Evidence for Chemical Bond Formation between Surface Treated Carbon Fibres and High Temperature Thermoplastics

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SYNOPSIS

The interaction between surface-treated carbon fibres and high temperature thermoplastics (polyethersulfone and polycarbonate) was studied by measuring the interlaminar shear strength of unidirectionally reinforced composites with a fibre volume content of 60%. The ILSS-values were correlated with the surface concentration of the acidic functional groups of the carbon fibres, as analysed by temperature programmed desorption and contact angle measurements using basic aqueous solutions (pH $\geq$ 12). Linear relationships were found with both the amount of carbon dioxide desorbed by decomposition of carboxylic surface groups and the work of adhesion calculated from the measured contact angles. This result could be interpreted as a consequence of acid–base interactions with the basic polymers. However, strongly acidic carboxylic groups are decomposed during processing of the composites. Therefore, the high ILSS-values can only be explained by chemical bonds being formed with the functional groups of the polymers during decomposition of the carboxylic surface groups. © 1994 John Wiley & Sons, Inc.

Carbon fibre reinforced polymers are mainly based on thermosetting resins and especially epoxy resins as matrix materials. As compared to these materials, carbon fibre reinforced high temperature thermoplastics are underdeveloped. This statement concerns both industrial applications as well as scientific investigations. The situation is remarkable because fibre reinforced high temperature thermoplastics as compared to composites with thermosetting resin matrices offer advantages related to the processing procedure, the mechanical properties, and additionally to environmental requirements: curing cycles are not necessary, the impact strength is significantly higher, and recycling is feasible.[1-3]

A fundamental problem of carbon fibre reinforced thermoplastics represents the carbon fibre–polymer interface.[1] High temperature thermoplastics only exhibit less reactive functional groups. For this reason, the interactions of these polymers with functional groups at carbon fibre surfaces should be limited to acid–base interactions. As compared to chemical bonds formed by thermosetting resins, such acid–base interactions are weak.[4] Consequently, the adhesion to the carbon fibre surfaces also should be weak. In order to clarify this problem, studies with carbon fibres of various surface treatments and different high temperature thermoplastics were performed. These studies were focused on a careful analysis of both the carbon fibre and the polymer surfaces. The surface chemistry of the carbon fibres was analysed by temperature programmed desorption of the surface groups, wetting studies, and XPS. The polymer surfaces were analysed by wetting studies. For evaluating correlations between the surface properties of both the carbon fibres and the polymers, unidirectionally reinforced composites with a fibre volume fraction of 60% were produced. The adhesion was tested with the aid of the short beam test.

This article summarizes main results of a fundamental study on this problem. Within the study evidence for chemical bond formation in the carbon fibre–high temperature thermoplastic interface was found.[5]

EXPERIMENTAL

Materials

The results presented in the following were obtained with unsized Celion G30-500 carbon fibres (BASF AG). These high tenacity fibres were available without and with commercial surface treatment. Unoxidized fibres were treated with 0.75% ozone in oxygen at 100°C for 60 s. The high temperature thermoplastics polyethersulphone (Ultrason E1010) and polycarbonate (Markrolon 2400) were obtained from BASF AG and from Bayer AG, respectively.

Fabrication of Composites

For the fabrication of unidirectionally reinforced composites with thermoplastic matrices four or five plies of carbon fibres were wrapped on a frame. The fibres were subsequently impregnated with a solution of 13 wt % of the polymer in methylene chloride. For evaporating residual solvent, the impregnated fibres were dried in air and treated in a vacuum at 110°C for 6 h. The resulting prepregs were moulded in a die at temperatures of 330°C (polyethersulphone) and between 260 and 320°C (polycarbonate) applying a pressure of 10 MPa. The fibre volume fractions of the composites varied between 57 and 62%.

Analytical Methods

The temperature programmed desorption (TPD) experiments were performed by heating carbon fibre samples with a rate of 10 K/min to 1050°C in pure argon (oxygen content < 0.1 ppm) applying a flow rate of 0.35 cm/s related to ambient conditions. Carbon dioxide desorbed from the fibre surfaces was continuously analysed by ND-IR-analysers (Leybold-Heraeus, Binos 1.2).

Wetting studies of fibres were performed according to the Wilhelmy technique with the aid of a Sartorius micro-balance (sensitivity: 1 μg).[6] The measurement of the wetting force F_W and the tear-off force F_{TO} directly yields the contact angle θ:

$$\frac{F_W}{F_{TO}} = \cos \theta. \qquad (1)$$

With the value of $\cos \theta$ the work of adhesion W_{SL} can be calculated if the surface tension of the test liquid γ_L is known:[7,8]

$$W_{SL} = \gamma_L \cdot (1 + \cos \theta). \qquad (2)$$

Contact angle measurements on plane polymer surfaces were conducted using the sessile drop technique.[8] The contact angle was measured every minute for a period of 10 min. A decrease of the contact angles was found until a plateau was reached after 6–10 min. By extrapolating the curve back to zero time, the advancing contact angle was obtained. The work of adhesion W_{SL} was calculated according to eq. (2).

The feature of the wetting studies performed represents the test liquid. Due to the application of aqueous solutions with pH values from 1 to 14, well-defined acid–base complexes (Brønstedt type) are formed with functional groups at the surface of the solid. Such acid–base complexes are reflected by a decrease of the contact angle θ or an increase of the work of adhesion W_{SL}. A decisive prerequisite for comparing the work of adhesion obtained with solutions of different pH values represents the independence of the surface tension γ_L of the pH value. All test liquids exhibit a value of 72.8 mN/m according to the value of pure water.[9,10]

For measuring the interlaminar shear strength (ILSS) the short beam test according to ASTM 2344 was applied (span-to-depth ratio: 4).

RESULTS AND DISCUSSION

Functional Groups at Carbon Fibre Surfaces

Oxygen containing functional groups at the carbon fibre surfaces exhibit different thermal stabilities. They are decomposed by formation of carbon dioxide and/or carbon monoxide.[11,12] For this purpose, TPD is an appropriate method for a quantitative analysis of the functional groups. Most important is the de-
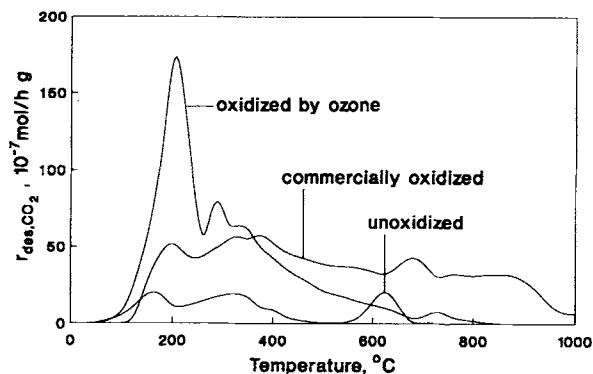

Figure 1 Desorption rates of carbon dioxide of fibres with different surface treatments as a function of the desorption temperature.

sorption of carbon dioxide below 250°C because it can exclusively be attributed to the decomposition of the most reactive strongly acidic carboxylic groups.[11] Desorption rates of carbon dioxide with unoxidized, commercially oxidized, and ozone treated fibres are presented in Figure 1. From the surface of the unoxidized fibre, only a small amount of carbon dioxide is desorbed below 250°C. A characteristic peak at 600°C is due to the desorption of peroxidic groups.[13] The commercially oxidized fibre shows enhanced desorption rates, but compared to the unoxidized fibre the structure of the desorption spectrum is similar. A significantly different desorption spectrum is found with the ozone treated fibre. It is characterized by a pronounced peak at about 200°C. Only a little carbon dioxide is split off at higher temperatures.

Work of Adhesion at Carbon Fibre Surfaces

The work of adhesion according to eq. (2) is a direct measure of the interactions between the surface of a solid and an adjacent liquid. On a molecular basis, dispersion and nondispersion forces determine the extent of the interaction.[8] Thus, the work of adhesion changes if the chemical nature of the solid surface or the liquid is altered. The work of adhesion of unoxidized, commercially oxidized, and ozone treated carbon fibres as a function of the pH value of the applied aqueous test liquids is presented in Figure 2. An increase of the work of adhesion with increasing pH value indicates the formation of acid–base interactions due to acidic surface groups of the fibres.[9,10] More pronounced than the steps are the
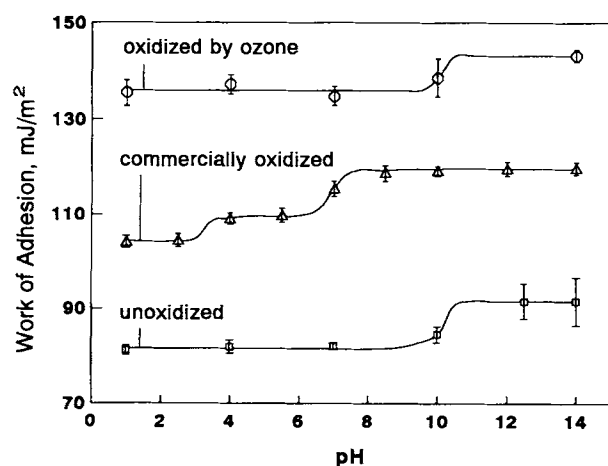

Figure 2   Work of adhesion of fibres with different surface treatments as a function of the pH value of the test liquid.
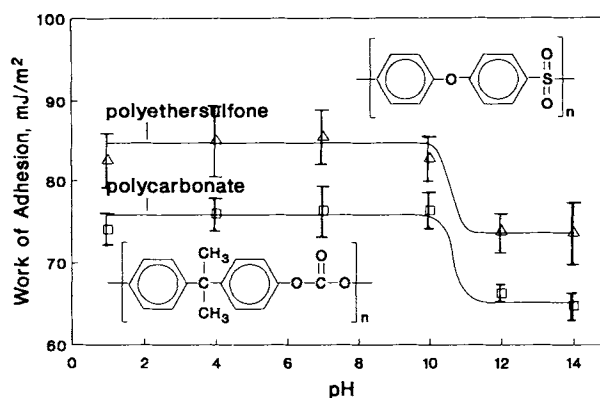

Figure 3   Work of adhesion of the high temperature thermoplastics, polycarbonate and polyethersulfone, as a function of the pH value of the test liquid.

levels of the work of adhesion if the surface treatment is regarded. As the dispersion fraction of the work of adhesion (according to London forces) of pure water is nearly independent of the surface chemistry of the fibres,[9,10] the different levels of the measured work of adhesion may be attributed to nondispersion, that is, acid–base interactions of water with the functional groups. In accordance with the low concentration of surface groups found by the TPD studies, the unoxidized fibre exhibits only low values of the work of adhesion over the total pH range. On the other hand, the highest values up to 140 mJ/m^2 were found with the ozone treated fibre. These results are in accordance with the amount of carbon dioxide measured in the TPD experiments.

Work of Adhesion at Polymer Surfaces

As follows from Figure 3, the work of adhesion of both high temperature thermoplastics (polyethersulphone and polycarbonate) increases with decreasing pH value. Thus, it can be concluded that the surface chemistry of the polymers is determined by basic functional groups. The work of adhesion of polyethersulphone is about 10 mJ/m^2 higher than that of polycarbonate. The basic character of the polymer surfaces should favour the formation of acid–base complexes in the interface with the acidic carbon fibre surface. The meaning of these complexes for the adhesion will be discussed below.

Influence of Surface Groups on Work of Adhesion

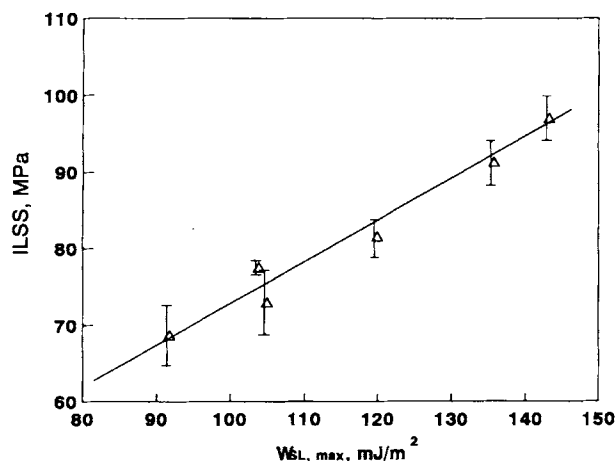In principle, the TPD results should be sufficient to correlate the functionality of carbon fibre surfaces

Figure 4 Interlaminar shear strength of polyethersulfone composites with differently treated fibres as a function of the maximum work of adhesion of the fibres.

with the adhesion of the basic polymers polyethersulphone and polycarbonate. However, the maximum work of adhesion as found by increasing the pH value is at least of similar relevance for the acidic functionality of the carbon fibre surfaces. This will be shown later. On the other hand, the maximum work of adhesion of differently treated fibres plotted as a function of the amount of carbon dioxide desorbed up to 250°C gives a fairly linear relationship. That indicates that the increase of the maximum work of adhesion of the fibres mainly results from carboxylic groups.
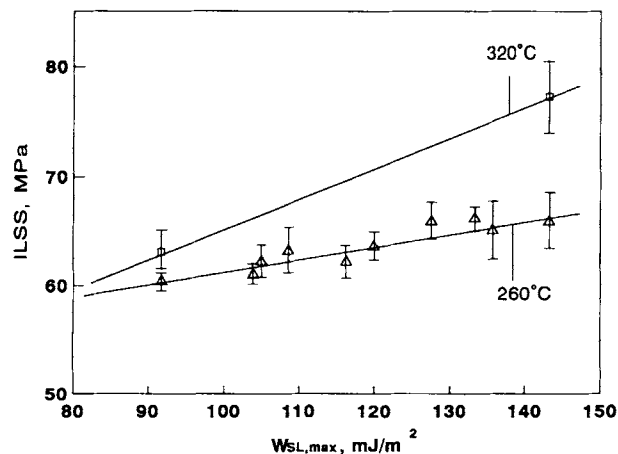

Figure 5 Interlaminar shear strength of polycarbonate composites with differently treated fibres as a function of the maximum work of adhesion of the fibres and the processing temperature (260 and 320°C) during the fabrication of the composites.

Relevance of Surface Chemistry of Fibres in Adhesion of High Temperature Thermoplastics

Figures 4 and 5 show the ILSS values of the composites with polyethersulphone and polycarbonate matrix, respectively, as a function of the maximum work of adhesion of the fibres. Linear relationships can be observed in all cases. In other words, a direct relationship exists between the acidic functionality of the carbon fibre surfaces and the adhesion of the polymers. More remarkable is the steep increase of the ILSS with increasing work of adhesion, especially in the case of polyethersulphone (see Fig. 4). For polycarbonate, two straight lines are shown that are obtained for composites with two different processing temperatures (see Fig. 5). The steep increase of the ILSS in the case of the polyethersulphone matrix and the strong influence of the processing temperature in the case of the polycarbonate matrix suggest that chemical bonds are formed in the interface. For that two steps should be responsible:

1. an oriented adsorption of the polymer at the carbon fibre surface during the impregnation
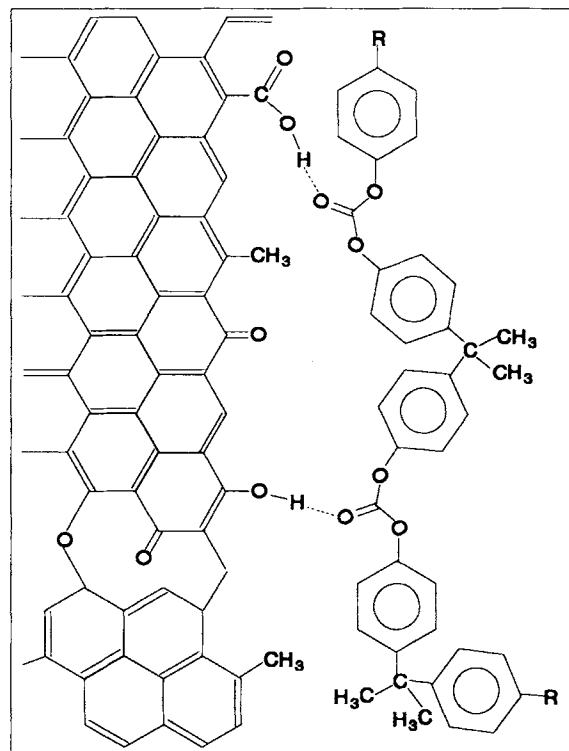

Figure 6 Model of possible acid–base interactions at the fibre–matrix interface in prepregs (i.e., for polycarbonate as matrix).
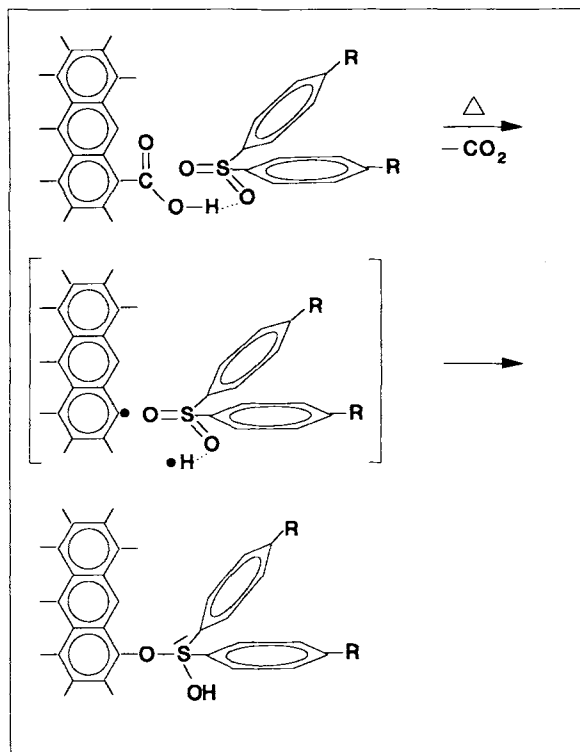
Figure 7 Model for postulated chemical reactions at the fibre–matrix interface that should occur during the fabrication of the composites (i.e., for polyethersulfone as matrix).

process due to acid–base interactions between acidic groups at the fibre surface and basic functional groups of the polymer;

2. chemical reactions between carboxylic groups at the fibre surface and sulphone or carbonate groups of the polymers, initiated by the decomposition of the thermally unstable carboxylic groups during the processing of the composites.

Similar observations about the oriented adsorption of polymers at the surfaces of different substrates and the formation of chemical bonds were reported already in earlier articles.[14,15] For polycarbonate, Figure 6 shows a model of acid–base interactions that should be formed in the first step. However, acid–base interactions cannot be considered directly responsible for the enhanced adhesion as follows from the small increase of the ILSS for a processing temperature of 260°C, but a strong increase for 320°C (polycarbonate, see Fig. 5). On the other hand, acid–base interactions should be most important for the formation of chemical bonds

namely in an indirect manner during the second step. This statement is explained in a model presented for polyethersulphone in Figure 7. It shows both steps, the interaction of an acidic carboxylic group with a basic sulphone group due to a preferred adsorption of the polymer and the reaction between the same groups. During processing of the composites at 330°C, the strongly acidic carboxylic groups are decomposed (see Fig. 1) and acid–base interactions can be transformed into chemical bonds. The mechanism shown in Figure 7 only represents an example, because many other types of reactions are conceivable. These considerations explain the above statement that acid–base interactions are indirectly decisive for the adhesion.

The formation of chemical bonds is strongly supported by the results with polycarbonate processed at a higher temperature of 320°C as compared to 260°C. Nevertheless, the ILSS values of polyethersulphone are not reached. This result is understandable because only in the case of polyethersulphone can charges and radicals be easily transferred to an oxygen atom of the sulphone group because they can be delocalized in the neighboured aromatic systems of the polymer.

CONCLUSIONS

The results obtained give a new view on the adhesion of high temperature thermoplastics to carbon fibre surfaces. The contribution of carboxylic surface groups for an enhanced fibre/matrix adhesion can mainly be attributed to reactions in the interface. These interface reactions are heterogeneous solid–liquid reactions, for which the adsorption as the primary step is decisive. The adsorption is favoured by acid–base interactions that necessitate the orientation of the interacting groups in a mutual steric favourable position. Chemical bond formation in the fibre–matrix interface is initiated by the decomposition of carboxyl groups at the fibre surface.

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