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

Part II *Surface chemistry*

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The paper is concerned with the surface chemistry of several different carbon fibres subjected to various surface treatments. The microstructure and nanostructures of these fibres were investigated in the Part I of this series of papers. For analysis of the surface chemistry of the fibres, X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) were employed; the first method was used for identification and semi-quantitative determination of functional surface groups, while the second method was used for a quantitative determination of these groups. The possible interactions of the various carbon-fibre surfaces due to different surface treatments (and therefore to different functional groups) were analysed by wetting studies using the Wilhelmy technique and aqueous solutions of different pH values as test liquids. By variation of the pH value of the test liquids, the distinct acid–base complexes that formed with the functional groups were identified. The same test liquids were used for characterization of the surface chemistry of the high-temperature thermoplastics (polycarbonate and polyethersulphone) used as matrix materials in the fabrication of the composites in this study. Acid–base interactions at the carbon-fibre surfaces are mainly determined by carboxylic groups of different acidity. The concentration of these groups as determined by desorption of carbon dioxide up to 500 °C is shown to be directly proportional to the measured work of adhesion of each group.

1. Introduction

The relevance of the surface structure and surface chemistry of carbon fibres for adhesion to and reinforcement of high-temperature thermoplastics was outlined in Part I [1]. In Part I, the surface structures of several high-strength carbon fibres subjected to different surface treatments were analysed by scanning electron microscopy (SEM) and scanning tunnelling microscopy (STM) techniques. The surface chemistry of these same fibres is analysed and characterized in this paper. Although numerous similar studies can be found in the literature [2–25], the objective of this study is unique in that it combines the results of the surface microstructure and nanostructure with results of the fibre surface chemistry. This will lead to a better understanding of the interactions at the interface between the carbon fibres and the high-temperature thermoplastics. Compared to thermosetting resins, high-temperature thermoplastics represent a very appropriate model, because they are a single-component system and possess only functional groups which have little reactivity. Thus, only acid–base interactions between the thermoplastics and the carbon-fibre surfaces are expected. The surface chemistry of the two polymers, polycarbonate and polyethersulphone, used in this study was also analysed.

For analysis of the surface chemistry, three experimental methods were applied in the present study. They include:

(i) X-ray photoelectron spectroscopy (XPS) for a qualitative or semi-quantitative determination of the functional groups,
(ii) temperature programmed desorption (TPD) for a quantitative analysis, and
(iii) wetting studies using aqueous solutions with different pH values for a direct analysis of possible acid–base interactions at the surfaces of interest.

2. Experimental procedure

2.1. Materials

The carbon fibres used, the various surface treatments, and the abbreviations chosen for these fibres are given in Table II of Part I [1].

TABLE I Selected properties of the high-temperature thermoplastics used

Properties	Polymer type	
	Polycarbonate Makrolon 2400 [26]	Polyethersulphone Ultrason E1010 [27]
Mechanical properties at room temperature		
Tensile stress at yield (MPa)	> 55	90
Young's modulus (MPa)	2300	2800
Strain at yield (%)	6	6.7
Other properties		
Coefficient of linear thermal length expansion (K^{-1})	65×10^{-6} (-50 to $+90$ °C)	55×10^{-6} (23–85 °C)
Density ($kg\,m^{-3}$)	1200	1370

TABLE II Binding energies and chemical shifts of electrons in C_{1s} orbitals of carbon atoms in graphitic or aliphatic carbon and in functional groups [19–24]

Binding energy (eV)	Chemical shift (eV)	Location of carbon atom	Symbol
284.7	–	Graphitic or aliphatic carbon	$-C-C-$
286.1	1.5	hydroxylic, ether and nitrogen-containing groups	$-C-O-R$, $-C-NR_2$
287.6	2.9	Carbonylic groups	$-C=O$
288.6	3.9	Carboxylic and related groups	$-COOR$

Polycarbonate (Makrolon 2400) was supplied by Bayer AG, in Leverkusen, Germany, while polyethersulphone (Ultrason E1010) was obtained from BASF AG, Ludwigshafen, Germany. Typical properties of these polymers are presented in Table I [26, 27].

The argon used in the TPD experiments had an as-received purity of 99.998% and was then further purified with an oxysorb cartridge (Oxisorb, Messer-Griesheim) to an oxygen content below 0.1 p.p.m. (parts per million).

The aqueous solutions used for the wetting experiments were prepared with double-distilled water and NaOH and HCl as the base and the acid, respectively. Methylene iodide with a purity of > 99.5 % was used as a non-polar test liquid.

2.2. Analytical methods

2.2.1. XPS and TPD measurements

The XPS measurements were carried out on a Leybold LHS 10 X-ray photoelectron spectrometer with an aluminium K_α X-ray source ($E_{\mathrm{AlK}_\alpha} = 1486.6$ eV). The vacuum in this instrument was maintained below 5×10^{-6} Pa. Bundles of carbon-fibre samples mounted to the header of the sample probe of the spectrometer were held at 100 °C for 10 min in an ultrahigh vacuum to remove physically adsorbed carbon dioxide and water. The C_{1s}, O_{1s} and N_{1s} photoelectron peaks were subsequently measured. In order to determine the different types of functional surface groups in a semi-quantitative manner, curve fitting of the C_{1s} peak was conducted using Gaussian functions. This procedure is relatively simple and should be sufficient to compare the surface chemistry of the differently treated fibres. Table II shows the binding energies and the chemical shifts of electrons in C_{1s} orbitals of carbon atoms in graphitic or aliphatic carbon and in functional groups given in the literature [19–24].

The TPD experiments were performed by placing 5 g of carbon fibres in a vertical reactor made of an alumina ceramic with an inner diameter of 30 mm. The samples were heated at a rate of 10 K min^{-1} to 1050 °C in pure argon (oxygen content < 0.1 p.p.m.) with a flow rate of 8 l h^{-1} at STP (standard temperature and pressure). The carbon dioxide and carbon monoxide that desorbed from the fibre surfaces were continuously analysed by a non-dispersive infrared analyser (Leybold-Heraeus, Model Binos 1.2). The calculated desorption rates of the analysed gases were plotted as a function of the desorption temperature.

2.2.2. Wetting studies

Contact-angle measurements, with the aid of the Wilhelmy technique, were used for determinations of possible physico-chemical interactions at the carbon-fibre surface [28, 29]. For this purpose, a Satorius microbalance with a sensitivity of 1 μg was employed. A small droplet of the test liquid was placed on a plate of polytetrafluoroethylene. After the filament was fixed to the balance, the test liquid was automatically lifted at a rate of 1 mm min^{-1}. The wetting force, F_w, and the tear-off force, F_{TO}, were measured with the balance. The contact angle, θ, was obtained according to the following equation

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

With this procedure it is not necessary to determine the circumference of the fibres. With the value of $\cos\theta$, the work of adhesion, W_{SL}, can be directly calculated if the surface tension, γ_L, of the test liquid is known [30, 31]. γ_L is about 72.8 mJ m^{-2} for water and aqueous solutions with pH values between 1 and 14.

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

Contact-angle measurements were used with the aid of the sessile drop technique for determinations of possible physico-chemical interactions at the polymer surfaces. For these measurements, an apparatus was available which allows a drop of a well-defined volume of the test liquid (aqueous solution or other liquid) to be automatically placed on the surface of the polymer [32]. To determine the advancing contact angle, photographs were taken every minute for a period of 10 min. The decrease of the contact angle was followed until a plateau was reached after about 6–10 min. By extrapolating the curve back to zero time, the advancing contact angle was obtained. Using this angle, the work of adhesion could be calculated using Equation 2.

3. Results

3.1. Functional groups at the carbon-fibre surfaces

Celion fibres with different surface treatments were used for the XPS investigations. A typical XPS spectrum showing the various binding energies of C_{1s} electrons in carbon atoms belonging to various functional groups is shown in Fig. 1.

The results are summarized in Table III, which presents the chemical surface composition of the fibres, expressed as a percentage carbon, resulting from the analysis of the C_{1s} photoelectron peak. Because simple Gaussian functions are used for fitting C_{1s} peaks, the hydroxylic groups are overestimated [19, 20]. This boundary condition has to be considered in the interpretation of the results.

Compared to the unoxidized Celion fibre (uu) a commerical-oxidation treatment (Celion fibre (ou)) leads to an equal increase of the surface concentrations of all oxygen-containing functional groups. The Celion fibre (uu) treated in pure oxygen (O_2/400 °C/0.5 h) shows the highest surface concentrations of hydroxylic and ether groups found in this study, while the concentration of carboxylic and lactone groups is small. This is due to the high treatment temperature of 400 °C – at which these surface groups are not stable. A treatment of the Celion fibres (uu) with ozone in oxygen (0.75% O_3/100 °C/60 s) is the most effective means of producing carboxylic groups with high selectivities.

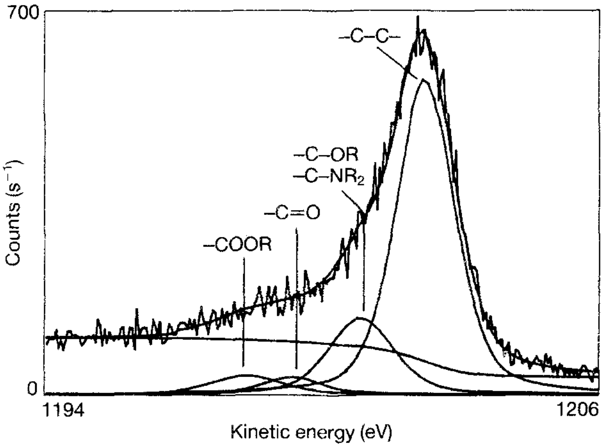

Figure 1 Typical XPS spectrum (1486.6 eV) showing the various binding energies of C_{1s} electrons in carbon atoms belonging to various functional groups.

The oxygen-containing functional groups shown in Table IV exhibit different thermal stabilities. For this reason, TPD is an effective tool for a quantitative analysis of the various functional groups which are desorbed by the formation of carbon dioxide and carbon monoxide. A correlation between the surface functional groups and the temperature regime of desorption is also given in Table IV. It can be seen that strongly acidic carboxylic groups are desorbed below 300 °C by formation of carbon dioxide. Neutral, weakly acidic, and peroxidic groups are desorbed at higher temperatures, up to 600 °C, but in defined temperature ranges. Their decomposition product is carbon dioxide. All the other surface groups of interest are decomposed by formation of carbon monoxide in the temperature range 400–900 °C. A quantitative determination of hydroxyl, hydroquinone, carbonyl, quinone and related groups, therefore, is difficult, but an analysis can be performed using a combination of XPS and TPD results.

Typical TPD results are shown in Figs 2 and 3. A comparison between Celion fibres of different surface treatments (namely, unoxidized (uu), commercially oxidized (ou), treated with ozone and treated in pure oxygen) is given in Fig. 2. Unoxidized Celion fibres (uu), by comparison, have small desorption rates (see Fig. 2a). Small amounts of carbon dioxide are split off around 180 and 320 °C resulting from carboxylic and lactone groups, while a characteristic peak at 600 °C is due to peroxidic groups [13]. The commercially oxidized Celion fibre (ou) shows enhanced desorption rates of both carbon dioxide and carbon monoxide, but the structure of the desorption spectra remains similar to the unoxidized fibre (uu) (see Fig. 2b). Peaks of carbon dioxide and carbon monoxide at 900 °C resulting from basic surface structures represent an exception [6].

Significantly altered desorption spectra are formed with ozone and oxygen-treated fibres. Typical of the ozone-treated Celion fibre (uu) (0.75% O_3/100 °C/60 s) is a sharp and high peak at about 200 °C corresponding to strongly acidic carboxylic groups (see in Fig. 2c). No carbon dioxide is desorbed in the

TABLE III Surface compositions expressed, as a percentage of carbon, of differently treated carbon fibres analysed by fitting of the C_{1s} photoelectron peak

Fibre	Treatment	Surface composition (% carbon)			
		-C-C- 284.7 eV	-C-O-R, -C-NR$_2$ 286.1 eV	-C = O 287.6 eV	-COOR 288.6 eV
Celion (uu)	None	76.9	18.4	3.4	4.4
Celion (ou)	None	65.9	23.8	3.8	6.5
Celion (uu)	O_2/400 °C/0.5 h	61.5	27.9	6.9	3.7
Celion (uu)	0.75% O_3/100 °C/60 s	65.8	18.3	6.3	9.7

TABLE IV Desorption temperatures, T_{des}, and gaseous decomposition products of different oxygen-containing surface groups

T_{des} (°C)	Desorption gas	Surface group	Reference
180–200, 300	CO_2	Carboxylic groups	[2,3,10,14,17]
250–600	CO_2	Neutral and weakly acidic groups carrying two oxygen atoms (i.e. different types of lactone groups)	[15–17]
500–600	CO_2	Neutral and peroxidic groups	[13]
400–900	CO	Hydroxylic and hydroquinonic groups	[2,3,13–15]
500–900	CO	Carbonylic and quinonic groups	[2,3,13–15]
900, 1200	CO, CO_2	Pyrone or chromene structures	[6,11,12]

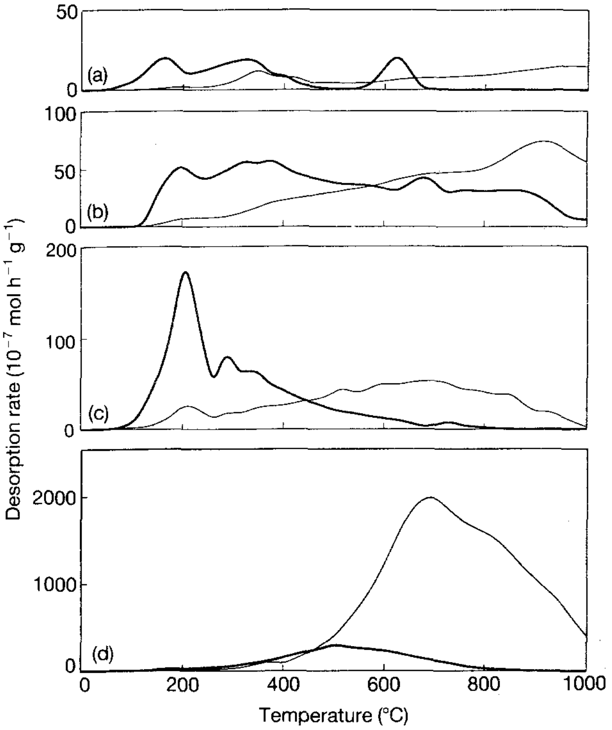

Figure 2 Desorption rates for (—) carbon dioxide and (—) carbon monoxide of differently surface treated and unsized Celion fibres as a function of the desorption temperature: (○) unoxidized fibre (uu), (△) commercially oxidized fibre (ou), (×) fibre (uu) oxidized with ozone (0.75% O_3/100 °C/60 s), and (□) fibre (uu) oxidized in pure oxygen (O_2/400 °C/0.5 h).

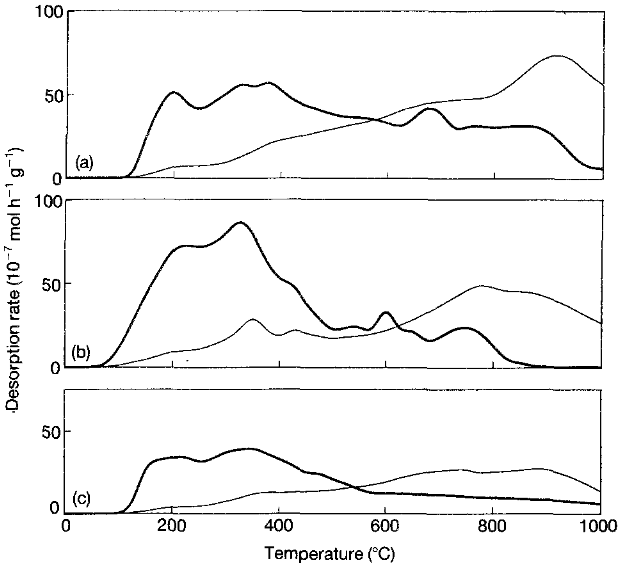

Figure 3 Desorption rates for carbon dioxide (—) and carbon monoxide (—) of different types of commercially oxidized fibres as a function of the desorption temperature: (a) Celion (ou), (b) Tenax (ou), and (c) AS4 (ou).

high-temperature range. In addition, some carbon monoxide is desorbed between 500 and 900 °C resulting mainly from carbonyl surface groups (see also the XPS results). Completely different desorption spectra result after treatment of the Celion fibre (uu) in pure oxygen (400 °C/0.5 h) as shown by Fig. 2d. Desorption only occurs at temperatures in excess of 400 °C where large amounts of carbon monoxide are formed. This desorption is associated predominantly with a high surface concentration of hydroxylic and ether groups as also found by the XPS investigations. Strongly acidic carboxylic groups which would be desorbed at about 200 °C are seen in only very small concentrations on the surface of this fibre. Nevertheless, carbon dioxide desorption is stronger than with other fibres, but mainly above 400 °C. The amounts of carbon dioxide and carbon monoxide desorbed up to 500 and 1000 °C (for all fibres) are summarized in Table V.

Fig. 3 compares the TPD spectra of three types of commercially oxidized carbon fibres (namely, (a) Celion (ou), (b) Tenax (ou) and (c) AS4 (ou)). All the fibres show medium desorption rates of carbon dioxide in the temperature range 150–500 °C due to the decomposition of the more-or-less acidic carboxylic and lactone groups. In comparison to the previously discussed Celion fibre (ou), the Tenax fibre (ou) shows more, and the AS4 fibre (ou) less, carbon-dioxide desorption in this temperature range up to 500 °C. Beyond 500 °C only the Celion fibre (ou) exhibits a considerable desorption of carbon dioxide. The temperature range between 500 and 900 °C is characterized by a strong desorption of carbon monoxide resulting from hydroxylic and carbonyl groups. This is especially true for the Celion fibre (ou), which shows some desorption of carbon dioxide and carbon monoxide at about 900 °C which can be associated with basic structures [6]. The desorbed amounts of carbon dioxide and carbon monoxide up to 500 and 1000 °C are also presented in Table V.

3.2. Wetting of fibres and polymers

The work of adhesion, W_{SL}, calculated according to Equation 2 is a direct measure of the interactions

TABLE V Desorbed amounts of carbon dioxide and carbon monoxide up to 500 and 1000 °C

Fibre	Treatment	Carbon dioxide, 10^{-7} mol g^{-1} desorbed up to		Carbon monoxide, 10^{-7} mol g^{-1} desorbed up to	
		500 °C	1000 °C	500 °C	1000 °C
Celion (uu)	None	8.0	10.4	3.2	11.0
Celion (ou)	None	28.7	54.1	9.3	51.3
Celion (uu)	O_2/400 °C/0.5 h	72.5	167.5	54.8	1115.7
Celion (uu)	0.75% O_3/100 °C/60 s	43.5	48.5	13.9	44.5
Tenax (ou)	None	38.5	51.8	10.3	38.9
AS4 (ou)	None	19.9	28.1	5.3	23.7

between the surface of a solid and an adjacent liquid. On a molecular basis, dispersive and non-dispersive forces determine the extent of the interaction. This means that the work of adhesion changes if the chemical nature of the solid surface or the liquid is altered.

This work of adhesion was obtained at various carbon-fibre surfaces with aqueous solutions having pH values between 1 and 14. In nearly all cases, an increase in the work of adhesion with increasing pH value was found. Therefore, it can be concluded that the surface chemistry of the fibres is determined by acidic surface groups. Moreover, it can be concluded from the stepwise increase that well-defined acid–base complexes are formed with aqueous solutions of distinct pH values. With the Celion fibres, the lowest values over the total pH range were obtained for the unoxidized samples (uu) as can be seen in Fig. 4. This signifies a low surface concentration of functional groups which is in accordance with the TPD results. In contrast, the highest values (up to 140 mJ m^{-2}) were found with the same Celion fibre (uu), after treatment with ozone (0.75% O_3/100 °C/60 s). This result again agrees with the TPD results, which showed the greatest concentration of strongly acidic carboxylic groups for the ozone-treated fibre. Medium values of the work of adhesion were observed for the commercially oxidized Celion fibre (ou) and the Celion fibre (uu) treated with oxygen. In the latter case, no dependence of the work of adhesion on the pH value exists. This may be due to the fact that no carboxylic groups are present, as shown by the TPD results.

A comparison of the wetting behaviour among three types of commercially oxidized fibres (Celion (ou), Tenax (ou), AS4 (ou)) is presented in Fig. 5. With increasing pH values, all fibres show a stepwise increase in the work of adhesion with two steps. The values of the work of adhesion at both pH 1 and at pH 14 are very similar for all fibres. However, the pH regimes in which the increases occur are different. Although the exact nature of the surface treatments by the producers of the fibres is not known, the treatment most likely consists of an anodic oxidation known to produce strongly acidic and also less acidic carboxylic surface groups [33, 34]. Therefore, it can be assumed that the steps in the work of adhesion in distinct regimes of the pH value correspond to Brønsted acid–base complexes between the carboxylic surface groups of different acidity and the acids as well as the bases. Details are explained in a model which was recently published elsewhere [35–37].

The total work of adhesion as calculated from Equation 2 and presented in Figs 4 and 5 is composed of a dispersive fraction, W_{SL}^{D}, and a non-dispersive, that is, acid–base fraction, W_{SL}^{AB} [38, 39]

$$W_{SL} = W_{SL}^{D} + W_{SL}^{AB} \qquad (3)$$

In order to derive the contribution of the dispersion interactions W_{SL}^{D} to W_{SL}, the dispersive component of the surface free energy of the fibre, γ_S^D, had to be determined. With the knowledge of this value W_{SL}^{D} can

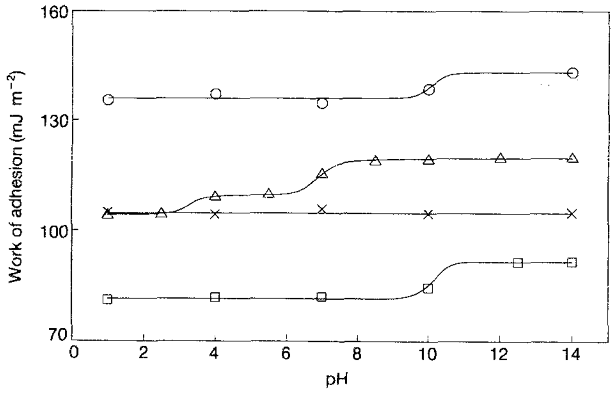

Figure 4 The work of adhesion of unsized and surface-treated Celion fibres as a function of the pH value of aqueous test liquids: (○) fibre (uu) oxidized with ozone (0.75% O_3/100 °C/60 s), (△) commercially oxidized fibre (ou), (×) fibre (uu) oxidized in pure oxygen (O_2/400 °C/0.5 h), and (□) unoxidized fibre (uu).

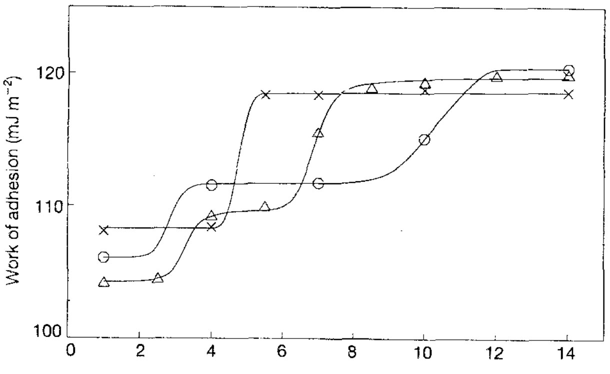

Figure 5 The work of adhesion of different types of commercially oxidized fibres as a function of the pH value of the aqueous test liquids: (×) Celion (ou), (○) Tenax (ou), and (△) AS4 (ou).

be calculated using Equation 4 [39, 40]

$$W_{SL}^{D} = 2(\gamma_L^D \gamma_S^D)^{1/2} \qquad (4)$$

The dispersive component of the surface free energy of the fibres, γ_S^D, was determined using methylene iodide as a non-polar test liquid ($\gamma_{CH_2I_2}^D = 51.0$ mJ m^{-2} [37]). It was found that the surface chemistry of the various fibres has a negligible effect on γ_S^D, because values from 47 to 50 mJ m^{-2} were obtained. Using the mean value of γ_S^D, the dispersive component of the work of adhesion between various fibres and pure water, W_{S,H_2O}^D, was calculated to be about 65 mJ m^{-2}. This value is significantly lower than the minimum values measured with all fibres (see Figs 4 and 5). Thus, it can be concluded that water itself (without the addition of any ions) strongly interacts with the fibre surface. This interaction is of a non-dispersive nature. The various steps in the curves are thus only additional specific interactions of ions of the aqueous solution with distinct functional groups at the fibre surface.

Wetting studies of polycarbonate and polyethersulphone surfaces were performed using the sessile-drop technique and aqueous solutions of different pH values. The results are shown in Fig. 6. For both polymers, a decrease of the work of adhesion can be observed at pH values of about 11 ($\Delta W_{SL} \approx 10$ mJ m^{-2}). This means that the surfaces of both polymers are controlled by basic functional groups. Although the work of adhesion of polyethersulphone is about 10 mJ m^{-2} higher than that of polycarbonate, the dispersive component of the work of adhesion, W_{SL}^D measured indirectly by the determination of γ_S^D with methylene iodide (see above) is similar in both cases (see Fig. 6). The difference between the lowest values of the work of adhesion, $W_{SL,min}$, and its dispersive component, W_{SL}^D, has to be attributed to non-dispersive interactions of pure water with the polymer surfaces.

The basic character of the polymer surfaces should promote good adhesion to acidic carbon-fibre surfaces because acid–base complexes can be formed. The relevance of such complexes will be shown in Part III.

4. Discussion

It was the aim of this part of the study to identify and determine the surface functional groups of carbon fibres with a broad variety of surface treatments and then to correlate these results with works of adhesion at the fibre surfaces. In addition to unoxidized and commercially oxidized fibres, samples were produced with selective oxidations of the fibres using oxygen and ozone in oxygen. It was shown in earlier papers that commercially oxidized fibres exhibit strongly acidic and less acidic carboxylic surface groups [2, 3, 10, 14, 17]. This result was confirmed with the aid of all the methods applied: XPS, TPD and wetting studies.

Additionally, two very specific methods of surface oxidation were applied, namely, treatment with molecular oxygen at 400 °C and with ozone in oxygen at 100 °C. In the first case, the attack of the fibre surface was very vigorous, but practically no carboxylic groups were formed. This result was expected, because carboxylic groups are nearly completely decomposed at a temperature of 400 °C. The surface groups that were formed under these conditions were hydroxyl and ether groups. A very different result was obtained with the ozone treatment, because the reaction of this gas with carbon is very selective in the formation of strongly acidic carboxylic groups.

In order to get an estimate of the surface concentration of strongly acidic and weakly acidic carboxylic groups, the amount of carbon dioxide up to 250 and 500 °C was calculated. Strongly acidic carboxylic groups are decomposed below 250 °C while both types of carboxylic groups are desorbed below 500 °C resulting in the formation of carbon dioxide. These results will be correlated with the work of adhesion below.

In principle, the TPD results should be sufficient to correlate the functionality of a carbon-fibre surface with its adhesion to basic polymers such as polycarbonate or polyethersulphone. Nevertheless, the possible interactions at the various carbon-fibre surfaces with adjacent liquids were investigated. For these investigations, wetting studies using aqueous solutions with pH values between 1 and 14 have been found to be very powerful [35–37]. By varying the pH value, specific acid–base complexes with relevant surface groups can be formed on the carbon-fibre surface. The formation of such a complex at a specific pH value results in a decrease of the contact angle or, according to Equation 2, to an increase in the work of adhesion, W_{SL}. This phenomenon is the reason for the stepwise increase in the work of adhesion shown in Figs 4 and 5. It has been demonstrated [35–37] that the strongest complexes, and thus the highest steps in the work of adhesion, are formed by carboxylic groups at the carbon-fibre surfaces.

As already mentioned, a step in the curve corresponds to a specific acid–base complex. The height of a step, ΔW_{SL}^{AB}, can be explained by the following equation

$$\Delta W_{SL}^{AB} = W_{SL,i}^{AB} = -n_i^{AB} \Delta G_i^{AB} \qquad (5)$$

From this equation it follows that the increase in the work of adhesion, $W_{SL,i}^{AB}$ at the step results from the free enthalpy of the complex formation, ΔG_i^{AB}, and the interface concentration of the particular complex, n_i^{AB}.

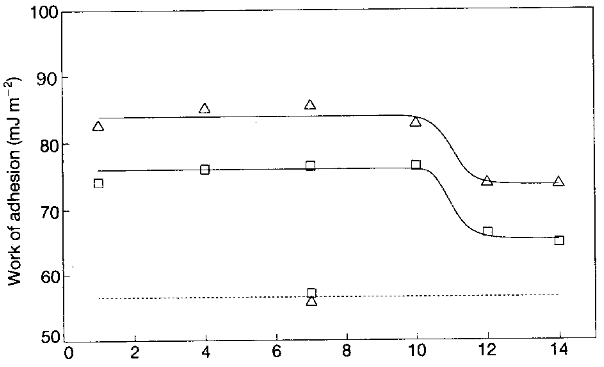

Figure 6 The work of adhesion of (△) polycarbonate and (□) polyethersulphone as a function of the pH value of (—) the aqueous test liquids and (---) the dispersive part of the work of adhesion of these polymers.

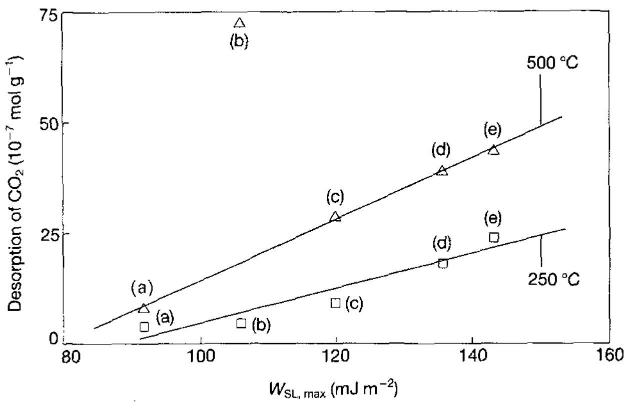

Figure 7 The amount of carbon dioxide desorbed from the surfaces of differently treated Celion fibres up to 250 and 500 °C as a function of the maximum work of adhesion of these fibres: (a) unoxidized (uu), (b) oxygen treated (c) commercially oxidized (ou), (d) weakly oxidized with ozone (not mentioned yet), and (e) oxidized with ozone.

Both of these quantities are responsible not only for $W^{AB}_{SL,i}$ but also for the pH value at which the complex is formed. For this reason, it is not surprising that fibres treated in different ways by various producers yield an increase in the work of adhesion at different pH values, although the functional groups are clearly similar. This phenomenon is presented in Fig. 5 and the details are given in recent publications [36, 37, 41].

With the knowledge that the dispersive component of the work of adhesion is equal for all fibres and that the increased works of adhesion result mainly from carboxylic groups, an attempt was made to correlate the maximum work of adhesion with the amount of carbon dioxide desorbed up to 250 and 500 °C. This relationship is presented in Fig. 7. It is based on Celion fibres subjected to various surface treatments. Except for the results of the fibre treated in oxygen, nearly linear relationships exist at both temperatures. In this case, the desorption of carbon dioxide between 250 and 500 °C is extremely high, but the work of adhesion is rather low. This clearly indicates that the desorption of carbon dioxide may not result from carboxylic groups. On the other hand, it is known from the literature that neutral and weakly acidic groups possessing two oxygen atoms are also decomposed between 250 and 500 °C resulting in the formation of carbon dioxide [15–17]. Such groups are obviously formed to a great extent by treatment with molecular oxygen.

Summarizing these results, it can be stated that carboxylic groups have a stronger interaction with basic materials than the other surface groups present on the carbon-fibre surfaces and are thus the groups principally responsible for the adhesion to basic polymers. It was found, however, that the amount of carbon dioxide desorbed up to 500 °C is not a definitive measure of the concentration of these surface carboxylic groups because other surface groups can also form carbon dioxide during this heating process. Thus, the work of adhesion resulting from carboxylic groups produces a better correlation with the adhesion of thermoplastic polymers to carbon fibres in composites than the amount of carbon dioxide desorbed during TPD. These results will be shown in Part III.

The basic character of the polycarbonate and polyethersulphone surfaces was also identified by our novel wetting technique. This was possible because the work of adhesion increased at a well-defined pH value as the pH of the aqueous test solution was lowered. As already mentioned, such changes in the work of adhesion correspond to Brønsted acid–base interactions between the basic functional groups of the polymers and the relevant aqueous solutions.

Acknowledgement

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