiber surface and interfacial shear stress (IFSS) in the case of H₂SO₄. The adsorbed NaOH interfered with the electrochemical reaction that takes place on the fiber surface. Moreover, IFSS decreased as the amount of adsorbed NaOH increased. Further experiments must be carried out to characterize the surface even more thoroughly, but also to explore all the potentials and possibilities offered by cyclic voltammetry.

3.6. References

2. Wake W.C., Polymer 19, 291 (1978)
Chapter 4

Adsorption of the electrolyte and its effect on interfacial adhesion

4.1. Introduction

Good adhesion of the polymer matrix and the fiber is usually achieved by electrolytic oxidation and chemical coupling [1-7]. A number of electrolytes can be used in the oxidation process including nitric acid, sodium carbonate, sulphuric acid, sodium hydroxide, etc. [8,5] and various functional groups form on the surface of the fiber in amounts depending on the conditions of oxidation [10-12]. Interfacial adhesion usually increases as a result, although quantitative correlation could be seldom established between the chemical composition of the fiber surface and matrix-fiber interaction [12-14].

In Chapter 2 a PAN based carbon fiber was subjected to electrochemical oxidation under a wide range of conditions (see also Ref.15). The type of the electrolyte, its concentration, the potential and the duration of the treatment were changed; altogether 160 different sets of conditions were used for oxidation. Close, quantitative correlations were found among the chemical composition of the fiber, its electrochemical activity and interfacial shear stress (IFSS) for fibers oxidized in sulphuric acid. However, the treatment in sodium hydroxide led to controversial results, which indicated the adsorption of the electrolyte onto the fiber surface resulting in inferior adhesion [16]. One of the main goals of the present study was the verification of this unexpected observation.

4.2. Preliminary experiments, considerations

The previous chapter proved that the chemical composition of the fiber surface changes considerably as an effect of electrolytic oxidation. New functional groups appear in the IR spectrum compared to that of the virgin fiber. Although the study of the chemical composition of the fiber by FTIR is difficult because of its intense absorption and interference, difference spectra allow even quantitative evaluation. Several broad vibration bands were identified in the spectrum, which were assigned to sodium phenoxides, carboxylates and sodium hydrogen carbonate. A sharp vibration appeared at 1338 cm\(^{-1}\), which could be detected with varying intensity on all fibers treated in NaOH; it was assumed to result from NaOH adhering to the fiber surface [16]. Several indirect observations supported this assumption: The intensity of the absorption increased strongly with increasing concentration of the electrolyte, but was almost completely independent of the potential of oxidation. The electrochemical activity of most fibers oxidised in NaOH was very low [16] and interfacial shear stress decreased with increasing intensity of this vibration, i.e. the amount of bonded sodium hydroxide. The lowest amount of adsorbed NaOH was accompanied by the largest IFSS of
37.7 MPa, while lower values of 24-25 MPa were measured on fibers containing more NaOH on their surface. Obviously, the continuous washing procedure used in the experiments removed most of the other electrolytes, but it was inefficient in the case of NaOH, which seems to adhere more strongly to the surface.

4.3. Experimental

The characteristic of the fiber used in the study, oxidation condition and sample preparation were described in Chapter 2. Most of the experiments reported in this paper were carried out on fibers oxidized in NaOH of 20 wt%, at 5 V and 20 cm/min. Various experiments were carried out to check the eventual adsorption of NaOH on the fiber surface and determine its effect on surface characteristic and adhesion. A bundle of fibers was soaked in 30 cm$^3$ distilled water as a function of time in order to determine the amount of adsorbed NaOH. After each soaking time the water was evaporated and the residues were dissolved in 20 cm$^3$ distilled water. The pH of the solution was determined by potentiometry and its sodium ion content by atomic absorption (Plazma Lab ICP-OES). The chemical composition of the treated, as well as the washed fiber was studied by Fourier transform infrared spectroscopy (Mattson Galaxy 3020, Unicam) in the diffuse reflectance mode (DRIFT). The local sodium content of the fiber surface was analyzed by an X-ray photoelectron spectrometer (Röntec EDR 288) attached to a Hitachi S-570 Scanning Electron Microscope (SEM). The fiber bundles soaked for various periods were used in cyclic voltammetry as working electrodes and current vs. potential correlations (CV traces) were recorded with 100 mV/s scan rate. A platinum plate was used as counter electrode and the measurements were done in 1 M KNO$_3$ solution with benzenesulphonic acid ($2\cdot10^{-3}$ M) as electroactive probe molecule. The interfacial shear stress was determined by the fragmentation of fibers embedded into an epoxy matrix. The details of the measurement can be found in Chapter 2.

4.4. Results

4.4.1. Dissolution

Bundles of fibers of approximately equal length and weight were soaked for predetermined periods of time in distilled water. The pH of the solutions obtained after the evaporation of the water and repeated dissolution was measured and the results are plotted against time in Fig. 4.1. A drastic increase of pH is observed at relative short times, at least compared to the total time scale of the experiment. In less than 10 hours the pH increases from 7 to about 9.5. After about two days, basicity reaches a constant value of around pH $\cong$ 10. Both the significant increase and the existence of a constant, saturation value indicate the dissolution of NaOH from the fiber surface. The significant deviations from the general tendency may be explained by the heterogeneity of the surface, the uneven distribution of adsorbed NaOH. An empirical function (Eq. 4.1) was fitted to the experimental points to describe the correlation quantitatively, i.e.
Adsorption of the electrolyte and its effect on interfacial adhesion

\[ pH = pH_0 + A (1 - e^{-bt}) \]

4.1

where \( pH_0 \) indicates the pH of distilled water, \( A = pH_\infty - pH_0 \) and \( b \) is a constant related to the rate of pH change. Because of the significant scatter of the points, the fit is relatively poor (\( R^2 = 0.7979 \)), but the correlation reflects well the time dependence of pH, indeed. The equation indicates that 95 % of the adsorbed NaOH dissolves from the surface in about 5 hours. This result proves that NaOH adheres strongly to the surface and the usual washing technology cannot remove it completely. Besides the pH of the solution, its sodium ion concentration was also determined. The time dependence of Na\(^+\) concentration is similar to that of pH, the number of ions continuously increases with time. However, the scatter of the values is even larger than for pH (\( R^2 = 0.6826 \)) and the rate of concentration change seems to be somewhat different than in Fig. 4.1. If we fit an equation similar to Eq. 4.1 to the experimental points, 95 % dissolution is reached in about 40 hours. In spite of the large scatter and the uncertainty, these results strongly corroborate our initial assumption and prove that NaOH is adsorbed to the surface of the fiber during oxidation and it dissolves slowly in water.

![Figure 4.1](image.png)

**Figure 4.1** Dissolution of NaOH from the surface of fibers oxidised at 5 V and 20 wt% Dependence of pH on soaking time. (O) experimental data, ——— fitted correlation
4.4.2. Fiber characterization

The fiber soaked in water was characterized by various techniques. The comparison of the spectra taken from the oxidized and the washed fiber, respectively, indicates some changes in their surface characteristics. Among other changes, the absorption band assigned to NaOH at 1338 cm$^{-1}$ almost completely disappears from the spectrum. The intensity of this vibration is plotted against time in Fig. 4.2. The correlation resembles very much those presented in Figs. 4.1 and 4.4, but with changes in the opposite direction. Intensity sharply decreases at short times, then it reaches a constant, equilibrium value. If a slightly modified equation, similar to Eq. 4.1, is fitted to the data ($R^2 = 0.9864$), it shows that 95% dissolution is reached at around 23 hours. These results supply a further proof for the dissolution of NaOH from the surface. Significant amount of sodium could be detected on the surface of the oxidized fiber by EDR analysis and the concentration of this element decreased drastically on washing. However, large differences were observed in the local concentration of sodium, which corroborates our conclusion about the heterogeneous, uneven distribution of NaOH, which was drawn from the results of pH measurements. Soaked fibers were also studied by cyclic voltammetry. If oxidation-reduction of electroactive groups occurs on the fiber surface, a characteristic peak appears on the voltammogram. The peak potential is determined by the type of the electrochemical reaction, while peak current by its intensity, i.e. the number of reactions taking place on the surface of the electrode [17-
Several voltammograms are presented in Fig. 4.3. The oxidized fiber and the one soaked for 1 hour (not shown) do not have any activity, electrochemical reaction does not take place at their surface. With increasing soaking time a characteristic peak appears on the CV trace, and its intensity continuously increases with time. We assume that water dissolves NaOH from the fiber surface, active groups become free and enter into reaction during the measurement. The traces indicate irreversible reaction of the probe molecule, which is in accordance with literature data [21].

![Figure 4.3 Cyclic voltammograms taken on carbon fibers soaked in distilled water for different times, —— 0 hour, ----- 2, ······ 4, 8 hours](image)

4.4.3. Interfacial adhesion

As described in the previous chapter, interfacial adhesion decreases with increasing intensity of the vibration at 1338 cm$^{-1}$ assigned to adsorbed NaOH. The removal of sodium hydroxide was expected to improve interfacial adhesion. The results presented in Fig. 4.4 strongly support this assumption. The time dependence of IFSS is very similar to that of pH. IFSS rapidly increases and reaches a constant value at longer times, which remains the same even after 240 hours. The very high value of 44 MPa corroborates our earlier observation that oxidation in NaOH is very efficient, sufficient number of reactive groups form on the surface, but adsorbed NaOH covers the active surface and/or creates weak sites and deteriorates IFSS. An equation similar to Eq. 4.1 was fitted to the experimental points also for IFSS. The fit is excellent ($R^2 = 0.9768$), the calculated correlation is presented in Fig. 4.4 as a solid line. The parameters of the equation allow the calculation of the time to remove 95 % of adsorbed NaOH, or more
exactly to achieve 95 % of maximum IFSS. This time is around 20 hours indicating very strong adsorption of NaOH to the fiber surface. Only long and very intensive washing is able to remove the adsorbed electrolyte from the surface.

4.5. Discussion, correlation

Practically all results point to the same direction and prove that NaOH strongly adsorbs to the surface of carbon fibers during their continuous electrolytic oxidation. Adsorption is indicated by the appearance of the vibration at 1338 cm\(^{-1}\) in the DRIFT spectrum of oxidized fibers. The adsorbed electrolyte can be removed by washing with water during which the pH and Na\(^+\) ion concentration of the water continuously increases. As a result of washing the above mentioned adsorption band disappears from the IR spectrum and the intensity of other vibrations increases. The electroactivity of the fiber increases with soaking time, a peak appears on the cyclic voltammogram recorded on washed fibers. Finally, interfacial adhesion improves drastically with the removal of adsorbed NaOH. Useful information for practice and further proof for the adsorption of NaOH is supplied by the analysis of the time dependence of its removal. Very similar correlation were obtained from several experiments, the pH of the washing water, the intensity of the vibration related to adsorbed NaOH, the peak current detected by CV, and IFSS changed according to similar functions. This similarity is unambiguously

![Figure 4.4](image)

**Figure 4.4** Dependence of interfacial adhesion of epoxy/carbon fiber microcomposites on the soaking time of fibers oxidised in NaOH at 5 V and 20 wt%. (○) experimental data, (●) omitted from the fitting procedure, ——— fitted correlation
proved by fig. 4.5 where IFSS is plotted against the pH of the water used for washing the fibers. A clear, practically linear correlation exists between the two quantities measured independently from each other proving that the changes are related to the same phenomenon, the removal of NaOH from the fiber surface. Although the phenomenon is clear, the reason for the strong adsorption needs further study and explanation.

Figure 4.5  Linear correlation of the pH of the washing water and the IFSS of epoxy microcomposites prepared from the washed fibers

4.6. Conclusions

The study proved that sodium hydroxide electrolyte adsorbs to the surface of carbon fibers oxidized in a continuous anodic electrochemical process. NaOH is removed slowly, more than 20 hours are needed to create a relatively clean surface. The adsorbed NaOH blocks reactive groups and hinders coupling between the matrix and the fiber. Its removal increases both the chemical and the electrochemical activity of the fiber and leads to a significant improvement of interfacial adhesion. Interfacial shear stress of epoxy microcomposites prepared with the neat, unoxidized fiber is 17.3 MPa, which increases to 27.5 MPa after oxidation in NaOH of 20 wt% at 5V and becomes 44.8 MPa after thorough washing. Although NaOH is a very efficient electrolyte for the anodic oxidation of carbon fibers, it cannot be used without the appropriate technology, which removes the NaOH adhered to the fiber surface.
4.7. References

Chapter 5

Chemical modification and coupling

5.1. Introduction

The application of carbon fiber reinforced composites is expected to increase in all fields of life. While earlier military and aerospace applications dominated, today these materials are used for the production of sports wares, but they are also applied in increasing quantities by the building and automotive industries [1]. The advantages of fiber reinforced composites, i.e. high stiffness and strength, can be fully utilized only if the adhesion between the fiber and the matrix material is excellent. Strong adhesion of the components is achieved by surface treatment and chemical coupling. Bonding of the fiber to the matrix is straightforward in glass fiber reinforced composites, since the active hydroxyl groups located at the fiber surface react readily with functionalized silane compounds [2].

Chemical coupling is more complicated in carbon fiber reinforced composites since the fibers are rather inactive after carbonization. As a consequence, before treating with a sizing material the fibers must be modified in order to form reactive groups on their surface [3-5]. The most often used technique of activation is the electrochemical, anodic oxidation, which results in the formation of active hydroxyl, carboxyl, phenolic hydroxy, quinone type carbonyl, lactone, carboxylic acid anhydride, cyclic peroxide, etc. groups [6-13]. The effect of oxidation on the surface chemistry of fibers and interfacial adhesion, as well as its dependence on the conditions of oxidation were reported in Chapter 2-4 of this Thesis. However, oxidation alone does not make possible the use of fibers as reinforcements in advanced composites, they are covered with a sizing, which contains an appropriate coupling agent. Epoxy or amino compounds are used the most often for coupling carbon fibers to epoxy matrices [14-17], but other proprietary treatments are also used [18,19].

The possible coupling of carbon fiber (CF) to an epoxy matrix with various compounds was investigated in this part of study. The bonding of four potential coupling agents onto the surface of an oxidized carbon fiber was determined by a dissolution technique. The four compounds contained reactive amino, epoxy and isocyanate groups. The chemical structure of the adsorbed layer and the possible coupling reactions were studied by FTIR spectroscopy. An attempt was made to correlate the amount and structure of the bonded coupling agent layer with the strength of fiber/matrix interaction in CF/epoxy microcomposites.
5.2. Experimental

The same non-treated, anodically oxidized carbon fiber described earlier was used in the experiments. The matrix polymer was also the same, as well as the preparation of epoxy microcomposites (see Chapter 2). Four different compounds were used as coupling agents in the experiments. Triglycidyl isocyanurate (TGIC) and 3-glycidoxy-propyl-triethoxysilane (EPS) contained reactive epoxy groups, while N-(3-trimethoxysilane-propyl)ethylene diamine (AMS) a primary and a secondary amino group. The fourth coupling agent was 4,4’-diphenylmethane-diisocianate (MDI). The grade, supplier and chemical structure of the coupling agents are listed in Table 5.1. The fiber was treated with various amounts of the coupling agents, with 0.5, 1.0, 1.5, 2.0 and 3.0 wt% of TGIC and MDI, while with 1, 2, 3, 4 and 5 wt% of the silanes.

Table 5.1 Compounds used as coupling agents in the experiments

<table>
<thead>
<tr>
<th>Abbr.</th>
<th>Formula</th>
<th>Grade</th>
<th>Producer</th>
<th>Treatment (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGIC</td>
<td>![TGIC structure]</td>
<td>Araldit PT 810</td>
<td>Ciba Geigy</td>
<td>0.5, 1, 1.5, 2, 3</td>
</tr>
<tr>
<td>EPS</td>
<td>(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;O)₃Si+CH₂=CH-C≡N</td>
<td>GF 82</td>
<td>Wacker</td>
<td>1, 2, 3, 4, 5</td>
</tr>
<tr>
<td>AMS</td>
<td>NH₂-CH₂-CH₂-NH-CH₂-CH₂-Si(OCH₃)₃</td>
<td>GF 91</td>
<td>Wacker</td>
<td>1, 2, 3, 4, 5</td>
</tr>
<tr>
<td>MDI</td>
<td>O=C=N-CH₂-O=N=C=O</td>
<td>M 48</td>
<td>Borsod-chem</td>
<td>0.5, 1, 1.5, 2, 3</td>
</tr>
</tbody>
</table>

A 1 m long bundle of fibers containing 48000 individual filaments was placed into a solution containing the coupling agent at a given concentration. The solution was stirred for 10 min, then the solvent was evaporated at room temperature. The fibers covered by TGIC were reacted at 120 °C for 24 hours, while the treatment with the silanes was followed by condensation in saturated water vapor at ambient temperature also for 24 hours. The amount of bonded coupling agent was determined by dissolving the excess, non-reacted material with an appropriate solvent, then measuring the concentration of the solution with FTIR spectroscopy [20-22]. Also the chemical reactions at the fiber surface and the structure of the bonded coupling agent layer were analyzed by FTIR. Both
transmittance and DRIFT spectra were used for the characterization of the treated fiber. The intense absorption caused by the black color of the carbon fiber and the relatively small amount of coupling agent on its surface rendered the measurement and evaluation very difficult, the quality of the spectra was rather poor in most cases. Interfacial shear stress (IFSS) was determined by fragmentation as described earlier. IFSS was calculated by the Kelly-Tyson equation [23].

5.3. Results

The experimental results are presented in three sections. First dissolution curves are shown, which are related to the adsorption and/or chemical bonding of the four compounds onto the surface of the carbon fiber. Chemical changes during surface treatment are analyzed with the help of FTIR spectra. The effect of treatment on matrix/fiber adhesion is shown in the last section. The correlation of the results obtained in various measurements is discussed in a separate section together with the consequences on composite strength and practical applications.

![Figure 5.1](image.png)  
**Figure 5.1** Dissolution curve of two coupling agents; (○) EPS, (□) TGIC
5.3.1. Bonding

The dissolution technique applied here proved to be a very efficient tool for the study of the surface treatment of particulate fillers [20-23]. The adsorption of surfactants used in non-reactive treatment usually increases up to a saturation value [20, 21, 24], while in the case of reactive treatment more complicated correlations were observed between the amount of coupling agent used for the treatment and that bonded irreversibly to the surface [22]. The results of dissolution experiments supply valuable information about the interaction of the treated surface and the surfactant or coupling agent. The technique can be used also for the optimization of surface treatment technology and surface coverage [21].

Although both TGIC and EPS contain active epoxy groups in their structure, they are assumed to bond to the surface by different coupling mechanisms. Nevertheless, their dissolution curves are very similar (Fig. 5.1). Proportional bonding occurs up to a certain coupling agent concentration, i.e. all the material applied strongly adheres to the surface, it cannot be dissolved with the solvent used. A slight maximum can be observed in the dissolution curve of EPS. Since the maximum is not very pronounced, it might be an artifact due to the standard deviation of the measurement. On the other hand, the association or reaction of the coupling agent molecules with each other might also result in the appearance of such a maximum on the dissolution curve.

The maximum in the amount of bonded TGIC is much more pronounced, it cannot be explained with experimental error. Moreover, this maximum is much more difficult to understand than in the case of EPS. Initially we assumed that the epoxy groups of this compound react with the active -OH functionality of the surface, on the one hand, and with the amine hardener of the matrix polymer, on the other. However, the maximum can be explained only with the reaction of the coupling agent molecules with each other. The probability of such reactions, if they exist at all, increases with increasing surface coverage. The exact nature of the reaction or reactions leading to the observed dissolution curve are not known at the moment, one can only speculate, at most. Nevertheless, Fig. 5.1 reveals that both coupling agents bond irreversibly to the surface of the carbon fiber up to a certain, not very high concentration.

The other two compounds used in these experiments, i.e. AMS and MDI show a completely different behavior (Fig. 5.2). The amount of bonded material increases continuously as the quantity used for the treatment increases. At the highest concentration of AMS almost all coupling agent is bonded to the surface. Also MDI is bonded in increasing amounts, but a part of this compound is obviously dissolved by the solvent, the dissolution curve runs far below the broken line indicating proportional bonding. The dissolution curves observed in Fig. 5.2 indicate the polymerization of the coupling agents on the surface of the fiber. Similar behavior was observed during the treatment of CaCO₃ with two aminosilane coupling agents of different structures [22]. Moreover, it is known that silane coupling agents readily form polysiloxanes on solid surfaces [25-29] and MDI is also very reactive, it takes part in various reactions yielding urethanes and related compounds. The dissolution curves shown in Figs. 5.1 and 5.2 forecast considerably different coupling efficiency of the various compounds used in these experiments.
5.3.2. Reactions, coupling

The four compounds were selected as potential coupling agents with definite ideas and reaction mechanisms in mind. Literature references indicate that a large number of active groups form on the surface of CF in anodic oxidation [12]. Hydroxyl and acid groups are very active, thus we assumed that TGIC reacts through its epoxy groups with them, i.e.

\[
\begin{align*}
\text{CH}_2\text{CHCH}_2\text{O} &+ \text{CF}\text{OH} \rightarrow \text{CH}_2\text{CHCH}_2\text{O}\text{CF} \\
\end{align*}
\]

Scheme 5.1

The epoxy group may react also with the acid groups of the surface in a very similar way. However, such reactions take place only at high temperatures, thus the fibers covered with TGIC were heat treated in an oven at 120 °C for 24 hours. In further reaction steps the remaining epoxy groups of TGIC may react with the secondary -OH group formed in the reaction of Scheme 5.1

![Figure 5.2](image-url)  
**Figure 5.2** Dependence of the amount of bonded coupling agent on the quantity used for the treatment; (∇) AMS, (Δ) MDI
Coupling to the matrix may occur in similar reactions, the free epoxy groups of TGIC react both with the amine hardener and the secondary -OH groups of the polymer. At high surface coverage such secondary reactions might lead to the polymerization of TGIC, which may be further promoted by moisture traces adsorbed on the fiber surface.

**Figure 5.3** FTIR spectra of TGIC, non-treated and treated carbon fiber. A) carbon fiber (DRIFT), B) TGIC in KBr (absorbance), C) CF treated with 3.0 wt% TGIC (difference spectrum, DRIFT)
Chemical modification and coupling

The FTIR spectra of the non-treated and treated fiber as well as TGIC are compared to each other in Fig. 5.3. The poor quality of the spectra taken on the fibers is obvious from the figure. Nevertheless, the most important absorption bands can be always identified. The strong absorption of the fiber at around 3450 cm\(^{-1}\) indicates the presence of associated -OH groups, which can be related to adsorbed water, but also to the active -OH groups of the carbon fiber. The presence of water is supported by the vibration detected at 1630 cm\(^{-1}\) on the spectrum of the fiber, as well by the absorption band appearing at 3450 cm\(^{-1}\) on the spectrum of TGIC recorded in KBr. This latter spectrum and also that of the treated fiber are dominated by the strong \(\nu\)C=O vibration at 1690 cm\(^{-1}\) and by the \(\beta\)\textsubscript{CH\(_2\)} absorption at 1464 cm\(^{-1}\), both characteristic for the isocianurate ring of TGIC. A closer analysis of the spectra shows that the vibration of the epoxy ring at 3068 cm\(^{-1}\) disappears from the spectrum of TGIC during treatment and also the skeleton vibrations of the isocianurate ring detected at lower frequencies (1330-850 cm\(^{-1}\)) change considerably. Although these changes do not prove, but they at least indicate that TGIC reacts with the

Figure 5.4 Polycondensation of EPS on the surface of carbon fiber. A) EPS in cyclohexane, B) DRIFT difference spectrum of CF treated with 5.0 wt% EPS
functional groups of the carbon fiber and the reaction goes through the epoxy ring, as expected.

![Figure 5.5](image)

**Figure 5.5** Surface treatment of CF with AMS. A) AMS in cyclohexane; DRIFT difference spectra of CF treated with B) 1.0 wt%, C) 3.0 wt% D) 5.0 wt% AMS

A much simpler scheme and a better explanation can be given for the bonding of EPS onto the fiber surface. As it was indicated before, organofunctional silane coupling agents undergo polycondensation in the presence of moisture and form a polysiloxane layer
Although EPS also contains an active epoxy group, this latter reacts only at high temperatures. The structure of the formed polysiloxane layer depends on the structure of the organofunctional group [22]. In spite of the poor quality of the spectrum, the above mentioned reactions are shown clearly by Fig. 5.4. After treatment, the well defined spectrum of the monomeric silane changes into a broad, diffuse band characteristic for polysiloxanes. The spectrum is dominated by the $\nu_{as}$ vibration of the Si-O-Si bonds appearing in the 1250-1080 cm$^{-1}$ range. Coupling to the epoxy matrix is expected to take place through the reaction of the epoxy functionality of the silane and the amine group of the hardener. The maximum in the dissolution curve can be explained by the loose structure of a polysiloxane of relative small molecular mass formed from EPS on the surface of the fiber [30,31] and by the dissolution of unattached, physisorbed polysiloxane layers.

The chemistry of the aminosilane is very similar to that of EPS. A polysiloxane layer develops on the surface of the fiber also in this case (Fig. 5.5), but the structure of this layer differs considerably form the one forming from EPS. The comparison of the spectra obtained in this study to those published in the literature shows that EPS forms a loose polycyclic structure [30,31], while the treatment with AMS results in a hard ladder type polymer layer [32]. The quantitative analysis of the spectra shows a linear correlation between the IR intensity determined in the range of 1190-950 cm$^{-1}$ and the amount of coupling agent used for the treatment (Fig. 5.6). The strong correlation proves that the entire amount of aminosilane used for the treatment is bonded strongly to the carbon fiber, it cannot be dissolved. Beside the $\nu_{as}$ Si-O-Si vibrations in the range indicated above also absorption bands related to the vibration of the amino groups can be detected in the spectra: the $\beta$NH$_2$ vibration at 1551 cm$^{-1}$ and the $\nu$C-N absorption in the range of 1320-1250 cm$^{-1}$. Coupling to the matrix is supposed to take place through the reaction of the reactive amino groups.
When MDI was selected as a potential coupling agent we assumed that the extremely reactive isocyanate group reacts with the active sites of the fiber and especially with the -OH and -COOH groups, i.e.

\[ R_1 N\equiv C\equiv O + HO \rightarrow R_1 NH-C-O \]

**Scheme 5.4**

The isocyanate molecules may react further with the active hydrogen of the formed urethane, leading to the formation of an allophanate group.

**Figure 5.6** Dependence of the amount of bonded polysiloxane determined by FTIR in the range of 1190-950 cm\(^{-1}\) on the quantity of AMS used for the treatment
The reactions with carboxyl groups created on the fiber surface during anodic oxidation lead practically to the same result. The fiber may be coupled to the polymer matrix through the secondary -OH groups formed during the curing of the resin.

Further reactions of the -NCO group with secondary -OH and amine groups lead to the cross-linking of the interlayer. Beside the formation of a bonded coupling agent layer, also some unattached polymer may form especially in the presence of moisture traces. This latter would explain the less than proportional bonding of MDI to the fiber surface (see Fig. 5.2).

The above presented reaction schemes are strongly corroborated by the analysis of the FTIR spectra. The spectrum of MDI is dominated by the very strong $\nu\text{N}=\text{C}=\text{O}$ vibration appearing at 2280 cm$^{-1}$ (Fig. 5.7). This band is absent in all spectra taken from the treated fibers indicating the complete reaction of the isocyanate. A series of new vibration bands can be detected on these spectra instead. A thorough analysis indicates the presence of $\nu\text{C}=\text{O}$ vibrations in the range of 1700-1615 cm$^{-1}$, $\delta\text{NH}$ deformation out-of-plane vibrations between 1600 and 1500 cm$^{-1}$, and $\nu\text{C}-\text{N}$ absorptions in the range of 1340-1200 cm$^{-1}$, all characteristic for urethane chemistry. A quantitative analysis of the spectra shows
that the intensity of the $\nu$C-N vibration increases linearly with the amount of MDI used for the treatment, while that of the $\delta$NH absorption displays a well defined maximum around 1.5 wt% coupling agent concentration (Fig. 5.8). The appearance of the maximum indicates the transformation of the primary structure formed by the reaction of the active surface of the fiber and MDI.

![Figure 5.7](image)

**Figure 5.7** Chemical transformation of MDI during treatment; A) MDI in KBr, B) DRIFT difference spectrum of CF treated with 3.0 wt% MDI

In spite of the difficulties encountered in FTIR analysis, valuable information was obtained about the reactions taking place on the surface of the fibers during treatment. The reactions assumed in advance take place as expected, but also secondary reactions occur in all cases. The formation of a polymer layer was unambiguously proved in the case of the silanes and MDI, but the maximum in the dissolution curve of TGIC also indicates the occurrence of side reactions. According to the spectra, the structure of the polysiloxane layer formed from AMS and EPS, respectively, seems to be different. A rigid layer of high cross-link density forms from the former, while a loose, low molecular weight polymer develops from the latter. The thickness and properties of these coupling agent layers must be related to the strength of fiber/matrix interaction.
Figure 5.8 Changes in the amount of functional groups on the surface of CF as a function of MDI quantity used for the treatment; (Δ) νN-H vibration at 1508 cm\(^{-1}\), (∇) νN-C absorption at 1313 cm\(^{-1}\)

Figure 5.9 Dependence of IFSS on the amount of coupling agent used for the treatment; (○) EPS, (□) TGIC
5.3.3. Adhesion

The strength of adhesion between the fiber and the matrix polymer was determined by fragmentation. Similarly to the dissolution study, the fiber was covered with different amounts of the four compounds, embedded into the epoxy matrix and tested by the standard method. The dependence of interfacial shear stress (IFSS) on surface coverage is presented in Fig. 5.9 for EPS and TGIC. A maximum is observed in IFSS as a function of the amount of coupling agent used for the treatment. Both correlations resemble very much the dissolution curves presented in Fig. 5.1. IFSS increases strongly when the fiber is treated with EPS, but some improvement is observed in adhesion also when TGIC is used. The increase in IFSS seems to be closely related to the amount of proportionally bonded coupling agent. Stronger adhesion can be achieved with EPS, because more of this compound bonds to the surface of the fiber than TGIC.

![Graph showing the correlation of IFSS with coupling agent concentration for APS and MDI.](image)

**Figure 5.10** Effect of surface coverage on matrix/fiber adhesion; (V) AMS, (Δ) MDI

Fig. 5.10 presents the correlation of IFSS with coupling agent concentration for the other two compounds. The same scale is used for IFSS as in the previous figure. The treatment by this two compounds results only in a marginal increase of adhesion. A small maximum is observed when MDI is used, at higher surface coverage the strength of interfacial adhesion falls below the value obtained with the non-treated fiber. The aminosilane coupling agent does not improve adhesion, only a very slight increase is observed in IFSS with increasing surface coverage. The correlations presented in Fig. 5.10 do not resemble the dissolution curves shown in Fig. 5.2. The relative coupling efficiency of the four compounds, as well as optimum surface coverage can be clearly
established from the results, but it is very difficult to find a correlation between adsorption and adhesion.

5.4. Discussion

A close correlation was observed between the dissolution curve and the dependence of fiber/matrix adhesion on surface coverage in some cases, while no similarity whatsoever existed between these quantities for other compounds. In order to obtain a better insight into the interrelation of the results, IFSS was plotted against the amount of bonded coupling agent in Fig. 5.11. A very close linear correlation was obtained for EPS and TGIC. The relationship proved to be valid for all values both before and after the maximum observed either in IFSS or on the dissolution curve. This result clearly shows that reactive coupling takes place, as expected, and the number of attached functional groups determines IFSS. Surface coverage has an optimum, which is determined by the chemical reactions taking place at the fiber surface. The amount of bonded material is limited mostly by the secondary reactions of the coupling agents.

![Figure 5.11](image)

**Figure 5.11** General correlation between IFSS and the amount of bonded coupling agent. Symbols are the same as in Figs. 5.1 and 5.2

It is more difficult to find an acceptable explanation for the lack of coupling efficiency in the case of AMS and MDI. Similarly to EPS, also the aminosilane forms a polysiloxane layer on the fiber surface, moreover, active amino groups are available in this layer to react with the epoxy matrix during curing (see Fig. 5.5). However, coupling does
not occur, IFSS is independent of the amount of bonded AMS. The tentative explanation developed is based on the different structure of the polysiloxane layers formed from the two silanes. The strong, hard layer developed from AMS as well as its high cross-link density hinder the amino groups in taking part in coupling reactions. A similar phenomenon was observed by Hamada et al. [29] in aminosilane treated glass fiber reinforced epoxy composites. As a consequence, only a few of the amino groups react with the matrix polymer. Moreover, these must compete with the amine hardener for active epoxy groups. On the other hand, the epoxy groups in the loose polymer layer formed by EPS possess a much higher reactivity, thus their reaction with the amine hardener leads to the coupling of the fiber and the matrix and to better adhesion.

At low surface coverage MDI behaves similarly to EPS and TGIC, it improves interfacial strength proportionally to the amount of bonded surfactant. With increasing layer thickness IFSS decreases sharply indicating the formation of a weak boundary layer. Such weak interphases were observed in epoxy/CF composites before [19]. Obviously failure occurs in this thick interlayer and not at either of the interfaces. This conclusion is strongly corroborated by the SEM micrograph taken from the surface of a fiber pulled out from the matrix in the fragmentation test (Fig. 5.12). The micrograph clearly shows the inhomogeneous distribution of the coupling agent on the surface of the fiber, as well as the rupture of the interlayer.

Figure 5.12  SEM micrograph taken from the surface of a fiber after the fragmentation test; treatment: 1.5 wt% MDI
5.5. Conclusions

The four compounds selected as potential coupling agents for epoxy/carbon fiber composites show completely different coupling efficiencies. All four react at the surface of the fiber more or less according to the chemistry assumed in advance, before the experiments. EPS, AMS and MDI form a polymer layer on the surface, but TGIC also enters into secondary reactions during treatment. The amount of bonded coupling agent depends very much on the chemistry taking place on the fiber surface and also on the structure of the formed layer. The results prove the importance of the optimization of surface treatment; both the type and the amount of the coupling agent affects strongly interfacial adhesion. IFSS is determined by the thickness and properties of the formed coupling agent layer. The combination of dissolution experiments with the fragmentation test yields valuable information about the processes taking place on the surface of the fiber during treatment, facilitates the selection of the best coupling agent, as well as the development of an optimum surface treatment technology.

5.6. References

Chapter 6

Coupling of carbon fibers to polycarbonate

6.1. Introduction

As mentioned before the appropriate adhesion of the components is a basic requirement for the preparation of all fiber-reinforced composites. Adhesion and coupling is especially important in thermoplastic matrices, because they usually contain very few reactive groups, if any [1-3]. In thermoplastics, interfacial adhesion and the properties of the composites are strongly influenced also by the characteristics of the matrix polymer [4] and by processing conditions [5-9]. Because of the potential and excellent properties of thermoplastics (improved impact resistance, lower sensitivity to water, higher prepreg stability, etc.) [10], intensive research is being done on their carbon fiber reinforced composites. Polycarbonate can be used as matrix both in advanced composites [11], but especially in injection molded short fiber reinforced parts [12,13]. Although several studies were carried out to reveal the factors influencing the properties of these composites and to improve interfacial adhesion of the components [2,14,15], a number questions remained open.

Polycarbonate is a semicrystalline polymer, its properties are also influenced by the crystalline structure. Several studies focussed on the formation of a transcrystalline layer on the surface of the fiber [16,17] and on its effect on properties [8]. The results showed that such a layer forms under isothermal conditions, indeed, but only in a very long time [16,17]. Almost hundred hours are needed to form a transcrystalline layer, which can be detected by polarization optical microscopy. Ranghavedran et al. [9] showed that polycarbonate is amorphous in composites prepared under practical conditions, transcrystallinity can be neglected as a factor influencing properties [5,9]. The effect of processing conditions and matrix properties proved to be more important in the determination of composite properties. Interfacial adhesion increased with increasing processing time and temperature [5-9] and larger interfacial shear stress was measured also with increasing molecular weight of the matrix [9]. This latter effect was explained with the increased entanglement density of the resin at higher molecular weight leading to increased yield stress and improved stress transfer [9].

Less information is available about the mechanism of interaction and coupling of polycarbonate and carbon fiber [15,18]. The experiments mentioned above were carried out on oxidized, but non-treated fibers [5]. However, sizing is used practically always in order to facilitate the production and processing of the fibers at a high rate [19]. The sizing material influences interaction, the chemical reaction of the fiber and the matrix becomes even more difficult, coupling is used to promote adhesion. The goal of this paper was the study of the reactions of some potential coupling agents with the surface of oxidized carbon fiber and a polycarbonate matrix. An attempt was made to determine the influence of these reactions on interfacial adhesion and on the extent of improvement in IFSS, which can be achieved in PC/CF micro-composites. The effect of
processing temperature and the molecular weight of the matrix was also checked on composites prepared with a fiber, which was treated with one of the coupling agents studied.

### 6.2. Experimental

Makrolon 2805 (Bayer AG) injection molding grade PC was used in most of the experiments as polymer matrix. Three other resins were also used in a series of measurements directed towards the determination of matrix properties on interfacial adhesion. The most important information related to these polymers is listed in Table 6.1. The anodically oxidized Panex 33 carbon fiber (diameter 7 µm, tensile strength 3.6 GPa, modulus 250 GPa) was obtained from Zoltek Co. The fiber was oxidized, but not sized. Four compounds were selected as possible coupling agents with specific coupling reactions in mind. Their chemical structure and some other relevant information are listed in Table 6.2.

#### Table 6.1 Polycarbonate grades used as matrix in the study

<table>
<thead>
<tr>
<th>Grade</th>
<th>Producer</th>
<th>Molecular weight (g/mol) $10^4$</th>
<th>$M_w/M_n$</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$M_n$</td>
<td>$M_w$</td>
<td></td>
</tr>
<tr>
<td>Lexan 101</td>
<td>General Electric</td>
<td>1.21</td>
<td>3.28</td>
<td>2.71</td>
</tr>
<tr>
<td>Makrolon 2805</td>
<td>Bayer AG</td>
<td>1.34</td>
<td>3.12</td>
<td>2.33</td>
</tr>
<tr>
<td>Makrolon 3105</td>
<td>Bayer AG</td>
<td>1.42</td>
<td>3.32</td>
<td>2.34</td>
</tr>
<tr>
<td>Xantar F 22 UR</td>
<td>DSM</td>
<td>1.92</td>
<td>3.41</td>
<td>1.77</td>
</tr>
</tbody>
</table>

The surface treatment of the fibers was carried out in solution to determine adsorption and coupling of the compounds to the fiber surface. Increasing amounts, i.e. 0.5, 1.0, 1.5, 3.0 and 4.0 wt% calculated for the weight of the fiber, of coupling agent was dissolved in an appropriate solvent then a bundle of fibers of 1 m length was placed into the solvent in a Petri dish. The solvent was completely evaporated then the fibers were dried to constant weight. The amount of adsorbed and/or coupled compound was determined by dissolution experiments [20]. A weighed amount of fiber was immersed into excess solvent to dissolve the non-bonded coupling agent from the fiber surface. Chemical reactions taking place on the surface were studied by diffuse reflectance infrared spectroscopy (DRIFT).
Table 6.2 Compounds used as coupling agents in the experiments

<table>
<thead>
<tr>
<th>Abbr.</th>
<th>Compound</th>
<th>Formula</th>
<th>Grade</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDI</td>
<td>4,4’-diphenylmethane-diisocianate</td>
<td>![Image of MDI structure]</td>
<td>M 48</td>
<td>Borsod Chem</td>
</tr>
<tr>
<td>TGIC</td>
<td>triglycidyl isocyanurate</td>
<td>![Image of TGIC structure]</td>
<td>Araldit PT 810</td>
<td>Ciba-Geigy</td>
</tr>
<tr>
<td>EPS</td>
<td>3-glycidoxy-propyltriethoxysilane</td>
<td>![Image of EPS structure]</td>
<td>GF 82</td>
<td>Wacker Chemie GmbH</td>
</tr>
<tr>
<td>SAS</td>
<td>3-triethoxypropyloct succinic acid anhydride</td>
<td>![Image of SAS structure]</td>
<td>GF 20</td>
<td>Wacker Chemie GmbH</td>
</tr>
</tbody>
</table>

Figure 6.1 Setup for the preparation of single fiber coupons for the fragmentation test. 1) stainless steel plate, 2) upper matrix sheet, 3) lower sheet of matrix with carbon fibers
The possible coupling reactions of the selected compounds and the polymer were studied through model reactions. Various amounts of the coupling agents were extruded with the polymer in a single screw laboratory extruder at 280 °C. The reactions were followed by transmission infrared spectroscopy (FTIR) on compression molded films of 40 µm thickness prepared on a Fontijne SRA 100 machine at 280 °C.

Specimens for fragmentation were also prepared by compression molding. Sample preparation was carried out according to the setup shown in Fig. 6.1. First, two sheets were compression molded from PC then single fibers were attached to one of them with appropriate spacing. Subsequently the sheets were placed between chromium plates into a frame and then they underwent a second compressing molding step. All processing operations were carried out at 280 °C. The same procedure was followed in the series of experiments directed towards the determination of the effect of processing temperature on interfacial adhesion. Specimens for fragmentation were cut from the compression molded plates. Interfacial shear stress (IFSS) was calculated from the average fragment length by the Kelly-Tyson equation [21].

6.3. Results

The coupling of the fiber and the matrix assumes that the coupling agents react both with the fiber and the matrix polymer. As a consequence, separate series of experiments were carried out to determine the reactions of the coupling agents first with the surface of the fiber then with the matrix. The results obtained are presented in separate sections, followed by the discussion of the effect of these reactions on interfacial adhesion. The influence of the molecular weight of the matrix, as well as processing temperature on interaction is presented in the last section for fibers treated with the epoxy silane coupling agent (EPS).

6.3.1. Adsorption and coupling

As described in Chapter 5, the adsorption of surfactants and other non-reactive compounds can be successfully studied by a simple dissolution technique [22,23]. In this procedure a filler or fiber is covered with increasing amounts of the surfactant then it is washed with an appropriate solvent. The analysis of the obtained solution makes possible the determination of the amount of bonded compound. The simple technique was developed for surfactants [22,23], but it was successfully applied also in the case of coupling agents [20,24]. The obtained bonding isotherms give valuable information about the behavior of the compound used for the treatment and in the case of coupling agents they offer hints about the coupling reaction as well.

Fig. 6.2 shows the bonding of the coupling agents to the surface of the carbon fiber. The isotherms differ considerably from each other. The bonded amount of TGIC is rather small and it approaches a saturation value with increasing amount of the compound used for the treatment. The treated fiber was put into an oven at 120 °C for 24 hours to promote the reaction of the coupling agent with the surface, but the applied temperature might be insufficient to initiate the coupling reaction. The observed
Coupling of carbon fibers to polycarbonate

dependence on the amount of TGIC used for the treatment may result from purely physical adsorption or from the limited number of active sites found on the surface of the fiber. The amount of bonded MDI is somewhat larger than that of TGIC, what may be the result of the higher reactivity of MDI. The continuous increase of bonded coupling agent indicates the polymerization of the isocyanate on the surface of the fiber. Although the relative magnitude of bonding is larger for MDI than for TGIC, it is rather low in absolute quantities. Only about 1.5 wt%, i.e. less then 40 % is bonded to the surface when 4.0 wt% is used for treatment. The chemical reactions taking place on the fiber surface, as well as the related DRIFT spectra were discussed in detail in Chapter 5 for TGIC, MDI and EPS thus we refrain their repeated presentation here. On the other hand, the silane containing an anhydride functional group has not been used before for the treatment of carbon fiber. This coupling agent was selected because we assumed that its functional group might react with active –OH groups both on the fiber surface and in the matrix polymer. As a consequence, the bonding and reactions of the silanes are discussed more in detail in this section.

![Figure 6.2](image)

**Figure 6.2** Bonding of coupling agents to the surface of carbon fiber; dissolution curves. Symbols: (□) TGIC, (◊) MDI, (○) EPS, (Δ) SAS, ----- complete coverage

The dissolution curves presented in Fig. 6.2 show that silanes are bonded to the fiber surface in larger amounts than the other two coupling agents are. However, the dissolution characteristics of the two compounds are different. SAS used for the treatment is bonded almost completely to the surface shown also by the small deviation of the measured values (Δ) from the line indicating complete bonding. Such a dissolution correlation was shown earlier to result from the polycondensation of the
silane and the formation of a hard polymer layer [24]. The correlation of EPS indicates physical adsorption or the formation of polysiloxane layer with a different, looser structure. This loose, physisorbed layer can be dissolved relatively easily from the surface resulting in the saturation curve obtained.

The reactions of EPS were discussed in the previous chapter, those assumed for SAS are presented in Scheme 6.1 below

\[
\begin{align*}
(C_2H_5O)_3Si(CH_2)_3CH_2O & \xrightarrow{H_2O} (C_2H_5O)_3Si\left(CH_2\right)_3CH_2OH \\
(C_2H_5O)_3Si(CH_2)_3CH_2OH + HO & \rightarrow HO\left(CH_2\right)_3CH_2OH
\end{align*}
\]

Scheme 6.1

The spectra taken from the surface of the treated fibers are shown in Fig. 6.3. The appearance of the strong carbonyl band at 1718 cm\(^{-1}\) (A) in Spectrum 1 proves that either the reaction of Scheme 1 and/or the hydrolysis of the anhydride group take place on the fiber surface. The intensity of the peak increases proportionally to the amount of silane used for the treatment (Fig. 6.4) supporting both the scheme and the results of the dissolution experiments presented in Fig. 6.2. However, besides coupling reactions, silanes also polymerize on the surface of fibers and fillers (see Scheme 6.1); it may occur simultaneously with coupling, but also independently of it. The multiple peaks appearing between 1230 and 1030 cm\(^{-1}\) (B) in Fig. 6.3 clearly prove the formation of a polysiloxane layer on the fiber surface. Similar vibrations can be detected in this wavelength region in the spectra taken from the fibers treated with both silanes. However, the comparison of the spectra indicates that the chemical structure of the polysiloxane is different in the two cases. EPS forms a looser small molecular weight polycyclic structure, as mentioned above [24,26].

The dissolution experiments and the study of the chemical structure of the treated fibers show that all four coupling agents are bonded to the surface of the fiber. However, the amount of the bonded material is different, it covers a wide range. Only small amounts of TGIC can be found on the surface after treatment and dissolution; chemical coupling could not be proved unambiguously. MDI and the silanes seem to form a polymer layer on the fiber surface, but the thickness and the structure of the layer is different in each case.
6.3.2. Reactions of the matrix

The number of reactive groups in polycarbonate is very small, it is practically limited to the hydroxyl groups at the chain ends. Moreover, also the reactivity of these groups is moderate. Nevertheless, the very reactive isocyanate groups of MDI are supposed to react vigorously with the chain-end –OH groups of the polymer according to Scheme 6.2

![Scheme 6.2](image)

Figure 6.3 DRIFT spectra of carbon fibers covered with 4 wt% silane coupling agent: 1) SAS, 2) EPS
The isocyanate groups may enter into further reactions with the secondary amine formed, which finally can lead to the formation of a network. The reaction of the two isocyanate groups of the same molecule with two different polymer chains may result in an increase of molecular weight and viscosity.

![Graph](image)

**Figure 6.4** *Intensity of the carbonyl vibration of SAS at 1718 cm⁻¹ plotted as a function of the amount of coupling agent used for the treatment*

The FTIR spectra of PC, MDI and the polymer processed in the presence of 5 wt% MDI, respectively, are presented in Fig. 6.5. The broad vibration appearing around 3400 cm⁻¹ (A) can be assigned to the -NH vibration of the urethane group forming in the coupling reaction. The intensity of the peak increases with MDI content (Fig 6.6). The saturation tendency of the correlation, as well as the presence of unreacted isocyanate groups appearing at 2272 cm⁻¹ (B) indicate that the number of the available reactive groups is limited in the polymer.

Triglycidyl isocyanurate (TGIC) contains three epoxy groups in one molecule. These may react with various functional groups including active hydroxyls. As a consequence, the coupling reaction assumed to occur between PC and TGIC is the following (Scheme 6.3):
Coupling of carbon fibers to polycarbonate

Figure 6.5 Formation of amine groups (A) in the reaction of PC and MDI; 1) PC, 2) PC + 5 wt% MDI (difference spectra), 3) MDI

Scheme 6.3

The reaction presented in Scheme 6.3 proceeds very slowly at ambient temperature, but the two functional groups are expected to react with each other more vigorously at the high temperature of processing.
The FTIR spectra of PC, TGIC the polymer extruded with 5 wt% TGIC, respectively, are presented in Fig. 6.7. A relatively broad peak of medium intensity appears at around 3500 cm\(^{-1}\) (A), which may be assigned to the vibration of secondary -OH groups formed in the reaction indicated by Scheme 6.3. The intensity of the vibration increases with increasing amount of TGIC, but the increase is not proportional to the amount of coupling agent added in the entire composition range. At high coupling agent content bonding seems to assume a constant value (Fig. 6.8) indicating that the number of reactions is limited, probably due to the fixed number of chain-end -OH groups in PC. The functions presented in Figs. 6.6 and 6.8, respectively, obviously differ somewhat from each other, but both approach to a saturation value. Although the differences need further study, the similarity proves unambiguously that the number of reactive groups available for reaction is limited. The epoxy silane (EPS) is assumed to enter into the same reaction with the polymer as TGIC, i.e. coupling should take place thorough its epoxy functionality. Unfortunately because of the intensive absorption bands of PC in the wavelength range below 1800 cm\(^{-1}\) (see Fig. 6.1, Spectrum 1), the detection of any reactions is extremely difficult. The same applies also to the reaction of the anhydride functional silane and PC. We assumed that this silane also reacts with the –OH groups of the polymer. However, neither the ester group nor the Si-O-C group of the silanes can be detected, because of the intensive vibrations of PC. A detailed analysis of the spectra indicates that the silane functionality of these coupling agents enter into different reactions even in the melt. Nevertheless, the mode and extent of coupling of the silanes to PC could not be defined unambiguously by the evaluation of

**Figure 6.6** Increasing intensity of the vibration of the amine forming during the model reaction of PC and MDI
the available data. Further experiments must be designed and carried out in order to obtain more information about the reactions of PC and functionalized silanes.

6.3.3. Interfacial adhesion

The effect of treatment on the interfacial shear stress of PC/CF microcomposites is presented in Fig. 6.9. Two different kinds of correlation were detected for the four coupling agents. IFSS of composites containing the fiber, which was treated with the anhydride functional silane does not change as a function of surface coverage. The constant value of adhesion indicates the lack of reaction between the matrix and the coated fiber. Such a behavior was observed before in epoxy composites containing fibers treated with an aminosilane coupling agent [20]. Both neat silanes, i.e. the amino and the anhydride functional compounds, condensed readily under ambient conditions forming a hard film, which indicates the catalytic effect of the organofunctional group on the polycondensation reaction. Obviously, the rigidity of the film decreases the reactivity of the remaining functional groups, interaction is created only by secondary forces and IFSS remains on the level of the neat fiber.

![Figure 6.7](image-url)  
**Figure 6.7** Model reaction of PC and TGIC, formation of secondary –OH groups. 1) PC, 2) PC + 5 wt% TGIC (difference spectra), 3) TGIC

6.3.3. Interfacial adhesion

The effect of treatment on the interfacial shear stress of PC/CF microcomposites is presented in Fig. 6.9. Two different kinds of correlation were detected for the four coupling agents. IFSS of composites containing the fiber, which was treated with the anhydride functional silane does not change as a function of surface coverage. The constant value of adhesion indicates the lack of reaction between the matrix and the coated fiber. Such a behavior was observed before in epoxy composites containing fibers treated with an aminosilane coupling agent [20]. Both neat silanes, i.e. the amino and the anhydride functional compounds, condensed readily under ambient conditions forming a hard film, which indicates the catalytic effect of the organofunctional group on the polycondensation reaction. Obviously, the rigidity of the film decreases the reactivity of the remaining functional groups, interaction is created only by secondary forces and IFSS remains on the level of the neat fiber.
Figure 6.8  Intensity of secondary –OH groups formed in the reaction of PC and TGIC plotted against the amount of coupling agent used in the reaction

Figure 6.9  Effect of various coupling agents on interfacial interaction in PC/CF microcomposites. Symbols: (□) TGIC, (◊) MDI, (○) EPS, (△) SAS
IFSS exhibits a maximum as a function of the amount of coupling agent used for the treatment for the remaining three compounds. The location of the maximum on the concentration scale is different in each case. The interpretation of the differences is difficult since the chemical reactions, the amount of bonded coupling agent, and especially the structure of the formed layer are completely different in the three cases. However, the fact that the maximum value of interfacial adhesion is approximately the same seems to be more important. We mentioned several times before, that coupling reactions are assumed to proceed through the chain-end –OH groups of polycarbonate and that the number of this latter is limited. The reaction of all or the majority of these groups with the functional groups of the bonded coupling agents would lead to the same IFSS value, assuming of course that the number of reactive groups is larger on the surface of the fiber than in the polymer.

Approximate calculations were carried out in order to determine the number of reactive groups on the fiber surface and in the polymer being in contact with it. We assumed that a layer of 0.1 µm thickness forms on the surface during treatment and the polymer could react with the functional groups within it. Taking into account the molecular weight and the functionality of the coupling agent, the number of functional groups were calculated for a fiber length of 1 cm. The results are listed in Table 6.3. The number of functional groups is at least twice as high for all four coupling agents than that of the –OH groups available in the polymer. Naturally, side reactions, the structure of the layer formed, the effect of processing conditions could not be taken into account during these calculations. Nevertheless, even these tentative values indicate the limited reactivity of PC in coupling reactions.

Table 6.3 Number of reactive groups on PC and the carbon fiber covered by various coupling agents at 0.5 wt %

<table>
<thead>
<tr>
<th>Component</th>
<th>Functional group</th>
<th>Type</th>
<th>No/molecule</th>
<th>No/cm³ interphase ·10²⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>–OH</td>
<td>1</td>
<td>5.65</td>
<td></td>
</tr>
<tr>
<td>MDI</td>
<td>–NCO</td>
<td>2</td>
<td>9.08</td>
<td></td>
</tr>
<tr>
<td>TGIC</td>
<td>epoxy</td>
<td>3</td>
<td>19.14</td>
<td></td>
</tr>
<tr>
<td>EPS</td>
<td>epoxy</td>
<td>1</td>
<td>19.85</td>
<td></td>
</tr>
<tr>
<td>SAS</td>
<td>anhydride</td>
<td>1</td>
<td>24.41</td>
<td></td>
</tr>
</tbody>
</table>

6.3.4. Temperature, molecular weight

Several research groups investigated the effect of processing parameters [5-9] and matrix characteristics on interfacial adhesion [4,9]. IFSS was shown to increase with increasing processing temperature, time [5-9] and cooling rate [14]. The effect of
Figure 6.10 Influence of temperature on interfacial adhesion between PC and CF covered with various amounts of EPS. Symbols: (□) 260, (○) 280, (△) 300 °C

Figure 6.11 Correlation of the tensile yield stress and molecular weight of various grades of polycarbonate
temperature and time was explained by the improved adsorption between the matrix and the fiber. On the other hand, increased cooling rate was claimed to result in increased internal stresses, which lead to an apparent improvement of IFSS.

The experiments cited above were executed mostly on neat, non-treated fibers; we carried out a similar series of experiments with fibers covered with EPS in different extents. IFSS is plotted against the amount of silane used for the treatment in Fig. 6.10. Interfacial adhesion increases with temperature in the same way as in the case of the neat fiber. However, the maximum cannot be explained either with the effect of cooling rate or improved adsorption; we believe that the number of coupling reactions and the structure of the formed siloxane layer is responsible for its appearance. Although a maximum was detected also in Fig. 6.9 as a function of surface coverage, its location differs significantly from that detected in Fig. 6.10. We must call attention here to the fact that a different polymer was used in the experiments of Fig. 6.9 (Makrolon 2805) than in those of Fig. 6.10 (Lexan 101), and also the plates were compression molded using a different machine. Since both molecular weight and processing conditions were proved to influence IFSS, the difference is not very surprising.

IFSS was claimed to improve with increasing molecular weight due to increased entanglement density [9], which leads to increased yield stress. Plates of the same thickness as used in the fragmentation experiments were compression molded and their tensile characteristics were also determined under the same conditions. The results are plotted in Fig. 6.11 showing that yield stress is independent of molecular weight. Meijer and his coworkers [27-29] carried out an extensive study on the deformation behavior of PC and other polymers. Based on the theory of Kramer [30,31] they calculated the entanglement density of PC and the molecular weight between entanglements proved to be around 2500. This means that in our case the number of entanglement points changes between 5 and 7 for the four polymers studied, thus this cannot be the reason for the assumed increase of interfacial adhesion.

IFSS is plotted against the amount of EPS used for the treatment in Fig. 6.12 for the four polymers selected for the study. The effect of molecular weight does not agree with the tendency claimed in Ref. 9. Moreover, the increase is not proportional with molecular weight even for the three polymers, for which IFSS seems to change according to the tendency claimed. We must call attention here to the fact that different producers supplied the polymers selected for the study (see Table 6.1). The number of –OH functionality depends strongly on the chemistry and conditions of the process used for their production and coupling reactions may be influenced also by the additives added to the final product. Producers usually do not supply information about these factors and their determination is very difficult because of the low concentration of both the functional groups and the additives. In spite of the very tentative character of the explanations given above, we believe that coupling efficiency of different grades depends on the number of active functional groups available on the polymer. This explanation is further supported by the strong similarity of the values measured on the neat fiber as well as at low surface coverages (see Fig. 6.12). Another proof is supplied by the results of Hüttinger et al. [18], who found that even uncoated carbon fiber enters
into chemical reaction with PC. Obviously, either the chemical structure or the additive package of Makrolon 2805 differs significantly from those of the other three polymers.

![Figure 6.12](image)

Figure 6.12 Effect of molecular weight and coupling on interfacial adhesion in PC/CF micro-composites. Symbols: (□) Makrolon 2805, (○) Lexan 101, (△) Makrolon 3105, (◊) Xantar F 22 UR

### 6.4. Conclusions

The results of the experiments focused on the determination of the coupling reactions taking place during the preparation of polycarbonate/carbon fiber composites showed that interfacial interaction can be improved in a limited extent in such materials. The amount of coupling agent bonded to oxidized carbon fiber depends on its chemical structure and on the reactions taking place on the fiber surface. Several of the coupling agents formed a polymer layer on the surface, the structure of which influenced also coupling to the matrix. The organofunctional groups of the coupling agents react with the chain-end hydroxyl groups of polycarbonate. The number of these latter is limited, much lower than the concentration of reactive groups available on the surface of the coated fiber. The limited number of reactive groups results in the same improvement of interfacial shear stress independently of the type of the coupling agent used if they could react with the polymer (i.e., TGIC, MDI, EPS). The silane having anhydride functionality obviously does not enter into coupling reactions with PC. Interfacial adhesion increased with processing temperature due to the increased rate of reaction. The effect of molecular weight on interfacial adhesion is not clear; the results published earlier could not be confirmed unambiguously. More experiments and a more detailed
analysis must be carried out in order to resolve some of the contradictions observed and answer the remaining questions.

6.5. References

Chapter 7

Impact resistance of short carbon fiber reinforced polyamide 6 composites

7.1. Introduction

Short fiber reinforced thermoplastic composites are used extensively in numerous engineering applications. Their properties are determined by their structure, which strongly depends on processing conditions and composition [1]. Parts from short fiber reinforced composites are produced almost exclusively by injection molding, the high shear that develops during processing results in the decrease of fiber length [2,3]. The prediction of composite properties is difficult because of the attrition of the fibers and due to the influence of numerous factors including component properties, injection rate, mould temperature, etc. [4-6]. The most important quantities that characterize structure are fiber length and length distribution, as well as orientation and orientation distribution [7,8]. Numerous studies have been carried out to determine the effect of processing parameters on these quantities [9,10] and attempts were made to relate them to composite properties [3,11,12]. Occasionally models were proposed to relate structure and fracture toughness quantitatively [12-14]. However, most of these studies were carried out on short glass fiber reinforced composites [4-12]; much less information is available about such correlations in carbon fiber reinforced thermoplastics.

This chapter discusses the effect of composition and injection rate on the structure of short carbon fiber (CF) reinforced polyamide 6 (PA) composites. Fiber length and orientation were measured and an attempt was made to establish correlations between the structure and mechanical properties, especially impact behavior of the composites.

7.2. Experimental

The polyamide 6 used as the matrix material was the Danamide E grade polymer of Zoltek Co., Hungary, while the polycrylonitrile-based carbon fibers (Panex 33) were produced by the same company. The fibers were treated with 4.3 % epoxy sizing, their original length was 3.2 mm, their diameter 7 µm. Composites of 0, 1.4, 1.9, 2.9, 4.4, 6.3, 9.4, and 16.1 vol% were prepared on a Werner Pfleiderer ZSK 30 twin screw extruder at 230, 250 and 260 °C zone temperatures. The composites were injection molded into standard dumbbell shaped tensile bars on a Battenfeld BA 200 CD machine. Set temperatures of the barrel were 235, 250 and 250 °C, the temperature of the mould was set to 80 °C. Injection rate varied between 10 and 100 % relative settings in 5 steps. Linear injection rates were derived from volumetric injection rate at the cross section of the specimen, where structure was determined. The calculated rates corresponded to 2.0, 3.3, 5.4, 14.2 and 22.6 cm/s.
In order to determine fiber length and length distribution the polymer was dissolved in formic acid and the dimensions of the fibers were determined by image analysis under a light microscope. Orientation and orientation distribution were also measured by optical microscopy on thin slices cut from the middle section of a specimen. The sections were photographed by a Polaroid DMC camera fitted to a Zeiss Dialux 20 microscope and they were analyzed by a Image-Pro Plus software. Orientation distribution was determined at different depths in the Y-Z plane of the specimen (see Fig. 7.1 in which Z is the mould-fill direction).

![Figure 7.1](image)

**Figure 7.1** *Definition of planes and mould-fill direction in the injection molded specimens*

Various mechanical tests were carried out on the injection molded specimens. Young's modulus (E), yield stress (σ_y) and strain (ε_y), as well as tensile strength (σ) and elongation-at-break (ε) were measured; also, flexural properties, [i.e. flexural modulus (E_f) and stress (σ_f)] were determined. Standard Charpy impact strength was determined on 80 x 10 x 4 mm bars cut from the injection molded bars. Instrumented impact testing was carried out at 2.9 m/s velocity, dynamic effects were damped by silicone rubber [15]. The specimens were notched to different depths by a saw and they were sharpened by an industrial razor blade to determine strain energy release rate by the method of Plati and Williams [16,17].
Figure 7.2  Dependence of average fiber length on composition in the extruded pellets

Figure 7.3  Composition dependence of average fiber length of CF in the injection molded bars at injection rates: (◊) 2.0, (□) 3.3, (Δ) 5.4, (☆) 14.1, (○) 22.6 cm/s
7.3. Results and discussion

In short carbon fiber reinforced composites, the determination of structure/property correlations is rather difficult because of the large number of parameters which influence both structure and properties. As a consequence, a comprehensive analysis of all factors is not attempted in subsequent sections, the attention is focused mainly on fiber length and orientation, on the one hand, and on fracture characteristics, on the other.

7.3.1. Structure

The first step in the processing of the composites was the homogenization of the fibers in the matrix polymer to produce granules for injection molding. Considerable attrition of the fibers takes place during this step, their original size decreases to an average value between 100 and 200 µm. Fiber content strongly influences the final length, as shown by Fig. 7.2. An approximately exponential decrease of fiber length was observed with increasing fiber content. The shortest average length is measured in the composite containing 16.1 vol% CF, its value is around 120 µm.

The length of the fibers decreased further during the injection molding of the specimens. Fiber content affected fiber length in a similar way as in extrusion. Increasing the injection rate led to decreased fiber length as expected (Fig. 7.3). However, the changes were much smaller during injection molding than in the first processing step; also, the effect of injection rate was moderate. Average fiber length varied between 80 and 110 µm depending on injection rate and composition. Nevertheless, the final length of the fibers seemed to change according to well-defined rules; its correlation with composite properties, if any, is expected to be easily discernible.

Figure 7.4 Schematic representation of fiber orientation in thermoplastic/glass fiber composites according to literature data [4-6,18,19]
Impact resistance of SCF reinforced PA6 composites

According to literature data gathered on glass fiber/thermoplastic composites the fibers are oriented into the direction of the flow near the wall of the mold and perpendicular to it in the middle of the specimen [4-6,18,19] (see Fig. 7.4). Rather surprisingly a completely different orientation distribution was observed in our PA/CF specimens. In these samples the fibers were aligned parallel to the wall, just like in the previous case, but they were either randomly orientated in the Y-Z plane or perpendicularly to the mold-fill direction (Fig. 7.5). On the other hand, their orientation was parallel to the flow direction in the midsection of the specimen. Although this

Figure 7.5 Schematic representation of fiber orientation in CF/PA composites in the X-Y plane of the specimen (a = skin thickness)

Figure 7.6 Effect of fiber content and injection rate on the thickness of the skin. Injection rate: (◊) 2.0, (□) 3.3, (Δ) 5.4, (☆) 14.1, (〇) 22.6 cm/s
distribution is surprising, a similar structure was observed in PA/LCP (liquid crystalline polymer) blends [20] with the only difference that the thickness of the external layer was considerably smaller there than in our case and it appeared also in PP/GF composites with increasing injection rate [6]. The two layers (i.e., layers of parallel [core] and perpendicularly [skin] oriented fibers) could be distinguished with acceptable accuracy at most values of the variables. Accordingly, the thickness of the skin layer indicated by $a$ in Fig. 7.5 was measured; the results are plotted as a function of fiber content in Fig. 7.6. The skin was surprisingly thick, but repeated measurements resulted in similar values. Increasing fiber content leads to the development of a thicker skin, while a thinner layer is measured if the rate of injection is increased. Composition dependence is more or less linear at high rates, and a saturation like correlation is observed at low injection velocities.

![Figure 7.7](image)

**Figure 7.7** Typical fiber orientations in the Y-Z plane at different distances from the wall, a) 0.08 mm, b) 2.00 mm. Fiber content: 4.4 vol%; injection rate: 14.1 cm/s

The orientation distribution of the layers is demonstrated in Fig. 7.7. Optical micrographs were taken from slices cut in the Y-Z plane at different depths. Fig. 7.7a presents the nearly random orientation of the fibers close to the wall at 0.08 mm, while the micrograph of Fig. 7.7b shows a slice taken beyond the skin layer, 2.0 mm away form the surface of the specimen. The parallel orientation of the fibers to the Z axis (i.e., mold-fill direction) is clearly seen in this figure. The angle closed by the fiber with the Z axis characterizes orientation quantitatively. Angles were determined for all fibers in slices taken from different depths. Three typical distributions are presented in Fig. 7.8 for slices cut at 0.08, 2.0 and 4.50 mm from the wall. The differences in the distributions are clear. The comparison of the distribution taken at 4.5 mm depth, close to the middle of the specimen (5 mm), to the one cut at 2.0 mm indicates that average orientation has a maximum at a point not too far from the wall.
Average orientation can be calculated from the individual orientations by various methods [11,12,14,21-23]. However, it was shown by Fakirov and Fakirova [24] that the Herman's orientation function can be calculated also from the average angle of orientation $\phi_a$:

$$f_p = 2\cos\phi_a - 1$$ \hspace{1cm} (7.1)

The parameter $f_p$ assumes the value of 1 if all fibers are orientated in the direction of the flow, -1 if they are perpendicular to it and 0 in the case of random orientation. Average orientation is plotted against the distance measured from the wall in Fig. 7.9. According to these results a large number of the fibers are oriented perpendicular to the direction of flow in the skin, indeed, in accordance with the qualitative picture presented in Fig. 7.5, while they are aligned into the direction of the Z axis in the core. After a maximum, a small decrease of $f_p$ occurs as we move closer to the middle of the specimen. These results indicate that the structure of CF/PA6 composites might be characterized by two
values, the average length of the fibers and the thickness of the skin layer, where the fibers are oriented perpendicular to the flow direction.

![Diagram](image)

**Figure 7.9** Dependence of average fiber orientation ($f_p$) in the Y-Z plane on the distance from the wall. Fiber content: 4.4 vol%; injection rate: 14.1 cm/s

### 7.3.2. Properties

The structure of the composites obviously determines their properties, but it is not clear, which factor has a stronger effect on them, fiber length or orientation. The Young's modulus of the neat polymer and that of the composites are presented in Fig. 7.10 as a function of composition. Stiffness increases continuously with increasing fiber content, as expected. Also increasing injection rate leads to a moderate increase of composite modulus. Since both fiber length and the thickness of the skin decrease with increasing injection rate, the effect of orientation seems to be stronger than that of fiber length; average orientation in the mold-fill direction increases with decreasing skin thickness.

Instrumented impact testing was carried out on all specimens produced at every combination of the variables (i.e., fiber content and injection rate). Typical load vs deflection traces are presented in Fig. 7.11. Fracture toughness increases with fiber content, as expected, and the traces are always triangular, indicating brittle fracture. In such cases the conditions of linear elastic fracture mechanics (LEFM) are fulfilled and size independent fracture characteristics (i.e., strain energy release rate $G_{IC}$ and critical stress intensity factor $K_{IC}$) can be determined from the load vs deflection traces.
According to the usual technique \cite{16,17}, $G_{ic}$ can be determined if fracture energy $U$ is measured on specimens notched to different depths. The correlation of $U$ and $G_{ic}$ is expressed as

$$U = U_0 + BD\phi$$ \hfill (7.2)

where $B$ and $D$ are the thickness and the width of the specimen, respectively, and $\phi$ is a geometrical parameter depending on notch depth. According to Eq. 7.2, if $U$ is plotted against $BD\phi$, a straight line should be obtained with the slope of $G_{ic}$ \cite{16,25}. Such a correlation is presented in Fig. 7.12 for a sample that was prepared at an injection rate of 22.6 cm/s and that contains 1.9 vol\% CF. The correlation is obviously not linear, its shape changes continuously. Similar correlations were obtained at all combinations of the variables indicating that $G_{ic}$ cannot be determined by this method for our composites. An obvious explanation lays in the specific structure of the specimens, in the development of the skin and core regions with drastically dissimilar fiber orientations.

Contrary to $G_{ic}$, the critical stress intensity factor can be determined from a single specimen, it can be calculated from the maximum force recorded on the force vs deflection trace (see Fig. 7.11). Since $K_{ic}$ was independent of notch depth average values were calculated for all combinations of the variables; they are plotted against fiber content in Fig. 7.13. Fracture toughness increases strongly with fiber content, but it
Figure 7.11 Typical load deflection traces of the neat PA and two composites of different fiber content. Injection rate: 2.0 cm/s

Figure 7.12 U vs BDφ correlation (Eq. 7.2) for the determination of Gk. Fiber content: 1.9 vol%; injection rate: 22.6 cm/s
Figure 7.13  Dependence of the critical stress intensity factor ($K_{IC}$) on fiber content and injection rate. Injection rate: (◊) 2.0, (□) 3.3, (Δ) 5.4, (☆) 14.1, (∙) 22.6 cm/s

Figure 7.14  Correlation of impact strength with composition and injection rate. Symbols are the same as in Fig. 7.13
improves also with increasing injection rate. Contrary to the continuous increase of modulus as a function of composition, a definite minimum appears in $K_{lc}$ at low fiber contents. A very similar correlation is obtained if the standard Charpy impact strength is plotted as a function of composition (Fig. 7.14). The general features are the same as for $K_{lc}$, but both the minimum and the effect of injection rate are more pronounced in this case.

7.3.3. Structure-property correlations

The properties of PA6/CF composites are obviously determined by their structure. Stiffness is expected to increase with increasing fiber length below the critical length and with increasing overall orientation parallel to the direction of the external load, which coincides with the direction of flow in our case. Decreasing skin thickness means increasing orientation, thus the results indicate that orientation of the fibers is more important in the determination of stiffness than fiber length.

Similarly to the dependence of modulus on the studied parameters (i.e., fiber length and orientation), the impact resistance also seems to depend differently on the two variables. Toughness is expected to decrease if the fibers are smaller, but to increase with their parallel orientation to the direction of flow. The dependence of length and orientation (i.e., thickness of the skin) on the injection rate indicates that the effect of orientation is much more pronounced also on this property than that of fiber length. This is not very surprising since average fiber length changes in a very narrow range, between 80 and 110 $\mu$m, while the change in the orientation of the fibers is more significant. Nevertheless, the thickness of the skin cannot be related directly to fracture toughness, what becomes obvious if we compare Figs. 7.13 and 7.14 to Fig. 7.6. A complicated correlation seems to exist between orientation and fracture resistance.

Nevertheless, several observations indicate the importance of the formation of the skin. The non-linearity of the correlation of $U$ vs $BD\phi$ of Fig. 7.12 may be a result of the different fiber orientation in the skin and the core. With increasing notch depth the relative area of the skin and the core changes continuously leading to a change in the compliance of the sample. In fact, the different orientation of the two layers leads to a modification of ligament stiffness. As a consequence, the changes in specimen compliance cannot be expressed by parameter $\phi$. An analysis of the data indicates that the fracture resistance of the skin and the core differs significantly from each other, that of the core exceeds the toughness of the outer layer. This conclusion is strongly supported by SEM micrographs taken from fracture surfaces in the two layers. The micrograph shown in Fig. 7.15a was taken from the skin. The fibers are oriented randomly and long fiber ends protrude from the surface. In the core, crack propagates perpendicular to the axis of the fibers, the length pulled out of the matrix seems to be much shorter than in the skin. Obviously, more fibers must be broken in the core than in the skin for the crack to propagate, which leads to increased toughness.

Finally, we must consider the decreased fracture resistance of the composites at low fiber content. The decreased fracture toughness and impact resistance is clearly
related to the mere presence of the fibers; the effect of injection rate is negligible in this region. Apparently the fibers promote fracture initiation, which can be understood since their diameter is in the range of the notch radius. Moreover, the epoxy sizing is known to be unfavorable in the PA matrix [26], debonding stress is low. The poor adhesion is shown also by the considerable length of the fibers pulled out of the matrix in Fig. 7.15a.

Figure 7.15 SEM micrographs taken from the fracture surface of a PA/CF composite: a) skin; b) core. Fiber content: 16.1 vol%, injection rate: 2.2 m/s
7.4. Conclusions

The study of the structure of short carbon fiber reinforced PA6 composites showed that in injection molded specimens average fiber length decreases with increasing fiber content and processing rate. The observed structure contradicts those reported in the literature for short glass fiber reinforced thermoplastic composites. Fibers are aligned along the wall, but they are oriented randomly relative to the mould-fill direction. On the other hand, most fibers are oriented parallel to this direction in the middle of the specimen. In these composites skin was defined as the thickness of the external layer containing randomly oriented fibers. The thickness of the skin decreased with increasing injection rate and decreasing fiber content. Instrumented impact testing indicated brittle failure at all combinations of the variables. Nevertheless, strain energy release rate could not be determined by the usual technique using varying notch depths. The non-linear dependence of $U$ on $BD\phi$ was explained by the different properties of the skin and the core. Also the mechanism of failure seems to be different in the two layers. A minimum appears in the fracture toughness and impact resistance at low fiber contents indicating that fibers might promote fracture initiation at such compositions. Fiber length changes in a narrow range in the studied composites, thus properties are determined mainly by orientation. As a consequence, both increased fiber content and injection rate lead to an increase of stiffness and toughness.

7.5. References

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Chapter 8

Summary

The most important goal of this study was the investigation of interfacial interactions developing between carbon fibers and various matrices, as well as their modification through the use of appropriate coupling agents. We intended to investigate the type and number of functional groups forming on the surface of carbon fibers during their electrolytic oxidation. We modified the surface composition of the fibers by changing the type of the electrolyte, its concentration, the potential and time of the oxidation in a wide range. The adhesion between the fiber and the matrix was changed through the use of various coupling agents. We wanted to follow the chemical reactions taking place on the surface of the fiber as well as the determination of the character of the chemical bonds formed in these reactions. We looked for a correlation between surface chemistry and the strength of interfacial interaction. In the case of short carbon fiber reinforced composites, which are also very important for practice, the goal of the research was the determination of the correlation between their structure developing during processing and the properties of the produced parts.

The research directed towards the determination of the role of interfacial interactions developing in carbon fiber reinforced composites as well as the attempts to modify them yielded numerous new results. We found that the conditions of electrolytic oxidation of carbon fibers significantly influence the type and number of functional groups formed on the surface. Type, concentration and potential of oxidation, all influence the composition of the surface. Close correlation was found between the number of certain functional groups formed on the surface during oxidation and interfacial adhesion.

The results which proved that sodium hydroxide electrolyte adsorbs on the surface of the fiber in an extent depending on the conditions of the oxidation, is important for practice. The adsorption of the electrolyte is strong, it can be removed only with thorough washing. The adsorption of NaOH deteriorates interfacial adhesion, the removal of the adsorbed material significantly improves interaction.

We found that cyclic voltammetry is an excellent technique for the characterization of the electrochemical activity of carbon fibers. We found close correlation among the peak current detected by cyclic voltammetry, the number of functional groups formed on the fiber surface and interfacial interaction.

The interaction between the fiber and the matrix can be modified by the application of coupling agents. Experiments carried out with various coupling agents proved that numerous chemical reactions take place on the surface of the fiber. The structure and properties of the coupling agent layer forming on the surface considerably influence the strength of adhesion and the properties of the composites. The coupling agents often take part in complicated polymerization reactions on the surface of the fiber. The structure of the polymer layer depends on the chemical composition of the
coupling agent and on the conditions of surface treatment. The obtained results proved that neither a rigid, stiff or a weak layer do not improve interfacial adhesion, both lead to composites with inferior properties.

In thermoplastic matrices the number of functional groups which makes possible coupling is usually very low. In polycarbonate the coupling agents may enter into chemical reaction only with reactive groups found at the end of the chains. Because of the low number of functional groups, the chain-end –OH groups in polycarbonate, which are available for chemical reactions, interfacial adhesion can be improved by coupling only in a limited extent.

Besides interfacial interactions composite structure plays also an important role in the determination of properties in short carbon fiber reinforced composites. Fiber orientation and orientation distribution as well as fiber length and its distribution influence the properties of the composites. A skin-core structure develops during the injection molding of a product, fiber orientation differs considerably in the two layers. The thickness of the skin depends on composition and on processing conditions. We found that the stiffness, strength and impact resistance of the composite increases with fiber content at moderate and high concentrations, but a small amount of fiber leads to decreased impact resistance because fibers behave like weak sites in the composite, they initiate fracture. Orientation distribution, which was determined by us in short carbon fiber reinforced polyamide composites differed from that published in the literature. This difference was reflected also in the properties of the composites, which proved again the determining role of structure in these materials.
List of symbols

\( a_n \) impact strength (kJ/m²)
\( f_p \) Herman’s orientation factor (average fiber orientation)
\( B \) thickness of the specimen (mm)
\( D \) width of the specimen (mm)
\( E \) Young’s modulus (GPa)
\( E_f \) flexural modulus (GPa)
\( G_{ic} \) strain energy release rate (kJ/m²)
\( I_p \) peak current
\( K_{ic} \) critical stress intensity factor (N/mm³/²)
\( U \) fracture energy (J)
\( \varepsilon \) elongation break (%)
\( \varepsilon_y \) yield strain (%)
\( \sigma \) tensile strength (MPa)
\( \sigma_y \) yield stress (MPa)
\( \nu_{as} \) asymmetric stretching vibration
\( \nu_s \) symmetric stretching vibration
\( \phi \) geometry factor
\( \phi_a \) average angle of orientation
\( \text{AMS} \) N-(3-trimethoxysilane-propyl) ethylene diamine
\( \text{CA} \) coupling agent
\( \text{CF} \) carbon fiber
\( \text{CV} \) cyclic voltammetry
\( \text{DRIFT} \) diffuse reflectance infrared spectroscopy
\( \text{EPS} \) 3-glycidoxy-propyl-trimethoxysilane
\( \text{FTIR} \) Fourier transform infrared spectroscopy
\( \text{IFSS} \) interfacial shear stress (MPa)
\( \text{LEFM} \) linear elastic fracture mechanics
\( \text{MDI} \) 4,4’-diphenylmethane-diisocianate
\( \text{PA} \) polyamide 6
\( \text{PAN} \) polyacrylonitrile
\( \text{PC} \) polycarbonate
\( \text{SAS} \) 3-triethoxysilylpropyl succinic acid anhydride
\( \text{SEM} \) scanning electron microscopy
\( \text{SIMS} \) secondary ion mass spectroscopy
\( \text{TGIC} \) triglycidyl isocyanurate
\( \text{XPS} \) x-ray photoelectron spectroscopy
\( \text{vol\%} \) volume percent
\( \text{wt\%} \) weight percent
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Curriculum vitae

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