Influence of fluorination on the properties of carbon fibres

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Abstract

Various fluorination methods were applied to modify the surfaces of carbon fibres. Mild fluorination techniques, such as low pressure fluorine at various temperatures and pressures, were compared with strong fluorination agents, such as HF–F_2 mixtures or ClF_3. The relationship between the degree of fluorination and the physical and chemical properties of two polyacrylonitrile-based carbon fibres (Torayca, FT 300 6000-99; Sigri, Sigrafil C320.00A) was studied using a combination of contact angle hysteresis, electron spectroscopy for chemical analysis (ESCA), resistivity measurements and X-ray diffraction (XRD).   © 1997 Elsevier Science S.A.

1. Introduction

Carbon fibres are widely used as reinforcements in composites, especially in composites with epoxide matrices. They combine a high stress factor and strength with a low density, which has led to their increasing use in high performance construction materials. To improve the fibre matrix adhesion, it is necessary to increase the surface polarity, create more sites for hydrogen bonding and improve the possibility for covalent linking between the fibre material and the surrounding polymer matrix in order to achieve good stress transfer from the matrix material to the filling fibre material [1].

The normally used oxidative methods for the modification of such non-polar carbon fibre surfaces include oxidation in various plasmas [2], oxidation in air [3], electrochemical oxidation of carbon fibres used as anodes in various electrolytes [4] or wet chemical methods [5], such as boiling in nitric acid. An alternative technique to increase the surface polarity of carbon is mild direct fluorination [6].

In recent years, several studies concerning fluorinated carbon fibres have been published [7,8]. The degree of fluorination depends on the nature of the fibres and the fluorination method used. Higher contents of intercalated fluorine can be obtained using either better graphitized structures or higher

fluorine pressures [9]. The reaction of fluorine and graphite at low temperature is kinetically hindered by the formation of covalent C–F bonds at the outer surface which prevents further migration of fluorine into the interplanar space and thus further fluorination [10]. The intercalation of fluorine into graphite at low temperature requires the assistance of fluorides to yield graphite intercalation compounds (GICs). In these GICs with the general formula C_xF ($1.3 < x < 20$), the sp^2 electronic structure of carbon is more or less preserved [11]. The fluorination of carbon fibres, in particular the formation of GICs or covalent and insulating graphite fluorides $(CF)_n$ or $(C_2F)_n$, has a strong influence on the physical properties, such as the layer structure, tensile strength and mechanical strength.

It is assumed that fluorination introduces hydrophobicity to the fibre surface. Li et al. [12] showed, by measurement of the adsorption isotherms of water and ethanol, that fluorinated carbon fibres possess water rejective properties. Fluorinated carbon micropores were presumed to repel water almost completely without the formation of water molecular clusters [12].

Recently, Tressaud et al. [9,11] have investigated the fluorination reaction in the presence of HF gas. They estimated the transport properties through electrical resistivity measurements, and the structure of the fluorinated compounds by X-ray diffraction (XRD) and electron spectroscopy for chemical analysis (ESCA).

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In this study, various fluorination methods were applied to modify the surfaces of carbon fibres in order to create fibres with special properties.

2. Experimental details

2.1. Starting materials

Two different types of starting carbon fibre were used without any additional surface sizing:
1. HT polyacrylonitrile (PAN)-based carbon fibres from Torayca (FT 300 6000-99);
2. HT polyacrylonitrile (PAN)-based carbon fibres from Sigri (Sigrafil C320.00A).

2.2. Fluorination procedure

A Monel high pressure bomb (Parr, series 4740, $V = 71$ ml), equipped with a Monel gauge block assembly and rupture disc and closed by Monel needle valves (Whitey), was rinsed several times with $CFCl_3$, dried and deactivated with F_2 (Solvay, 2 bar, 24 h, 100 °C).

The fluorination treatments were carried out on a calibrated Monel vacuum line. The exact reaction conditions are listed in Table 1. The fibre samples C2, C3 and T1 were stepwise fluorinated. In a typical experiment, a bunch of fibres was transferred into the prepassivated reactor. The oxidizer (F_2 (Solvay), ClF_3 (Air Products), HF (Fluka)) was condensed at -196 °C on the Monel vacuum line onto the fibres, and the mixture was warmed to room temperature. From outside the reactor was heated with compressed air by a system of three nozzles.

Caution: the generated heat may warm the outside surface of the bomb; every time the bomb is cooled or heated, the reactor head must be maintained close to room temperature.

2.3. Chemical and physical characterization

2.3.1. Surface analyses

Surface analyses were carried out on fibre bundles. ESCA measurements were performed with an M probe (small spot ESCA, spot sizes of (1000×400) 2–150 μm) from Surface Science Instruments (SSI) using focused monochromatic Al Kα radiation with an energy of 1486.6 eV [13]. The samples were fixed on an aluminium sample holder. The residual pressure inside the analysis chamber was about 10^{-9} mbar. To avoid charging of a non-conducting sample by the emission of photoelectrons, the sample was neutralized by a low energy electron beam (1–20 eV). A homogeneous charge distribution of electrons was achieved using a nickel net attached 2 mm above the sample leading to a better spectrometer resolution [14].

In the survey spectrum (0–1100 eV), the ESCA program package fixed the C 1s peak at 284.6 eV considering the neutralization. For the high resolution C 1s spectra, the exact position of the C 1s peak was not fixed. A more detailed description of the method and software used can be found in Ref. [15].

Scanning electron micrographs (SEMs) to show the eventual changes in the surface morphology of all the investigated fibres were obtained with a Hitachi S-2700 instrument.

2.3.2. Contact angle measurements

The technique and experimental details have been described elsewhere [16–18]. Since the contact angle θ of a test liquid on carbon fibres is not directly measurable because of the small fibre diameters (about 7 μm), a gravimetric method was used to estimate the contact angles to water (surface tension $\gamma = 72.8$ mN m^{-1}; polar component of surface tension $\gamma^p = 50.7$ mN m^{-1}; dispersive part of surface tension $\gamma^d = 22.1$ mN m^{-1}; polarity $X^p = \gamma^p / \gamma = 0.7$) and to methylene iodide ($\gamma = 50.8$ mN m^{-1}; $\gamma^p = 6.7$ mN m^{-1}; $\gamma^d = 44.1$ mN m^{-1}; $X^p = 0.13$).

Because of the very small mass change during the measurement of a monofilament, five fibres were placed parallel

Table 1
Reaction conditions during fluorination

Fibre	Type of fibre	Oxidizer	Reaction step	Reaction time (h)	Temperature (°C)	Pressure (bar)
C0	C320.00A	–	–	–	–	–
C1	C320.00A	F_2	1	1	110	3
C2	C320.00A	F_2	1	4	25	21
			2	2	100	26
C3	C320.00A	F_2–HF (10 : 1)	1	2	25	14
			2	2	100	18
			3	2	140	19
C4	C320.00A	ClF_3	1	60	25	1.3
C5	C320.00A	F_2–HF (9 : 1)	1	24	200	14
T0	Torayca	–	–	–	–	–
T1	Torayca	F_2	1	1	25	21
			2	2	100	26
T2	Torayca	F_2–HF (9 : 1)	1	24	200	15

to each other onto an aluminium carrier. The carrier was placed into a ultramicroelectrobalance (MP8, Sartorius, Göttingen, Germany; accuracy, 0.1 μg; reproducibility, 0.2 μg) so that the ends of the fibres were located above the test liquid surface. Weight recordings were obtained during the fibre immersion–emersion cycle at a stage velocity of 3 μm s^{-1}. After immersion of the fibres into the liquid, the same direction was maintained for 15 min, and then reversed until emersion. Immersion and emersion were performed using a reversible elevator operated with a direct current motor. The direct current was taken from a constant current source (Philips power supply unit PE1507).

For the contact angle θ calculation, the effective fibre diameters d were estimated from SEMs. Advancing θ_a and receding θ_r contact angles were calculated by the Wilhelmy equation from the mass changes Δm, which were detected during the immersion and emersion of the fibres in the test liquid

$$\cos \theta = \frac{\Delta mg}{U\gamma}$$

were g is the acceleration due to gravity, U is the fibre perimeter and γ is the surface tension of the test liquid.

Due to the very small fibre diameters, no buoyancy slope could be obtained. To check the reproducibility, all measurements were carried out ten times on fibres of the same sample. All contact angles are average values and the errors are standard errors. The contact angle measurements were performed in an air-conditioned room at a constant temperature of 20 °C.

2.3.3. X-Ray diffraction

The instrument used was a Guinier-type diffractometer (Siemens Guinier goniometer). The fibres were cut into pieces 5 cm in length and placed into the sample holder, so that the incident X-ray beam was perpendicular to the fibre axis.

2.3.4. Conductivity measurements

The four-point method was used to estimate the conductivity of a single filament, eliminating problems of contact resistance [19]. The input resistance of the voltage measuring device must be much higher than the resistance R of the filament. All measurements were performed at room temperature (20 °C). The current I was taken from the power supply (Gossen Konstanter T4 33 2) and measured with a Fluke 45 dual display multimeter. The input resistance of this was 200 TΩ. The voltage U was determined by a Keithley 617 programmable electrometer. A constant current of 100 μA was applied. The specific resistance of a single filament (ρ) was calculated using the fibre length l ($l = 2$ cm) and the fibre diameter d ($d \approx 7$ μm, estimated from SEMs) using the following equation

$$\rho = \frac{R\pi d^2}{4l} = \frac{U\pi d^2}{4Il} = \frac{1}{\kappa}$$

where κ is the specific conductivity. All measurements were repeated on ten samples of each fibre type to obtain average values.

2.3.5. Elemental analyses (fluorine)

The entire carbon fibre was burnt completely in a pure oxygen atmosphere. According to Schöniger [20], the combustion gases were passed through a Ce(III) solution precipitating Ce(III) fluoride. The remaining Ce(III) ions were back titrated.

3. Results and discussion

Highly oriented graphite reacts with fluorine at high temperatures (above 700 °C), with fluorination of all carbon layers, yielding carbon tetrafluoride. Depending on the temperature (400–600 °C), fluorination leads, in the ideal case (addition of F_2 to all carbon–carbon double bonds), to graphite fluoride $(CF)_x$, or to various graphite fluorides [21].

We have investigated the mild direct fluorination of carbon fibres using different fluorinating agents and different temperatures and pressures. The results of cerimetric analyses of the fluorinated fibres are shown in Table 2. Mixtures of F_2 and HF represent the strongest fluorinating agent, leading to a fluorine content of about 13%, followed by ClF_3 (6.6%), whereas pure fluorine gives fluorine contents of below 1%. ClF_3 is a much stronger fluorinating agent than pure fluorine. ClF_3 is one of the most reactive chemical compounds known, and reacts violently with many substances generally thought of as inert [22]. For example, it spontaneously ignites asbestos and reacts explosively with most organic substances. The reactivity can be moderated by dilution with an inert gas [23]. However, using ClF_3 results in a small amount of chlorine on the fibre surface (Table 3).

The intercalation of fluorine requires the presence of a Lewis acid, such as HF, because of its small polarizability. The Lewis acid forms a mobile anion. Fluorine intercalates easily into graphite as the mobile $HF_2^{\delta-}$ anion.

The oxidation of carbon fibres probably occurs more efficiently (i.e. faster) when the surface is acidic rather than basic. During fluorination (oxidation), however, the surface becomes less acidic (or more basic) by the adventitious occurrence of water from the reaction with the oxide surface. In addition, when F_2 is used as oxidizing agent, it is reduced

Table 2
Cerimetric analysis of the fluorinated fibres

Fibre	Fluorine content (wt.%)
C1	0.515
C2	0.525
C3	12.47
C4	6.645
T1	0.695
T2	13.41

Table 3
ESCA results: elemental contents of the fibre surface [a]

Fibre	Amount (at.%)				
	C	F	O	N	Rest
C0	95.0	0	5.0	0	
C1	59.3	30.5	10.2	0	
C2	50.5	39.8	9.8	0	
C3	35.3	62.7	2.0	0	
C4	56.1	30.9	7.9	1.7	Cl = 0.7 As = 2.7
T0	94.5	0	3.8	1.7	
T1	69.2	14.3	11.7	2.6	P = 1.2 Al = 1.0
T2	39.4	60.6	0	0	

[a] Survey spectra with fixed C 1s = 284.6 eV.

to give the basic F^- ion. Therefore the presence of HF in the reaction mixture acidifies the surface and makes it kinetically more approachable by the F_2 molecules.

To obtain information (up to a depth of 10 nm [24]) about the chemical composition of the fibre surface and the binding characteristics of the elements at the surface, ESCA measurements were carried out. The results are summarized in Tables 3 and 4.

In most fluorinated fibres, oxygen and nitrogen are found on the outer surface. This can be explained by the remaining starting components and contamination after F_2 treatment. According to their origin, the two types of carbon fibre have a slightly different surface composition. The carbon content is almost the same for both fibres, but the ESCA measurements give 1.7% N and 3.8% O for the surface of the Torayca fibre and 0% N and 5.0% O for C320.00A.

Consistent with cerimetry, the surface of the carbon fibres treated with an HF–F_2 mixture shows the highest degree of fluorination at about 60% (Table 3) and a C/F ratio between 1.5 and 1.8 (Table 4). In contrast with cerimetry, the amount

Table 4
C 1s, F 1s and O 1s binding energies, relative amounts [a] and C/F surface ratios of C320.00A and Torayca carbon fibres before and after fluorination

	Assignment	C0	C1	C2	C3	C4	T0	T1	T2 [c]
C 1s [d]	Graphite C	284.4	284.7	284.8	283.3	284.6	284.9	284.8	277.1
			38.8	28.8	49.2	42.1	86.8	54.8	34.5
	C-sec. [b]		285.6	285.7	284.4	285.5	–	285.7	278.4
			12.1	8.4	13.2	16.1		17.1	15.2
	C–O [f]		286.4	286.7	–	286.5	286.4	286.5	–
			10.5	9.2		12.8	13.2 [a]	11.3	
	C=O		287.7	288.2	–	–	–	–	–
			11.6	10.8					
	CF		288.7	289.4	285.5	288.0		287.6	279.6
			14.9	24.4	37.6	18.4		110.5	30.4
	CF₂		290.1	291.1	–	289.6		289.1	284.4
			7.9	12.9		7.8		6.3	16.4
	CF₃		291.8	292.8	–	291.3		–	288.8
			4.3	5.6		2.8			3.4
F 1s [c]	Ionic F–C				685.0				683.7
	Semi-ionic F–C		687.4			686.7	–	687.7	
	Covalent F–C			688.2					
O 1s [e]		531.7	533.2	533.9	524.5	532.7	532.9	533.1	–
C/F ratio [c]		–	0.5	0.8	1.8	0.6	–	0.2	1.5

[a] Due to the applied method for the intensity determination, the values are qualitative (deviation about 10%). Moreover, the difference between the fluorine contents in the survey and C 1s spectra can be explained by a slight modification of the sample surface due to X-ray radiation.

[b] C-sec. denotes a carbon atom with a carbon atom neighbour, on which fluorine is bonded. A chemical shift for this atom is detectable.

[c] Due to the fluorination of the fibre, the electrical conductivity of the surface decreases strongly. Therefore it is necessary to discharge the fibre with an electron beam (8 eV). On the other hand, the fluorination is not complete, so that parts of the fibre still conduct as normal. The values given for this particular fibre are therefore relative values only and rather low compared with fibre C3.

[d] High resolution C 1s spectrum, in relation to the absolute amount of carbon given in Table 3.

[e] Survey spectra with C 1s fixed at 284.6 eV.

[f] In some cases C–N.

of fluorine on the surface for C1 (fluorination with neat fluorine) is roughly the same as that for C4 (fluorination with ClF_3), which means that, in the case of ClF_3, deeper parts of the fibre are fluorinated and not only the surface.

As expected, fluorination progresses further the higher the temperature and pressure. The fluorination power increases from neat fluorine to ClF_3 to an $HF-F_2$ mixture.

In addition to the elemental composition of the surface, the bonding conditions of the elements involved were estimated. The correlation between the modification of the graphite structure, different chemical environments and the bond energy shift has been developed by several groups. The chemical shift of the binding energy is a useful tool for the investigation of the molecular environment of an element [25].

Table 4 summarizes the C 1s and F 1s core level photoelectron binding energies of all the investigated fibres, together with the relative amounts of C, F and O and an approximate assignment. Between non-fluorinated and fluorinated fibres, noticeable changes are observed in the C 1s high resolution spectrum due to new contributions at higher binding energies. Each electronegative element X polarizes the C–X bond, resulting in a shift in E_b towards higher energies compared with the C 1s peak of graphite carbon [13]. In our case, the first peak is shifted by +0.9 to +1.3 eV towards higher energy and can be assigned to secondary C atoms. The next two peaks at +1.5 to +3.0 eV are associated with C–O and C=O carbon atoms. Surprisingly, neither C–O nor C=O peaks could be detected for the $HF-F_2$-treated fibres (C3 and T2), which can be explained by the formation of water in the reaction of HF with the C–O groups, followed by the evaporation of water in high vacuum (see also Table 3). The next component of the C 1s band can be assigned to covalent C–F (+3.0 to +4.6 eV) for all fibres, with the exception of a semi-ionic C–F carbon atom for C3 and T2 (+2.2 to +2.5 eV). Finally, peaks corresponding to C–F2 and C–F3 carbon atoms are found at about +4.3 to +7.3 eV and +7.1 to +11.7 eV respectively. With an increasing amount of fluorine on the surface, the content of graphite-type carbon decreases. As expected, the relative amounts of C–F, C–F2 and C–F3 decrease from C–F to C–F3. This is due to kinetic reasons. Moreover, the fluorination of the bulk phase of the fibre must be considered.

The ionic character of the C–F bond in the $HF-F_2$-treated fibres (see above) can also be seen in the survey spectra (C 1s fixed at 284.6 eV), where the F 1s peak (C3, 685.0 eV; T2, 683.7 eV) lies in the region of an ionic C–F fluorine atom (E_b(LiF) = 684.5 eV, covalent graphite fluoride $E_b[(CF)_n] = 689.6$ eV) [26].

Next in our investigation, we carried out contact angle measurements and combined them with the ESCA results in order to obtain thermodynamic and chemical information on the outermost carbon fibre layer. In contrast with ESCA, data can only be obtained up to a depth of 1 nm [27]. We were particularly interested in the influence of surface fluorination on the physical properties, such as wettability, surface polarity and solid surface tension.
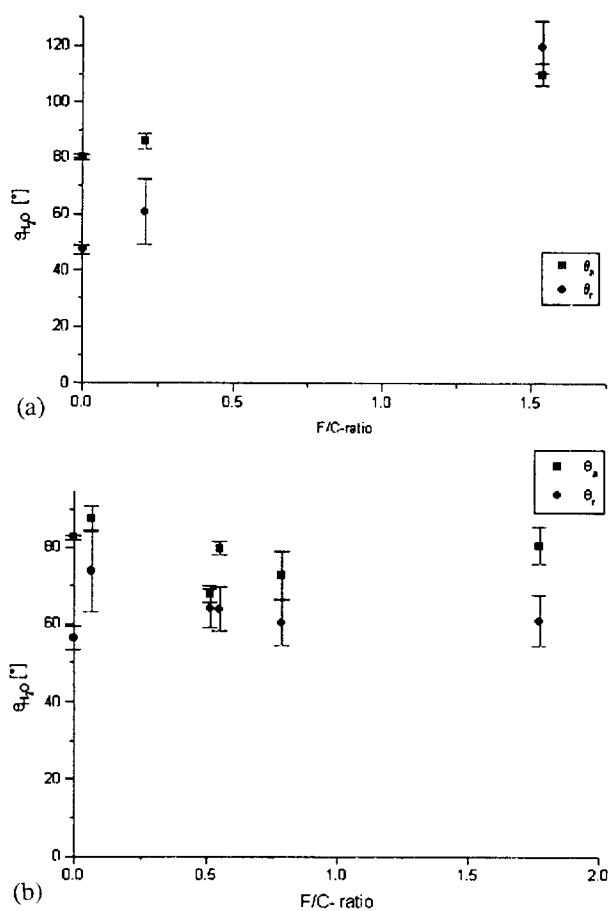

Fig. 1. Contact angle measured against water vs. fluorine content of modified fibres: (a) Torayca (T0–T2); (b) C320.00A (C0–C4).

For all the investigated fibres, a relatively large hysteresis was observed. This hysteresis phenomenon was not caused by swelling of the fibre material due to penetration of the test liquid. We can exclude this effect since each measurement was repeated several times and only a relatively small variation of the contact angle was observed. The hysteresis increases with surface roughness and chemical inhomogeneity, but when the surface becomes composite, the energy barriers decrease dramatically, and so does the hysteresis [18]. Both fibres can be regarded as real surface systems and thus both represent metastable systems.

Within error limits, the appearance of hysteresis (difference between advancing θ_a and receding θ_r contact angles) decreases for the fluorinated Torayca fibres as the fluorine content on the surface increases (Fig. 1(a), water as test liquid). This can be explained by the chemical modification of the surface composition due to fluorination. In an aggressive oxidizing environment, such as fluorine, ClF_3 or an F_2- HF mixture, the amorphous surface carbon atoms are transformed into fluorocarbons as indicated by ESCA measurements (Tables 3 and 4), resulting in a more homogeneous surface. Surprisingly, this effect cannot be detected for the C320.00A fibres (Fig. 1(b)). According to SEMs, "mild" fluorination (C1, C2) smoothes the surface, but the aggressive $HF-F_2$ mixture (C3) significantly damages the surface
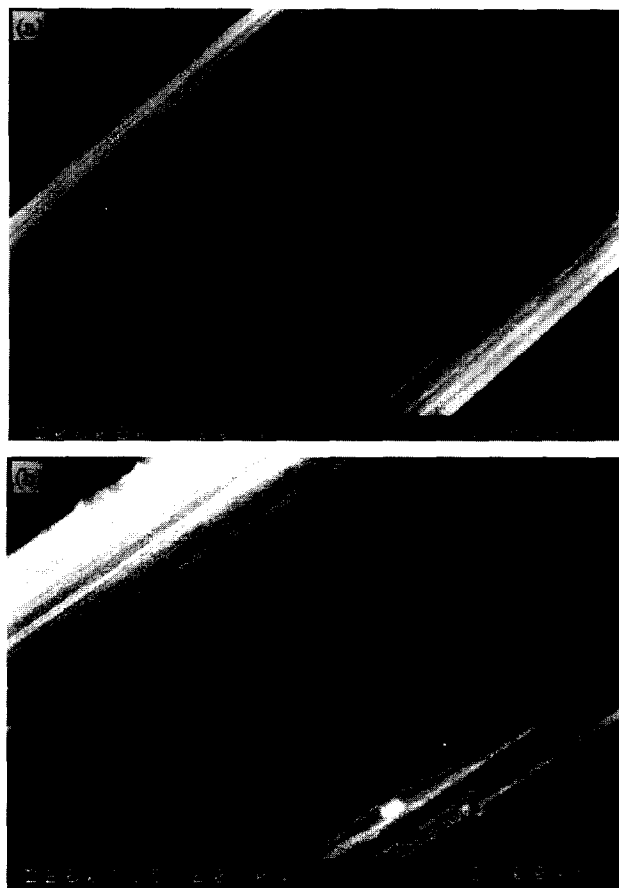
Fig. 2. SEMs of fibres: (a) pure C320.00A (C0); (b) HF–F$_2$-treated C320.00A fibre (C3).

(Fig. 2). In agreement with this, the advancing angle, which is characteristic of low energy surface areas [28], seems to be relatively constant with increasing fluorine content on the surface. However, in contrast with the Torayca fibres, the receding contact angle, which is more characteristic of high energy areas [28], decreases. This means that the surface is better wetted by the test liquid water and the polarity of the surface is slightly increased. In contrast with the C320.00A fibre, the wettability of the Torayca fibre decreases with increasing fluorine content leading to a reduced polarity.

The relatively large error limits of the contact angles are caused by the very high sensitivity of the Wilhelmy method to the measurement conditions; in addition, it is impossible to modify all of the fibre material equally.

The contact angles for C320.00A measured vs. methylene iodide (Fig. 3(a)) show a similar tendency. It is remarkable that the advancing contact angles are smaller than the receding angles. Methylene iodide has a very small polar component of surface tension, so that the polar interaction is small compared with that in water (with a fairly large polar component) and the major contribution should stem from dispersive interactions. The modified Torayca fibres show the same trend as discussed for water. Both contact angles increase with increasing amounts of fluorine (Fig. 3(b)).
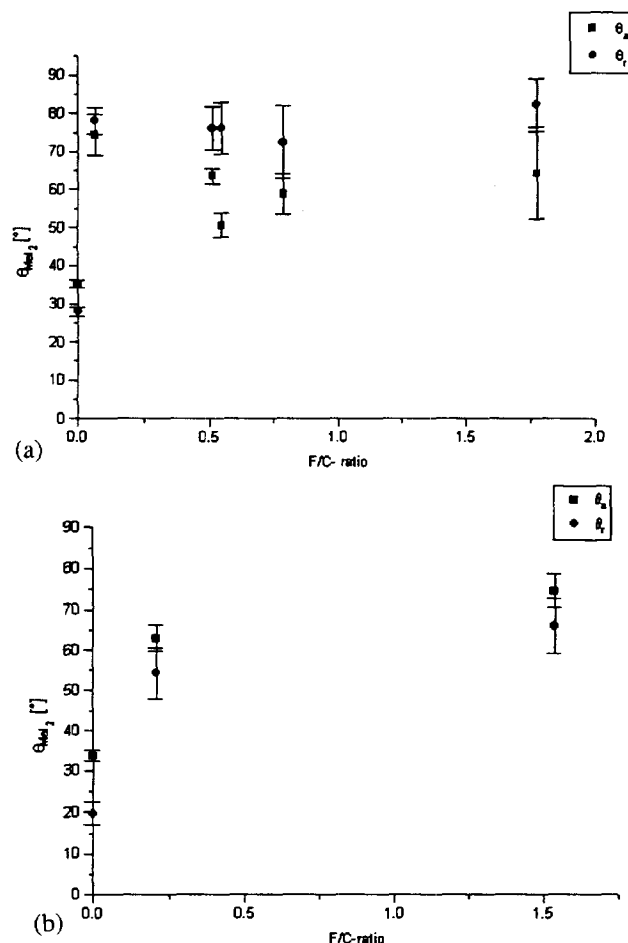

Fig. 3. Contact angle measured against methylene iodide vs. fluorine content of modified fibres: (a) C320.00A (C0–C4); (b) Torayca (T0–T2).

The combination of the harmonic mean equation [29], which is valid between low energy materials

$$\gamma_{sl} = \gamma_s + \gamma_{lv} - 4\left(\frac{\gamma_{lv}{}^d\gamma_s{}^d}{\gamma_{lv}{}^d + \gamma_s{}^d} - \frac{\gamma_{lv}{}^p\gamma_s{}^p}{\gamma_{lv}{}^p + \gamma_s{}^p}\right)$$

and the Young equation [17]

$$\gamma_{lv}\cos\theta = \gamma_s - \gamma_{sl}$$

leads to the following term

$$(1 + \cos\theta)\gamma_{lv} = 4\left(\frac{\gamma_{lv}{}^d\gamma_s{}^d}{\gamma_{lv}{}^d + \gamma_s{}^d}\right) + \left(\frac{\gamma_{lv}{}^p\gamma_s{}^p}{\gamma_{lv}{}^p + \gamma_s{}^p}\right)$$

From the measured contact angle data between fibres and water and methylene iodide, using the term above, we calculated the solid surface tension and the polarity X^p (Table 5)

$$X^p = \frac{\gamma_s{}^p}{\gamma_s}$$

The surface tensions for these test liquids are known as mentioned above.

For both kinds of fibre, a decrease in the surface tension is observed. The higher the fluorine content on the surface, the less the surface tension. In accordance with this, the smallest

Table 5
Solid surface tensions and polarity of investigated fibres

Fibre	γ (mN m^{-1})	γ^P (mN m^{-1})	γ^d (mN m^{-1})	$X^P = \gamma^P/\gamma$
C0	46.5 ± 1.3	7.7 ± 1	38.8 ± 0.9	0.17 ± 0.13
C1	40.0 ± 1.7	21.1 ± 1.5	18.9 ± 0.9	0.53 ± 0.08
C2	38.4 ± 4.6	16.8 ± 3.8	21.6 ± 2.6	0.44 ± 0.26
C3	33.3 ± 5.9	13.5 ± 3.5	19.8 ± 4.7	0.41 ± 0.31
C4	37.9 ± 1.9	11.5 ± 1.1	26.4 ± 1.6	0.30 ± 0.11
T0	42.9 ± 0.8	7.0 ± 0.5	35.9 ± 0.6	0.16 ± 0.07
T1	31.7 ± 2.3	10.3 ± 1.6	21.4 ± 1.7	0.32 ± 0.17
T2	24.9 ± 7.5	0.2 ± 2.6	24.7 ± 7.0	0.01 ± 13.0

Table 6
Resistance, conductivity and resistivity of fluorinated fibres [a]

Fibre	R (Ω)	κ (S cm^{-1})	ρ (mΩ cm)
C0	7325	530	1.89
C1	7297	597	1.74
C2	6674	627	1.59
C3	38300	109	9.15
C4	8005	523	1.91
T0	9254	593	1.68
T1	8956	467	2.14
T2	9053	487	2.05

[a] R, resistance; κ, conductivity; ρ, resistivity.

surface tension is observed for the HF–F$_2$-treated fibres (C3 and T2). It seems that the polar part of the surface tension increases (C1, C2, T1) (γ^P, Table 5) slightly at first, for a low degree of fluorination, and then decreases again for higher degrees of fluorination (C3 and T2). The nature of C–F bonding is affected mainly by the fluorination temperature and fluorine content. The results given in Table 5 are those usually observed for fluorinated carbon materials, because the C–F bonding varies from ionic to semi-ionic to covalent with increasing fluorination temperature and from ionic to semi-ionic with increasing fluorine content (for C$_x$F prepared at 100 °C or lower). In the case of C$_x$F synthesized below 100 °C, the C–F bond is mainly ionic at stage 2 or higher stages and semi-ionic at stage 1 with a higher fluorine content.

The strong decrease in the dispersive component γ^d of the surface tension may be caused by the destruction of the graphitic character of the fibre surface due to fluorination. The

γ^d values are usually assumed to be fairly independent of the method of surface modification [30]. It is assumed that the dispersive components reflect the essential surface characteristics of carbon or the partial graphitized carbon framework of the fibre material. In contrast, we observed a distinct dependence of the γ^d values on the fluorine content on the fibre surface. When a certain amount of fluorine is present on the fibre surface, the amorphous part of the surface is eliminated, and therefore the amount of graphite must decrease, in accordance with the ESCA results (Tables 3 and 4).

Conductivity measurements were carried out to check for possible changes in the π-electron system of the graphitic parts of the carbon fibre. Such changes in the π-electron system may be due to intercalation, resulting in an increase in the fibre conductivity, or chemical reaction, such as the formation of graphite fluoride, which will lead to a significant decrease in the conductivity [31]. The electrical conductivity changes according to C–F bonding, i.e. not only with the degree of fluorination.

The results of the conductivity measurements are summarized in Table 6. Slight fluorination increases the conductivity, whereas higher degrees of fluorination are associated with a lower conductivity. When only the surface area is fluorinated, almost no change in the (002) diffraction line of graphite is observed. Since no increase in the interlayer distance (Table 7) is observed, ion intercalation, which may cause a decrease in the specific resistivity, can be ruled out for C1 and C2. Assuming that the carbon fibres are made up of onion skin, ordered, graphite layers [1], the graphitic framework is relatively rigid and may resist intercalation or bulk fluorination when mild fluorination conditions are applied. According to the ESCA data and cerimetry results, strong fluorination conditions (ClF$_3$, HF–F$_2$) lead not only to fluorination of the surface, but also to fluorination of the bulk phase of the carbon fibre (cerimetric fluorine estimation of the whole bulk volume: HF–F$_2$, 12%; F$_2$, 0.5%–0.6%). In this case, the sp^2 state of the carbon layers generating a π-electron system is changed to an sp^3 state (fluorocarbon-like graphite fluoride) and the conductivity decreases considerably; this was observed in particular for the HF–F$_2$-treated C320.00A fibre (C3). The large conductivity difference between the two fibres treated with HF–F$_2$ may be explained by the considerable changes in the texture of the C320.00A fibre (C3), whereas the Torayca fibre still pos-

Table 7
2Θ values and calculated interlayer distances of fluorinated fibres

Fibre	$2\Theta_1$ (°)	$\Delta\Theta_{1/2}$ (°)	$2\Theta_2$ (°)	d_1 (Å)	d_2 (Å)
C0	–	2.4	25.2	–	3.53
C1	–	2.45	25.25	–	3.53
C3	21.1	–	25.4	4.21	3.51
C4	–	2.85	25.1	–	3.55
T0	–	2.43	25.15	–	3.54
T1	–	2.8	25.3	–	3.52
T2	–	3	25.5	–	3.49

sesses a relatively large part of the original sp^2 structure. Consistent with this, for the C3 fibre, a new very small but broad, peak at $21.1°$ (2Θ) is observed in the X-ray diffraction pattern. The diffraction peak at $21.1°$ probably indicates the formation of stage 3 C_x F. For all other investigated fibres, only the (002) reflection is obtained (Table 7). All of the fluorinated fibres have, within the error limits (the peak shape allows an accuracy of $\Delta\Theta_{1/2} = \pm0.2°$ resulting in $\Delta d = \pm0.03$ Å), the same interlayer distance. The halfwidth of the peak increases and the peak height strongly decreases after fluorination of the fibre material.

Furthermore, the material changes colour during fluorination from black to a shiny dark blue. The dark blue colour of fluorinated graphite is not due to the formation of covalent graphite fluoride, but to the partial formation of stage 1 C_x F with a semi-ionic C–F bond.

Acknowledgements

References

[1] W. Ruland, Adv. Mater. 2 (1990) 528.

[2] Y. Xie, P.M.A. Sherwood, Appl. Spectrosc. 44 (1990) 798.

[3] L.T. Drzal, Carbon 17 (1979) 375.

[4] A.D. Jannakoudakis, P.D. Jannakoudakis, E. Theodridou, J.O. Besenhard, J. Appl. Electrochem. 20 (1990) 619.

[5] S.S.J. Lin, Vac. Sci. Technol. A 8 (1990) 2412.

[6] Y. Chong, H.J. Ohara, Fluor. Chem. 57 (1992) 169.

[7] L. Fischer, U. Siemann, W. Ruland, Colloid Polym. Sci. 261 (1983) 744.

[8] M. Zayat, D. Davidov, H. Selig, Carbon 32 (1994) 485.

[9] A. Tressaud, V. Gupta, L. Piraux, L. Lozano, E. Marquestaut, S. Flandrois, A. Marchand, O.P. Bahl, Carbon 32 (1994) 1485.

[10] N. Watanabe, H. Touhara, T. Nakajima, N. Bartlett, T. Mallouk, H. Selig, in: P. Hagenmuller (Ed.), Inorganic Solid Fluorides, Academic Press, New York, 1985, p. 332.

[11] A. Tressaud, C. Guimon, V. Gupta, F. Moguet, Mater. Sci. Eng. B 30 (1995) 61.

[12] G. Li, K. Kaneko, S. Ozeki, F. Okino, R. Ishikawa, M. Kanda, H. Touhara, Langmuir 11 (1995) 716.

[13] R. Holm, S. Storp, Methoden zur Untersuchung von Oberflächen, Ullmanns Encyclopädie der Technischen Chemie, vol. 5. Verlag Chemie GmbH, Weinheim, 1980, Chapter 2, pp. 519–576.

[14] G. Barth, R. Linder, C. Bryson, Advances in Charge Neutralization for XPS Measurements of Nonconducting Materials, Surface and Interface Analysis, vol. 11, Wiley, New York, 1988, pp. 307–311.

[15] N.N. M-Probe Operator's Manual, Surface Science Instruments, Mountain View, CA, USA, 1991.

[16] A.W. Neumann, R.J. Good, in: R.J. Good, R.R. Stromberg (Eds.), Surface and Colloid Science, vol. 11, Plenum, New York, 1979. B.B. Sauer, T.E. Carney, Langmuir 6 (1990) 1002. S. Tuna, Dissertation, TU-Berlin, 1990. R.E. Johnson, R.H. Dettre, Adv. Chem. Ser. 43 (1964) 112. M. Tawaga, A. Gotoh, A. Yasukawa, M. Ikuta, Colloid Polym. Sci. 268 (1990) 598. M.E.R. Shanahan, Surf. Interface Anal. 17 (1991) 489.

[17] T. Young, Philos. Trans. (London) 95 (1805) 84.

[18] M. Morra, E. Occhiello, F. Garbassi, Adv. Colloid Interface Sci. 32 (1990) 79.

[19] DIN 53 482 (Methods of Test for Materials for Electrical Purposes; Measuring of Electrical Resistance of Non-metallic Materials).

[20] Element Analyses (Fluorine): Schöniger-Aufschluß, Indirect Complexometric Titration of Cerium IV Salts.

[21] A.F. Holleman, E. Wiberg, Lehrbuch der Anorganischen Chemie, 101 ed., Walter de Gruyter, Berlin, 1995, p. 846.

[22] L. Stein, Physical and chemical properties of halogen fluorides, in: V. Gutman (Ed.), Halogen Chemistry, vol. 1, Academic Press, London, 1967, pp. 133–224.

[23] N.N. Greenwood, A. Earnshaw, Chemistry of Elements, Pergamon, Oxford, 1984, pp. 968–973.

[24] A.W. Jache, in J.F. Liebman, A. Grennberg, W.R. Dolbier, Jr. (Eds.), Fluorine-Containing Molecules, Verlag Chemie, New York, 1988, Chapter 9, p. 165.

[25] G. Kämpf, Charakterisierung von Kunststoffen mit Physikalischen Methoden, Carl Hanser Verlag, München, 1982.

[26] P. Swift, D. Shuttleworth, M.P. Seah, in: D. Briggs (Ed.), Handbook of X-Ray and Ultraviolet Spectroscopy, Heyden, London, 1978. N. Watanabe, T. Nakajima, H. Touhara, Graphite Fluorides, Elsevier, Amsterdam, 1988. T. Nakajima, N. Watanabe, Graphite Fluorides and Carbon–Fluorine Compounds, CRC Press, Boca Raton, FL, 1991.

[27] T. Mallouk, N. Bartlett, J. Chem. Soc., Chem. Commun. (1983) 103.

[28] M. Zayat, Carbon 32 (1994) 490. C.T. Ho, D.D.L. Chung, Carbon 28 (1990) 524.

[29] Y. Uyama, I. Hiroyuki, I. Kazushi, A. Kishida, Y. Ikada, J. Colloid Interface Sci. 141 (1991) 275.

[30] S. Wu, Polymer Interface and Adhesion, Marcel Dekker, New York, 1982.

[31] K. Tsutsumi, S. Ishida, K. Shibata, Colloid Polym. Sci. 268 (1990) 31. J. Schultz, L. Lavielle, C.J. Martin, Chim. Phys. 84 (1987) 231.