JOURNAL OF MATERIALS SCIENCE 29 (1994) 3984–3992

The relevance of the surface structure and surface chemistry of carbon fibres in their adhesion to high temperature thermoplastics

Part III *Interface adhesion and reinforcement effects*

G. KREKEL, U. J. ZIELKE, K. J. HÜTTINGER*
Institute für Chemische Technik, Universität Karlsruhe, Kaiserstrasse 12, D-7500 Karlsruhe, Germany

W. P. HOFFMAN
Phillips Laboratory, OLAC PL/RKFE, Edwards Air Force Base, Edwards, CA, 93523-5000 USA

This paper has three principle thrusts: (i) the fabrication of unidirectionally reinforced composites made from carbon fibres subjected to different surface treatments in combination with various (polycarbonate, polyethersulphone and epoxy) matrices, (ii) a study of some of the mechanical properties (that is, the interlaminar-shear strength (ILSS) and the failure behaviour) of these composites; and (iii) determination of the correlations between the adhesion of the matrix polymers as measured by the ILSS and the surface structure as well as the surface chemistry of the various fibres. It will be shown that the surface structure of the fibres has a minor effect, while the surface chemistry appears to have an extraordinarily great influence on the adhesion of the fibres to high-temperature thermoplastics. The data clearly show that, depending on the processing temperature during the fabrication of the composites, chemical bonds can be formed at the fibre–polymer interface. This bond formation is initiated by the decomposition of carboxylic groups and, as a consequence, dangling carbon atoms are free to react with the functional groups of the polymer.

1. Introduction

It is well-established that the reinforcement effect of fibres in any composite is determined to a great extent by the fibre–matrix interface [1–3]. When thermoplastics and high-temperature thermoplastics are used as matrices, the interfacial adhesion should be maximized. The factors controlling these adhesion phenomena, namely the surface structure and surface chemistry of the carbon fibres, were investigated and discussed in Part I and Part II of this series [4, 5]. This last paper in the series is concerned with the influence of fibre surface structure and surface chemistry on fibre adhesion to polycarbonate and polyethersulphone, two high-temperature thermoplastics. For this purpose, unidirectionally reinforced composites with a fibre volume fraction of 60% were fabricated. These composites were used for measuring the interlaminar-shear strength (ILSS), the Young's modulus and the flexural strength. The data obtained, in particular the ILSS data, were correlated with the fibre surface treatments, or more specifically, with the surface structure and surface chemistry of the various carbon fibres. Composites made with an epoxy resin were also studied for comparison.

2. Experimental procedure

2.1. Materials

The nature of carbon-fibre surfaces and the surface treatments that they were subjected to were presented in Part I of this series [4]. The surface chemistry of the various fibres and the properties of the high-temperature polymers were given in Part II of this series [5].

The epoxy resin which was used, additionally, for the fabrication of composites in this paper is a product of Ciba-Geigy AG, Basel, with the trade mark LY556 (diglycidyl ether based on bisphenol A) for which the curing agent HT972 (4,4′-diaminodiphenylmethane) was used. The properties of the cured epoxy resin [6] are presented in Table I.

2.2. Fabrication of composites

For the fabrication of unidirectionally reinforced composites with high-temperature thermoplastic matrices, four or five plies of carbon fibres were wrapped on frames. Subsequently, the stretched fibres were impregnated with a solution of 13 wt% of the polymer in methylene chloride. After drying in air, the resulting prepregs were treated in vacuum at 110 °C for 6 h in

---

* Author to whom correspondence should be addressed.

0022–2461

TABLE I Properties of the epoxy resin [6]

Properties at room temperature	Type LY556/HT972
Tensile strength (MPa)	83–87
Young's modulus (MPa)	2800–3000
Elongation at break (%)	5.5–5.8
Compressive strength (MPa)	207
Density (kg m^{-3})	1.1–1.2
Viscosity of the uncured LY556, (mPa s) (25 °C)	3–10 × 10^3

order to evaporate any residual solvent. Next, the prepregs were moulded in a die at temperatures from 260 to 320 °C for polycarbonate and at 330 °C for polyethersulphone while applying a pressure of 10 MPa. The resulting composites had a fibre volume fraction of between 57 and 62%.

For the fabrication of composites with epoxy resin as the matrix, carbon fibres were wrapped on a frame which afterwards was placed in a die. The fibres were subsequently impregnated with a mixture of 79 wt % of the diglycidyl ether and 21 wt % of the curing agent at 70 °C. The epoxy resin was cured under a pressure of 2.5 MPa while held at 80 °C for 4 h followed by 120 °C for 2 h. The composites obtained had a fibre volume fraction of between 57 and 62%.

2.3. Analytical methods

For measuring the ILSS, a short-beam test conducted according to ASTM D2344 was employed, while for measuring the flexural strength, a three-point flexural test was conducted according to DIN 29971 (with a span-to-depth ratio of 40) was used. The fracture surfaces of the composites were characterized with a scanning electron microscope (Cambridge, Stereoscan S4-10).

3. Results

3.1. Interlaminar-Shear Strength

The ILSS was used as a measure of the adhesion phenomena, although it is known that this quantity is not very specific with respect to the interface adhesion resulting from physico-chemical interactions [1]. In spite of this fact, the ILSS is widely used in the literature and therefore our results can easily be compared to the work of others.

Results are presented for the Celion fibres only. The measured ILSS data with polycarbonate, polyethersulphone and epoxy resin as matrices are shown in Fig. 1. It can be seen that the influence of the surface treatment of the fibres is rather small using polycarbonate as the matrix. This result is really surprising when compared to the composites using polyethersulphone as the matrix. The reinforced polyethersulphone shows the very strong influence of the surface treatment of the fibres, this is manifested by the high values of the ILSS. These values are even higher than the values found for composites with an epoxy-resin matrix. With all matrices, the highest ILSS values were found for the ozone-treated fibres. Although the ILSS values of the polycarbonate and polyethersulphone composites are very different, the trends with respect to the surface treatment are the same. It was thought that the different recommended processing temperatures of 260 °C (polycarbonate) and 330 °C (polyethersulphone), applied during the fabrication of the composites, are responsible for the differences in the absolute values obtained for the ILSS.

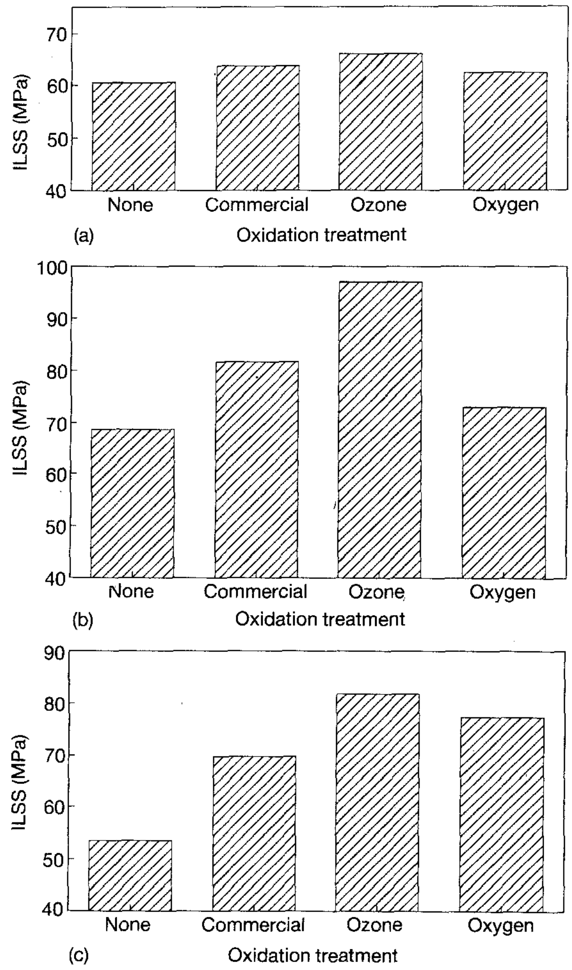


Figure 1 ILSS of composites with differently treated Celion fibres and different matrices: (a) polycarbonate, (b) polyethersulphone, and (c) epoxy resin.

For this reason, composites with polycarbonate as the matrix were fabricated at increased processing temperatures up to 320 °C, which was possible due to the thermal stability of this polymer. The results are presented in Fig. 2. ILSS values obtained from composites with unoxidized and ozone-treated Celion fibres (0.75% O_3/100 °C/60 s) are compared. With unoxidized fibres, a higher processing temperature has practically no effect. In contrast, a remarkable increase in the ILSS (with temperature) resulted from employing the ozone-treated fibre in the polycarbonate matrix.

3.2. Mechanical properties

The Young's modulus, flexural strength, and strain-to failure of the edge fibres in the composites, which are results from a three-point-flexural test, are shown in Table II. It can be seen that the Young's modulus is

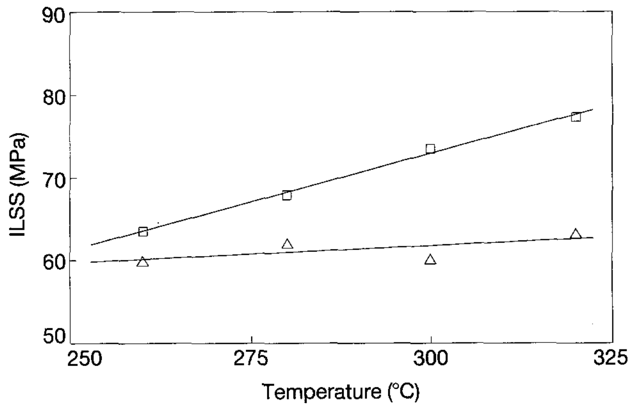


Figure 2 ILSS of composites with (△) unoxidized and (□) ozone-treated Celion fibres and polycarbonate as the matrix as a function of the processing temperature during the fabrication of the composites.

not significantly influenced by the surface treatment of the fibres nor by the nature of the matrix.

This, however, does not hold for the flexural strength which is mainly controlled by the matrix. The highest values of the flexural strength were found with the epoxy resin, while the lowest were observed with polycarbonate as the matrix. An effect of the surface treatment can be observed in the case of the polyethersulphone and the epoxy resin. With these matrix materials all the surface-oxidized fibres clearly demonstrate higher flexural strength values than those with the unoxidized fibre. On the other hand, the type of surface treatment has an insignificant effect in composites using the polyethersulphone matrix except in those with the oxygen-treated fibre which showed a slightly decreased flexural strength.

The flexural-strength values are reflected in the strain-to-failure data of the edge fibres in the composites (according to DIN 53452) and are given in Table II. For composites made from surface-treated fibres and polyethersulphone, strain-to-failure values of about 1.62% were found. These values correspond to those provided by the manufacturer (see Table I in Part I [4]). The surface-treated fibres in the epoxy resin yield slightly higher values of about 1.8%. This larger value may be attributed to a bridging of flaws or microcracks at the fibre surface by the epoxy resin. In contrast, the strain-to-failure of the edge fibres in composites with polycarbonate as the matrix is very poor with the fibres only being utilized to about 80%. This behaviour has been found to be due to a compression failure of the composites with a polycarbonate matrix [7, 8].

The dependence of the flexural strength on the ILSS for composites with polyethersulphone matrix is shown in Fig. 3. It can be observed that the flexural strength comes to a maximum value of about 1725 MPa which is already reached at an ILSS value of about 80 MPa. A further increase of the flexural strength is not observed, probably because the edge fibres in the composites are already elongated to their maximum.

3.3. Fracture behaviour

A discussion of the strength values and especially of the ILSS would be incomplete without consideration of the fracture behaviour. For this reason, some scanning electron micrographs of the fracture surfaces will be presented. For brevity, only the two extreme cases, namely the unoxidized Celion fibre (uu) and the ozone-treated Celion fibre, will be shown. In all cases only the section resulting from the tensile stress will be presented.

The results with the polycarbonate matrix can be seen in Fig. 4a and b. With the unoxidized fibre, a pure single-fibre pull-out is evident with no matrix adhesion at the fibre surface visible even at a higher magnification (Fig. 4a). With the ozone-treated fibre there is no single-fibre pull-out, but rather a pull-out of fibre bundles is the predominant fracture mode, because the fibres are linked together by the polymer (Fig. 4b).

Corresponding micrographs of the fracture surfaces with polyethersulphone as the matrix are presented in Fig. 5. It can be seen in Fig. 5a that the unoxidized fibres exhibit poor adhesion to the polyethersulphone matrix; that is, the fracture surface shows single-fibre pull-out as well as pull-out of some fibre bundles. However, when compared to the polycarbonate composites, the length of the fibres pulled-out is smaller

TABLE II Mechanical data of composites with differently treated Celion fibres and various matrices (where E_{b0° is the Young's Modulus, σ_{bB0° is the flexural strength, and ε_{RB} is the strain-to-failure of the edge fibres in the composites). The values in parentheses represent standard deviations

Polymer	Fibre treatment	E_{b0° (GPa)	σ_{bB0° (MPa)	ε_{RB} (%)
Polycarbonate	None	118.1 (2.6%)	1479.9 (4.6%)	1.28 (4.8%)
Polycarbonate	Commercial	114.7 (4.9%)	1503.5 (4.5%)	1.34 (4.6%)
Polycarbonate	In oxygen	116.8 (3.6%)	1434.3 (5.4%)	1.27 (5.5%)
Polycarbonate	With ozone	116.1 (6.1%)	1457.4 (4.7%)	1.27 (5.7%)
Polyethersulphone	None	114.6 (2.5%)	1438.8 (8.4%)	1.34 (5.3%)
Polyethersulphone	Commercial	118.3 (6.9%)	1717.4 (2.4%)	1.60 (4.3%)
Polyethersulphone	In oxygen	112.6 (2.9%)	1654.2 (2.6%)	1.60 (6.6%)
Polyethersulphone	With ozone	115.0 (4.8%)	1721.3 (2.4%)	1.60 (5.1%)
Epoxy resin	None	116.9 (0.9%)	1744.3 (4.8%)	1.59 (6.7%)
Epoxy resin	Commercial	117.4 (1.3%)	1966.5 (3.4%)	1.78 (11.4%)
Epoxy resin	In oxygen	118.6 (1.5%)	1994.6 (7.1%)	1.85 (9.6%)
Epoxy resin	With ozone	123.4 (4.8%)	1993.2 (4.2%)	1.76 (4.3%)

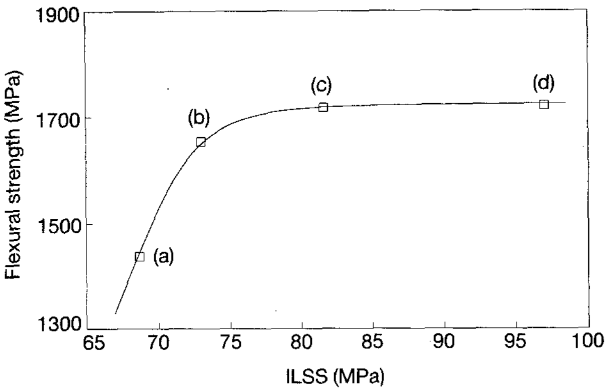


Figure 3 Flexural strength of composites with differently treated Celion fibres and polyethersulphone as the matrix as a function of the ILSS: (a) unoxidized (uu), (b) oxygen-treated fibres (O_2/400 °C/0.5 h), (c) commercially oxidized fibres (ou), and (d) ozone-treated fibres (0.75% O_3/100 °C/60 s).

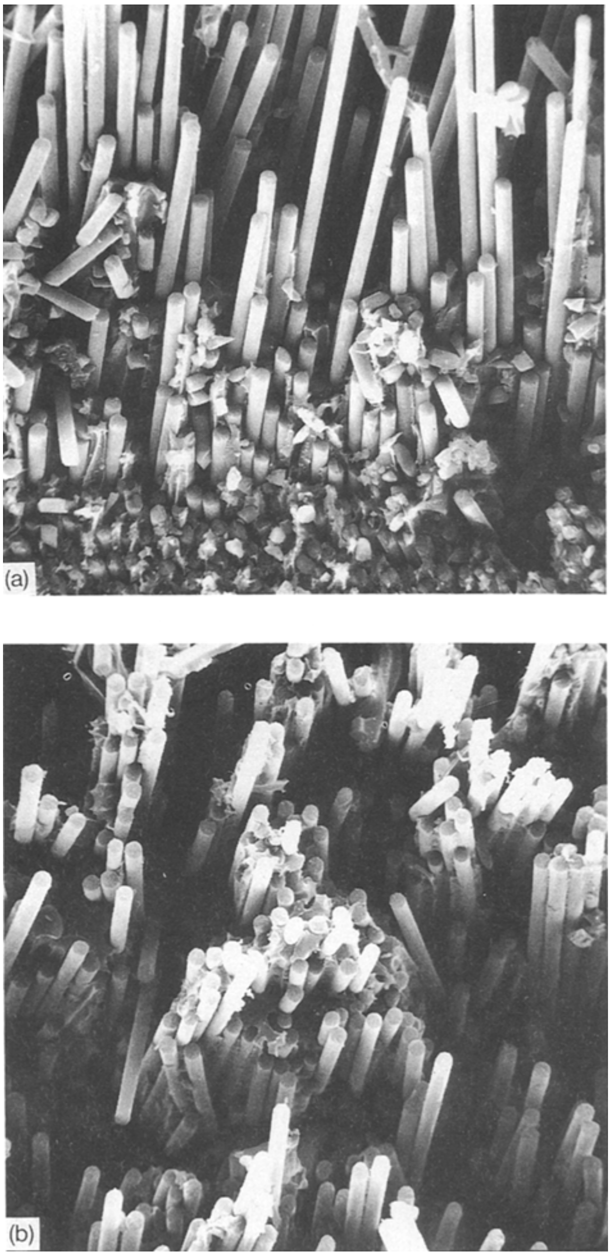


Figure 4 Fracture surfaces of composites with polycarbonate as matrix: (a) single-fibre pull-out with unoxidized Celion fibres (uu), and (b) pull-out of bundles of fibres with ozone-treated Celion fibres.

(Fig. 5a). A completely different fracture surface resulted with the ozone-treated fibres (Fig. 5b). In this case, a small pull-out of thick fibre bundles is dominant while a single-fibre pull-out represents the exception. The explanation of this failure mode can be seen in Fig. 5c which is a high-magnification view of a single fibre with strong matrix adhesion. This phenomenon corresponds to a cohesion failure of the matrix which can also be seen by the very high ILSS value of 97 MPa.

A typical fracture surface that is representative of composites fabricated with epoxy-resin matrix and various carbon fibres is presented in Fig. 6. In this instance, representative means that the micrograph shown could describe either the non-treated or the surface-treated fibre. With both of these surfaces, a considerable amount of fibre pull-out can be observed. In addition, the surfaces of the fibres are covered by small particles of matrix formed by brittle fracture. However, no matrix adhesion was observed with either fibre.

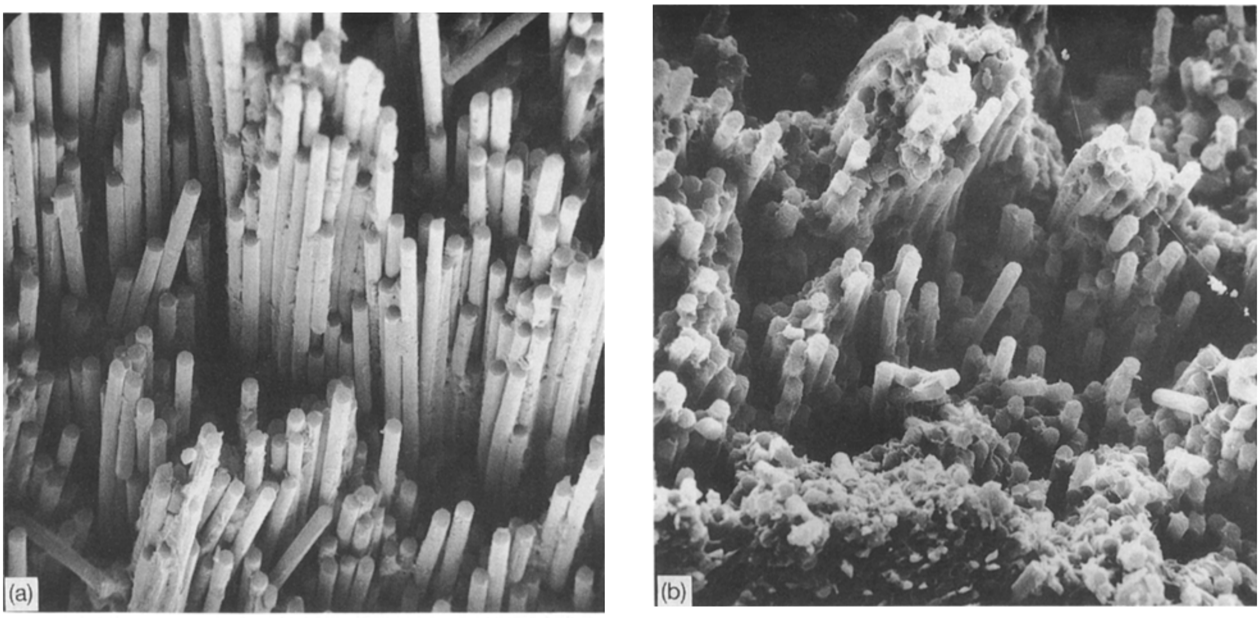
4. Discussion

The objective of this study included a detailed analysis of the surface structure and surface chemistry of selected polyacrylonitrile (PAN) carbon fibres in order to gain a better understanding of the adhesion and reinforcement phenomena of the fibres in high-temperature thermoplastics. In addition to scanning electron microscopy (SEM), scanning tunnelling microscopy (STM) was used to analyse the surface structure of the fibres down to the nanometre scale. The surface structure of these fibres is discussed in Part I [4] while the results of the surface chemistry of the fibres and the adhesion and reinforcement phenomena are presented in Part II [5] and in this paper, Part III. In the discussion that follows we will attempt to correlate the surface properties of the fibres with adhesion effects measured in composites manufactured with these fibres.

The most extensive investigations were performed with Celion fibres. For brevity, the discussion will be limited to these fibres. Figs 7 and 8 show the ILSS measured as a function of the maximum work of adhesion of the fibres for composites using polycarbonate or polyethersulphone as the matrix. As described in Section 2, the composites were manufactured using processing temperatures of 260 °C for polycarbonate and 330 °C for polyethersulphone. In the case of composites with polycarbonate as the matrix the results obtained by applying a higher processing temperature of 320 °C are also presented in Fig. 7. The values of the maximum work of adhesion have already been presented in Part II of this series [5].

Linear dependencies of the ILSS on the maximum work of adhesion can be observed for both matrices. The linear relationship of the ILSS with the maximum work of adhesion can be described by a simple equation

$$\mathrm{ILSS} = m\,W_{\mathrm{SL,max}} + C \qquad (1)$$



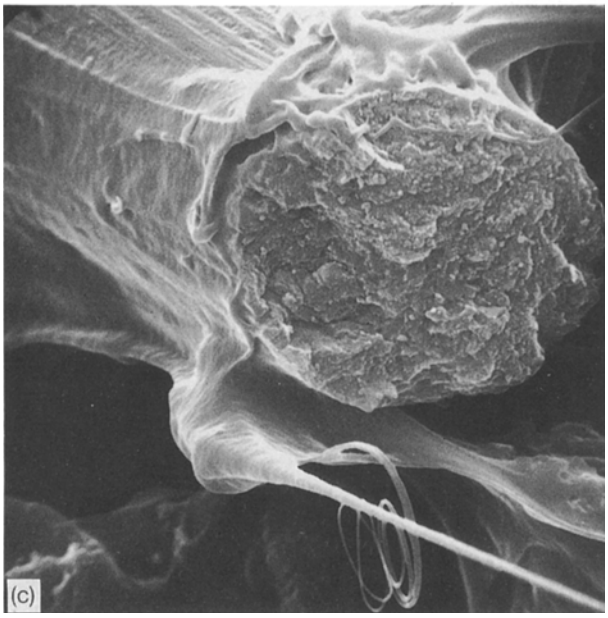


Figure 5 Fracture surfaces of composites with polyethersulphone as the matrix: (a) single-fibre pull-out with unoxidized Celion fibres (uu), (b) pull-out of thick bundles of fibres with ozone-treated Celion fibres, and (c) cohesion failure of the matrix in composites with ozone-treated fibres.

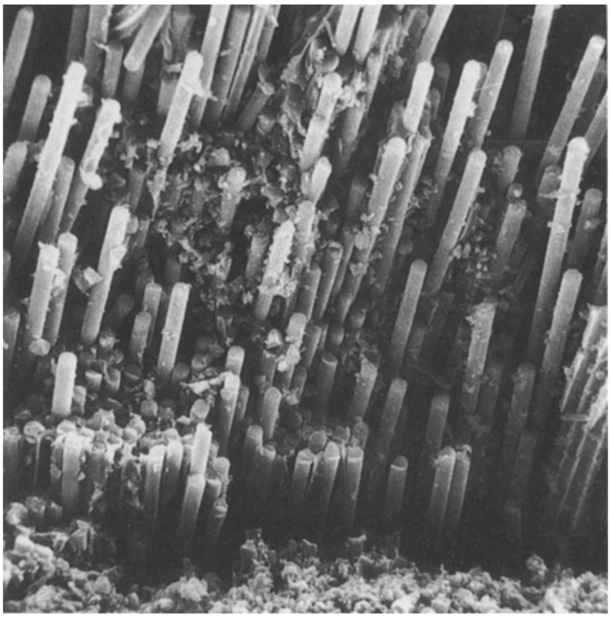


Figure 6 Fracture surfaces of composites with an epoxy-resin matrix with single-fibre pull-out and small particles of the fractured matrix.

The constant C has been defined as a work of adhesion of 85 mJ m^{-2}. This value corresponds to the work of adhesion of carbon fibres in the absence of functional groups [8–10]. The corresponding values of the ILSS are 60 MPa for the polycarbonate matrix and 64 MPa for the polyethersulphone matrix. These values can be seen to be nearly independent of the polymers, which should be expected.

The slope, m, in Equation 1 represents the slope of lines such as those in Figs 7 and 8 and it is the most significant part of Equation 1. A high value of m indicates a strong effect from functional groups at the carbon fibre surfaces on the adhesion to the polymer matrices, as measured by the ILSS. The values 0.14×10^{-9} and 0.28×10^{-9} m^{-1} were measured for m for composites with a polycarbonate matrix manufactured at 260 and 320 °C, respectively while a value of 0.54×10^{-9} m^{-1} was measured for composites with a polyethersulphone matrix manufactured at 300 °C. The effect of the processing temperature is apparent, but it is also clear that the interactions between the functional groups at the carbon-fibre surfaces and the polyethersulphone are stronger than those for the polycarbonate. The reasons for this will be explained below.

The surfaces of carbon fibres affect their adhesion to various matrix materials in different ways. On the surface of these fibres there coexist several types of oxygen-containing functional groups such as carboxyls, hydroxyls, carbonyls (see Part II) [5]. In Part II it was shown that these groups individually contribute

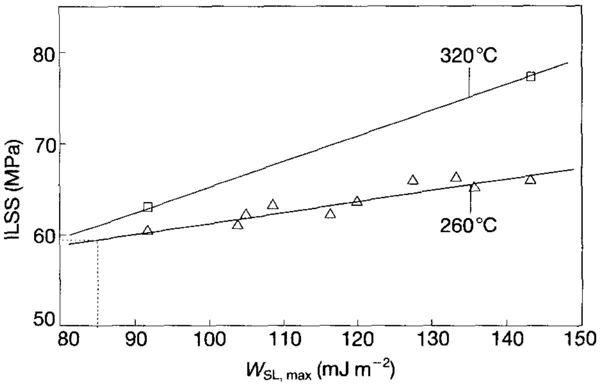


Figure 7 The ILSS of polycarbonate composites with differently treated Celion fibres as a function of the maximum work of adhesion of the fibres and the processing temperature (260 and 320 °C) during the fabrication of the composites.

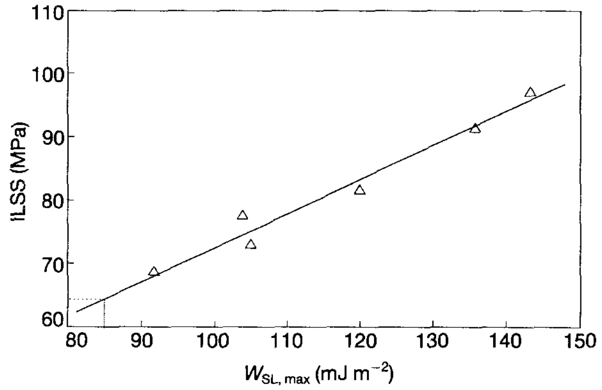


Figure 8 The ILSS of polyethersulphone composites with differently treated Celion fibres as a function of the maximum work of adhesion of the fibres.

to the total work of adhesion of the fibres obtained with aqueous solutions of different pH values. The influence of acidic carboxylic groups was clearly dominant, because a linear relationship was found to exist between the maximum work of adhesion and the number of carboxylic groups at the fibre surface (see Fig. 7 in Part II). This means that carboxylic groups should also have a significant influence on the adhesion of the fibres to polymers containing basic surface groups. Indeed, all composites which possess carboxylic surface groups fit the linear relationship between the ILSS and the maximum work of adhesion. In addition to the carboxylic groups, there should also exist acid–base interactions between other acidic surface groups, especially the hydroxyl groups, and the basic functional groups of the polymers (Fig. 9). However, it was found that their contribution to the overall adhesion is small. This conclusion was reached from the low values of the ILSS which were obtained with composites with an extremely high concentration of hydroxylic surface groups such as with the fibre treated in pure oxygen at 400 °C for 0.5 h (see Fig. 2 in Part II).

It should be noted, however, that the acid–base interactions between carboxylic groups at the carbon-fibre surface and basic functions of the polymers, which are possibly formed primarily during the fabrication of the prepregs, are not directly responsible for the enhanced adhesion at the fibre–matrix interface in the composites. Nevertheless, they have an indirect effect on the adhesion, as will be shown below. Section 2 described the fabrication of the composites using processing temperatures from 260 to 320 °C for polycarbonate and 330 °C for polyethersulphone. At these temperatures the majority of the carboxylic groups are decomposed and desorbed from the fibre surface.

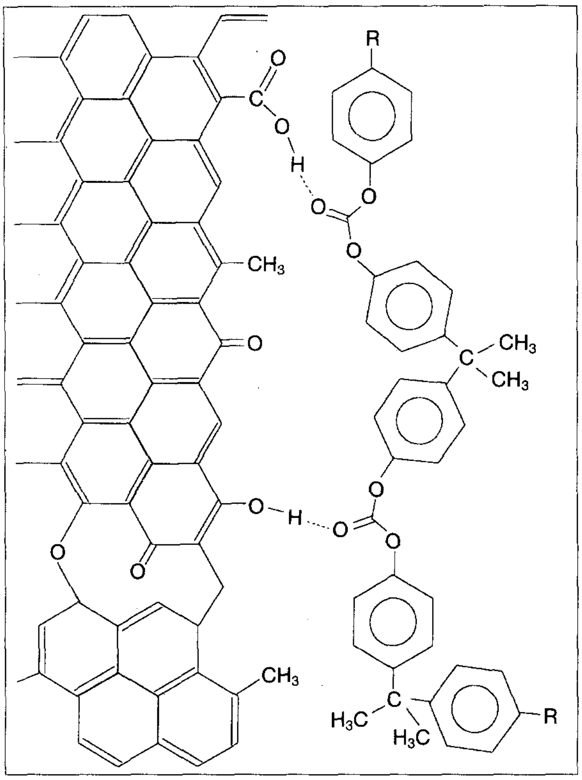


Figure 9 A model of possible acid–base interactions at the fibre–matrix interface in prepregs (that is for polycarbonate as the matrix).

The decomposition of a carboxyl group occurs by desorption of carbon dioxide and the formation of a C–H bond between the surface and the hydrogen of the carboxyl group. The mechanism of the reaction may be of ionic or of radical nature or it may even be a 1,3 rearrangement [11]. However, the high processing temperature should favour an ionic or radical mechanism. With these mechanisms a charge or a radical can be transferred during the decarboxylation reaction to the polymer. This charge adheres to the fibre surface and bonds the fibre to the matrix polymer. A model for such a mechanism with polyethersulphone is shown in Fig. 10.

The formation of these bonds is favoured if the transiently formed charges and radicals can be delocalized in both the aromatic systems of the carbon fibre as well as in the polymer. As Fig. 10 shows, acid–base interactions which already exist prior to the decomposition of the carboxyl groups should support the formation of bonds between the fibre surface and the matrix polymer. Thus, acid–base interactions can be transformed into chemical bonds. With respect to the heterogeneous reaction between the solid carbon-fibre surface and the fluid polymer, acid–base interactions are very important in controlling the

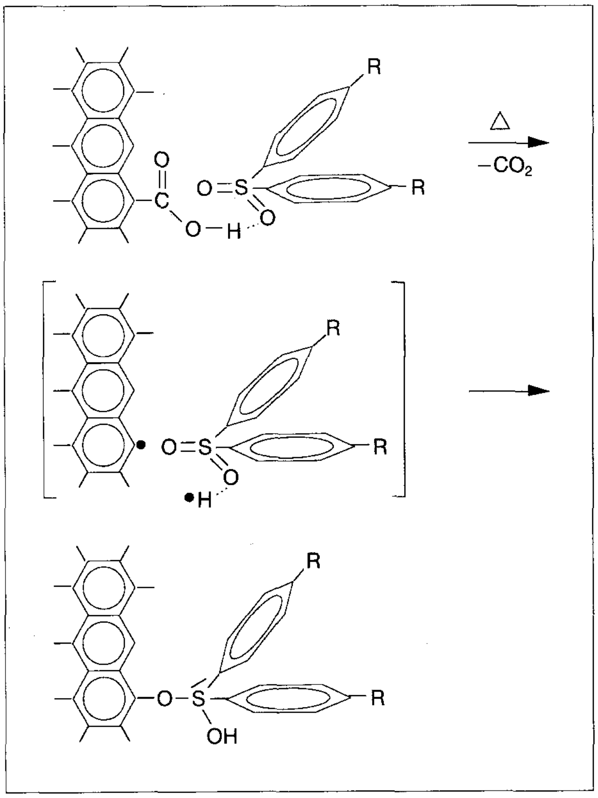


Figure 10 A model of possible chemical reactions at the fibre–matrix interface which are postulated to occur during the fabrication of composites with polyethersulphone as the matrix material.

alignment of the molecules of the polymer at the carbon-fibre surface. Furthermore, they should cause the displacement of adsorbates at the fibre surface. It is through this mechanism that the carboxylic groups can have an indirect effect on the adhesion.

The stronger influence of the surface chemistry of the carbon fibres on their adhesion to polyethersulphone, in comparison to polycarbonate, may be explained by the following factors.

1. As a consequence of the higher processing temperature, more groups (even the thermally more stable carboxylic groups) are desorbed from the carbon-fibre surface and are enabled to react with the matrix polymer.

2. Contrary to the 1,3-rearrangement reaction which does not lead to a reaction with the matrix, the ionic and radical decarboxylation reactions should be favoured by the higher processing temperatures.

3. The sulphur in polyethersulphone can be reduced and is able to form bonds beyond the eight-electron rule.

4. Charges and radicals which are transferred to an oxygen atom of the sulphone group can be delocalized in the neighbouring aromatic systems of the polymer.

As stated above, the value of C (Equation 1) is relatively independent of the nature of the matrix polymer. Values of about 60 MPa for polycarbonate and 64 MPa for polyethersulphone were determined. The value of C results from different components, which contribute to the adhesion and are independent of the nature and concentration of oxygen-containing surface groups. In the discussion that follows, these components will be summarized in light of the present results and their contributions to C will be roughly estimated as follows.

1. Dispersion interactions across the interface are present in all systems and they are always attractive forces. The effective range of these forces is usually small, because the interaction energy decreases with the sixth power of the radius of the interacting atoms or molecules [12]. The high polarizability of the macromolecules should favour these dispersive interactions. In this study, the dispersive component of the surface free energy of the fibres, γ_S^D, was shown to be independent of the surface treatment applied. Therefore, the adhesion due to dispersion interactions should be a constant in each fibre–matrix system. The contribution is estimated to be about 10 or 20%.

2. Acid–base interactions between the functional groups and the aromatic systems of the polymers and the aromatic system of the carbon-fibre surface are estimated to contribute 10 to 20% to the adhesion.

3. Friction in the interface between the fibres and the polymer matrices should be significant, but the change of the surface structure of the fibres due to the various surface treatments has no effect on the adhesion. Thus, the contribution of the mechanical interlocking to C should be constant and it is estimated to be 30 to 40%.

4. During the performance of the short-beam test the test specimens are plastically deformed. Although these deformation forces do not result from the adhesion between the fibres and the matrix their estimated contribution to the ILSS is 30 to 40% [8].

In summary, the ILSS of composites with thermoplastic matrices is composed of two components. A component which is independent from the surface chemistry of the fibres and a second component which is dependent on the surface chemistry. Dispersive interactions across the interface, acid–base interactions between the polymers and the carbon of the fibre and mechanical interlocking contribute to the component of the ILSS which is independent of the surface chemistry of the fibres. Deformation forces additionally enhance the ILSS. The contribution which depends on the surface chemistry of the fibres is predominantly determined by carboxylic surface groups. Furthermore, the processing temperature has a decisive influence on the resulting ILSS values. An increase in this temperature leads to an enhancement of the ILSS values if carboxylic groups are present on the carbon-fibre surface. Thus, a significantly higher contribution from the fibre surface chemistry to the interfacial adhesion can be obtained if higher processing temperatures are applied.

Carbon-fibre composites made with an epoxy-resin matrix were also studied in order to compare the adhesion properties of these composites with composites fabricated using thermoplastic matrices. As Fig. 11 shows, a linear relationship between the ILSS and the maximum work of adhesion of the fibres can also be observed with this system. The slope of the line is about $0.48 \times 10^{-9}\,\mathrm{m}^{-1}$. This value is in the range of the values found with composites using polyethersulphone as the matrix. The ILSS value at $W_{\mathrm{SL,max}}$

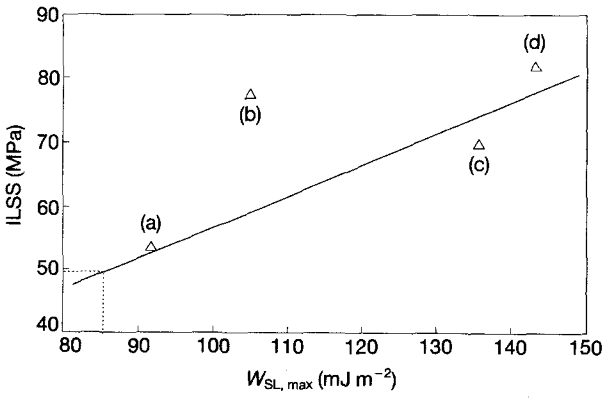


Figure 11 ILSS of epoxy-resin-matrix composites as a function of the maximum work of adhesion of the Celion fibres subjected to various surface treatments which were used to fabricate the composite.

$= 85$ mJ m^{-2} is about 50 MPa, which is significantly lower than the value obtained from composites with thermoplastic matrices.

The linear increase of the ILSS, as a function of the maximum work of adhesion in the epoxy system, can again be explained by the dominant influence of the carboxyl groups. However, in contrast to composites fabricated with thermoplastics as matrices, the processing temperature of the composites is below the desorption temperature of the carboxyl groups. Therefore, chemical bonds between the matrix and the fibre surface can result from a direct reaction of the components of the resin (epoxy compound and curing agent) with the carboxyl groups. Such reactions have been frequently described in the literature [13, 14] as was detailed in Part I [4] (see Fig. 3 in Section 1 Part I). These reactions should be favoured by the high mobility of the molecules of the uncured epoxy resin due to the low viscosity.

In contrast to composites manufactured with high-temperature thermoplastic matrices, both carboxyl and hydroxyl groups have an important influence on the adhesion properties of composites using epoxy resin as the matrix. This is shown by the high ILSS values of composites with oxygen-treated fibres, which exhibit a high surface concentration of hydroxyl groups. These groups form covalent bonds with the epoxy-resin matrix. The formation of these bonds is similar to the reactions of the carboxyl groups shown in Fig. 3 in Section 1 of Part I [4].

Compared to composites with a thermoplastic matrix, a smaller value for C was found for composites with an epoxy matrix. The reason for this is that the test specimens are not deformed during the performance of the short-beam test. This may be a consequence of the three-dimensional network and a higher compressive strength of the cured epoxy-resin matrix. This is thought to be the case because the contribution of the mechanical interlocking and the dispersion interactions to the ILSS of composites with an epoxy-resin matrix should be similar to that for the composites with thermoplastic matrix.

5. Conclusion

The investigations of the present study confirmed the well-known fact that the interactions across the interface between fibres and polymers are complex. They are individually determined by the surface structure and surface chemistry of the fibres and the nature of the selected polymer.

With the use of high-temperature thermoplastic polymers as matrices, a relatively simple but, from the technical viewpoint, attractive system was chosen. It has been shown that the adhesion in composites with thermoplastic matrices can be divided into a component which is independent from the surface chemistry of the fibre and a further component which depends on its surface chemistry.

This result, which is already known in the case of composites made with thermosetting matrices, could not be predicted. However, the contribution of the surface chemistry of the fibres to the adhesion at the interface depends considerably on the kind of thermoplastic polymer that is used. Thus, with fibre surface treatment, only a small (10%) increase of the ILSS from 60 to 66 MPa was observed with polycarbonate as the matrix. In contrast, the increase of the ILSS due to fibre surface treatment in the case of a composite with a polyethersulphone matrix was considerable, for it amounted to more than 40% (from 68 to 97 MPa). In addition to the differences caused by the matrix material, the adhesion between fibres and thermoplastic matrices can be enhanced by applying high processing temperatures. As shown above, composites using a polycarbonate matrix fabricated at 320 °C (rather than 260 °C) exhibit an increase of the ILSS from 63.1 to 77.3 MPa, which represents a 23% increase.

The main result of the present study is that the contribution of acidic surface groups, and especially carboxyl groups, to enhanced adhesion can be attributed principally to reactions at the interface. These interface reactions are heterogeneous solid–liquid reactions, for which adsorption as the primary step is decisive. This adsorption is favoured by acid–base interactions which necessitate the alignment of the interacting groups in a mutually sterically favourable position. However, although a strong and aligned adsorption is necessary, it is not enough to augment the adhesion. The high ILSS values result, only because the decomposition of the acidic carboxyl groups leads to the formation of chemical bonds between fibre and matrix. The reaction shown in Fig. 10 is only one possible example, because other ionic or radical mechanisms are conceivable. Nevertheless, the existence of the chemical reactions in the interface is clearly confirmed by the results with polycarbonate and polyethersulphone matrices. In particular, the enhancement of the adhesion obtained by an increase of the processing temperature can only be explained by chemical-bond formation at the interface.

The results of this study present a new aspect of the reinforcement of high-temperature thermoplastics with carbon fibres. The processing temperature was found to be an important factor not only with respect to the infiltration of the fibres [15, 16], but also because the stability and reactivity of the functional groups at the carbon-fibre surface will be influenced by this temperature. However, in elevating the temperature to enhance the interfacial bond, the thermal stability of the thermoplastic polymer used has to be taken into account. For polymers which cannot be subjected to higher temperatures, catalysis for the interface reactions would be most attractive.

Acknowledgement

Financial support for this study from the German Research Foundation (DFG) is gratefully acknowledged.

References

1. P. J. HERRERA-FRANCO and L. T. DRZAL, *Composites* **23** (1992) 2–27.
2. A. HAMPE in "Haftung bei verbundwerkstoffen and werkstoffverbunden" (DGM Informationsgesellschaft mbH, Oberursel, 1989) pp. 33–44.
3. F. P. GERSTLE in "Encyclopedia of polymer science and engineering", edited by H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz. Vol. 3, (Wiley, New York, 1988) pp. 776–820.
4. G. KREKEL, K. J. HÜTTINGER, W. P. HOFFMAN and D. S. SILVER, *J. Mater. Sci.* in press.
5. G. KREKEL, K. J. HÜTTINGER and W. P. HOFFMAN, *ibid.* in press.
6. CIBA-GEIGY AG, Product information: Araldit LY556, Basel (1988).
7. S. W. YURGATIS and S. S. STERNSTEIN, *J. Mater. Sci.* **23** (1988) 1861–1870.
8. G. KREKEL, PhD thesis, University of Karlsruhe (1992).
9. K. J. HÜTTINGER, S. HÖHMANN-WIEN and G. KREKEL, *Carbon* **29** (1991) 1281–1286.
10. *Idem. J. Adhesion Sci. Tech.* **6** (1992), 317–331.
11. N. L. ALLINGER, M. P. CAVA, D. C. DE JONGH, C. R. JOHNSON, N. A. LEBEL and C. L. STEVENS, "Organische chemie" (de Gruyter, Berlin, 1980) pp. 825–830.
12. P. W. ATKINS, "Physikalische chemie", 1st Edn, Verlag Chemie, Weinheim (1987), 598–602; and *Idem. Carbon* **28** (1990) 221–228.
13. E. FITZER and R. WEISS, *Carbon* **25** (1987) 455.
14. P. EHRBURGER, J. J. HERQUE and J. B. DONNET, *London, Soc. Chem. Ind* **1** (1978) 398.
15. E. FITZER, K. H. GEIGL, W. HÜTTNER and R. WEISS, *Carbon* **18** (1980) 389–393.
16. J. MATSUI, *Crit. Rev. Surface Chem.* **1** (1990) 71–130.

Received 5 April
and accepted 8 October 1993