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X-ray photoelectron spectroscopic analysis of barium-labelled carbon fibre surfaces

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A technique for labelling acidic functional groups on carbon fibre surfaces with barium has been developed for X-ray photoelectron spectroscopy analysis of the surface acidity of commercial Type II fibres, with differing degrees of oxidation. As the dibasic barium is believed to label adjacent monobasic groups, the results show that up to 58% of the surface oxygen, on the commercially treated fibres, is present in the acidic form.

1. Introduction

It is generally accepted that the strength of the bond at the fibre surface–resin interface is an important factor in determining the mechanical properties of carbon fibre reinforced plastics. The true nature of this interfacial bond is the subject of some controversy, as it may have both physical and chemical contributions. A physical bond could arise through the surface roughness of the fibre, at a scale of $\leqslant 0.1\,\mu m$, with an associated mechanical keying effect. However, the interaction between mutually reactive functional groups on the fibre surface and in the resin could, in contrast, produce a chemical bond. Ehrburger and Donnet [1] found that the interlaminar shear strength (ILSS) of unidirectional composites increases with the degree of surface acidity of the fibre, as determined by potentiometric titration.

However, it must be remembered that the relationship between the ILSS of a fibre composite and the interfacial bond strength is probably complex, and dependent upon the strength of the resin itself, the degree of fibre oxidation and other factors, such as voids in the matrix. The above interrelationship is being investigated by observing interfacial debonding effects in a scanning electron microscope straining stage. (This technique has been applied to glass fibre reinforced composites by Bailey and Parvizi [2].) For correlation purposes, chemical characterization of fibre surfaces is required.

A literature survey shows that a range of experimental techniques have been used to investigate carbon fibre surface chemistry, e.g. titration of acidic groups [1], mass spectroscopic analysis of species obtained during programmed thermal desorption from fibres [3, 14] and X-ray photoelectron spectroscopy (XPS) [4]. It is apparent from these results that a range of oxygen-containing species are present on the surfaces of oxidized fibres, e.g. COOH, C=O and C–OH, together with more complex structures such as lactones. Thus a complex surface chemistry, which is dependent upon the mechanism of oxidation, exists. Proctor and Sherwood [4] showed that by using curve-fitting techniques a detailed analysis of the C1s peak in the XPS spectrum reveals the presence of the different C/O functional groups. We have investigated an alternative technique in which the groups are specifically labelled, with for example a heavy metal which can readily be detected by XPS. Acidic groups, such as COOH and C–OH, probably constitute a significant proportion of the total number of C/O groups present on a given unit area of fibre surface, and they can be reacted with a metallic base which could provide an easily detectable label.

Monobasic labelling of such groups with

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Ag^+,

$$-COOH \xrightarrow{AgNO_3} -COO^- Ag^+$$

has been investigated in earlier work by Watts [5]. However, this method was found to be unsatisfactory, since the subsequent silver signal was observed to be critically dependent upon the degree of post-labelling rinsing with water, (to remove excess $AgNO_3$) and it was assumed that chemically bound Ag^+ was also lost during the rinsing process, e.g.

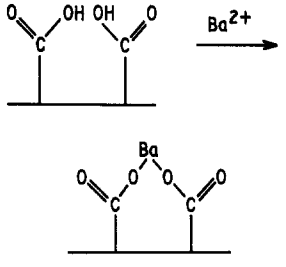
$$COOH \xrightarrow{AgNO_3} COO^- Ag^+$$

$$\xrightarrow{H_2O\ rinse} COOH + Ag^+ \downarrow$$

Note that the monobasic Ag^+ is bound to only one COO^- group.

In contrast, Bradley and Czuha [6] labelled the surface acidic groups on modified plastics with Ba^{2+} to produce a subsequent barium XPS signal which could be correlated with the degree of titratable surface acidity, even when the specimens had been given a very thorough post-labelling rinsing to remove excess barium salts.

The binding of Ba^{2+} to two adjacent monobasic groups:



accounts for its retention during rinsing. In this paper we report the application of the barium labelling technique to carbon fibre surfaces.

2. Experimental details

2.1. Specimen preparation

A set of three Type II carbon fibre samples, taken from the same batch but with differing levels of surface treatment, were supplied by Dr J. Harvey, Royal Aircraft Establishment, Farnborough, and originated from a manufacturer (see Table I). From each of these samples two specimens were prepared for analysis: a "control" specimen, which was rinsed in cold distilled water for 1 min prior to drying in a cold air stream and storage in a desiccator, and a "barium-labelled' specimen, which was treated by the following method:

(i) Washed in H_2O at room temperature for 1 min.

(ii) Immersed in weak (10^{-3}M) HCl, whilst gently boiling for 30 min. As a result of the production process, it is known that an alkaline sodium salt is present on the fibre surface. Since some of the acidic groups may have been neutralized, this weak acid treatment is intended to convert any –COONa back to its original form, as COOH.

(iii) Washed in H_2O for 1 min.

(iv) Immersed in a saturated solution of $BaCl_2$, containing 20 gl^{-1} of $Ba(OH)_2$, whilst gently boiling for 1 h.

(v) Thoroughly rinsed in three separate portions of distilled water, to remove excess barium salts.

(vi) Dried in a stream of cold air and in a desiccator.

2.2. XPS analysis

Six specimens were prepared for XPS by mounting the fibres across gaps in the metal holders. The spectra were obtained on a VG Scientific ESCA 3 MkII, operating at a vacuum of $< 10^{-9}$ torr, with Al($K\alpha$) radiation ($h\nu$ = 1486.6 eV). The analyser pass energy was set at 50 eV, and 4 mm entrance and exit slits were used.

The spectrometer was interfaced to a VG 3040 data system, based on a PDP8e computer. Each specimen was analysed by a combination of 1000 eV survey, and 20 eV high-resolution scans for all the relevant elements that could be present: carbon, oxygen, nitrogen, barium and chlorine. The presence of sodium, to any significant

TABLE I Materials used

Fibre sample No.	Treatment	Notation
1	Nominally untreated	UT
2	Treated with 1.25 × a nominal degree of surface treatment	1.25 NST
3	As No. 2, but with 2 × NST	2 NST

degree, would be identified by a sodium Auger peak at 497 eV on the XPS survey scans.

The surface atomic percentages for each element were calculated from the peak areas (after linear background subtraction), using published sensitivity factors [7].

3. Results and discussion

The results of the analysis are given in Fig. 1 and Table II in the form of survey scans and calculated surface atomic percentage concentrations. As expected, there is an increase in the atomic fraction of oxygen as a result of the oxidative treatment:

$$\frac{\Delta O\%\ (UT \rightarrow 1.25\,NST)}{\Delta O\%\ (UT \rightarrow 2\,NST)} = \frac{6.0}{9.5} = 0.632$$

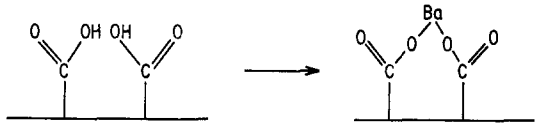
(see Table I for definitions) which compares very well with the ratio of the degrees of surface treatment, 1.25/2 = 0.625. There is no real significance in the average changes in nitrogen content of $\leqslant 0.3\%$ since there is an uncertainty in the values of $\simeq 0.3\%$. It is, however, apparent that as the oxygen level increases there is a corresponding trend in the percentage of barium for the labelled specimens. Note that with the labelled 2 NST sample the chlorine narrow scan revealed the presence of a small quantity of excess $BaCl_2$. 0.5% chlorine implies that 0.25% of the total barium is due to excess $BaCl_2$, hence the labelled barium amounts to 2.14 − 0.25 = 1.89%.

Rand and Robinson [8] evaluated the surface micropore volume of commercial HT (Type II) fibres by N_2 absorption–desorption tests, and obtained values of 2×10^{-5} and $7 \times 10^{-5}\,cm^3\,g^{-1}$ for untreated and treated samples respectively, after degassing at 110° C. Their results therefore imply that commercial treatment causes an increase in surface microporosity.

The retention of a detectable excess $BaCl_2$ on the labelled 2 NST specimen, as mentioned above, may therefore be due to the presence of a relatively high degree of microporosity on this treated fibre. The surface concentration of micropores on the UT and 1.25 NST samples may, however, be too low for detection of adsorbed $BaCl_2$ ($\equiv 0.12\%$ Cl) in these two cases.

It is interesting to note that there is an increase in oxygen concentration after immersion in the aqueous labelling medium, the magnitude of which, ΔO%, is relatively high for the two treated fibre samples (1.25 NST and 2 NST). This effect may also be attributed to adsorption of H_2O during labelling, at activated areas or micropores which form during commercial oxidation. The effect has been observed with other aqueous, trial labelling solutions, regardless of solution composition (see for example in Fig. 2).

Consider the barium and oxygen atomic percentages. There are three possible neutralization reactions of surface acidic groups by Ba^{2+}:

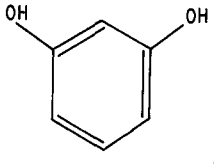


(i) 1 Ba ≡ 4O as COOH

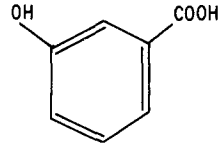
(ii) 1 Ba ≡ 3O as COOH –OH

(iii) 1 Ba ≡ 2O as OH

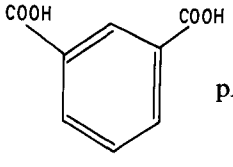
However, from the dissociation constants, pK_a, of some relevant aromatic acids, it is likely that phenolic–OH groups pairs on fibre surfaces are so weakly acidic that Reaction (iii) probably does not occur to any significant degree, e.g.



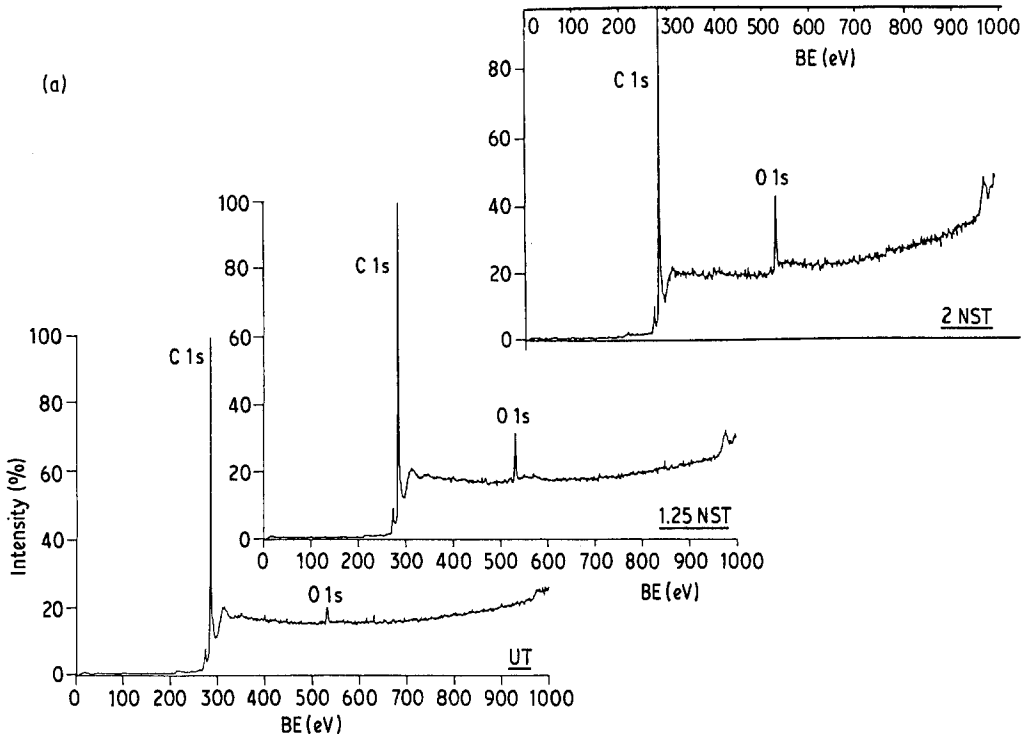
pK_a = 9.1 (1) and 11.3 (2)



pK_a = 3.9 (1) and 9.8 (2)



pK_a = 3.6 (1) and 4.6 (2) [9]



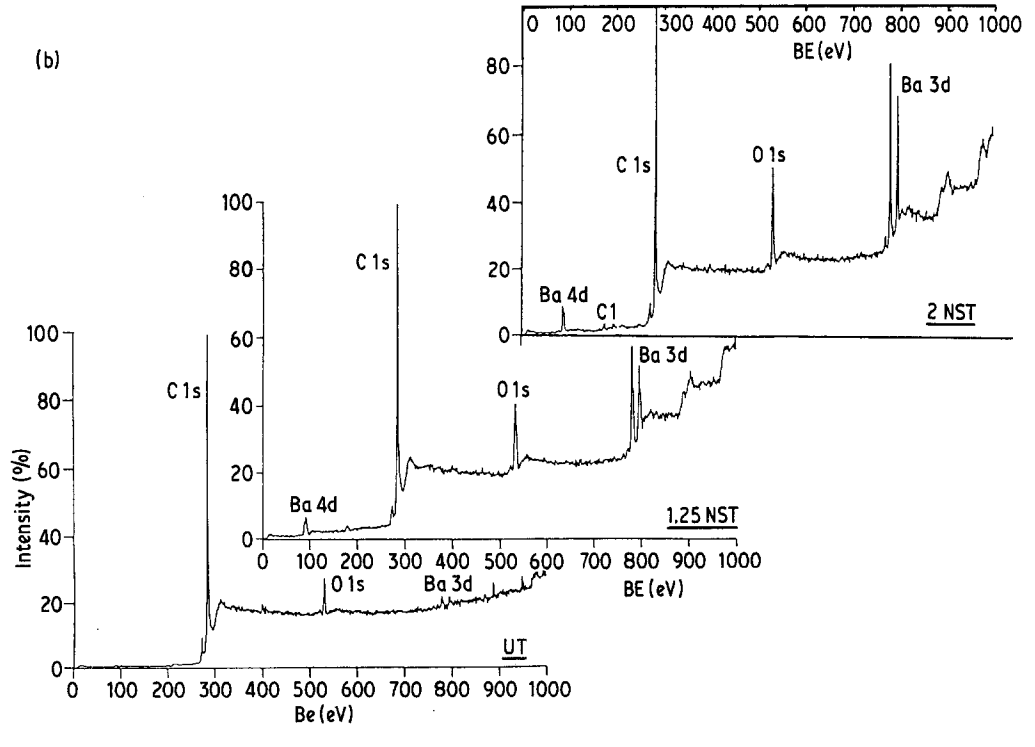


Figure 1 Survey spectra of (a) control and (b) barium-labelled specimens.

TABLE II Surface atomic percentages before and after fibre surface treatment

Treatment before XPS	UT					1.25 NST						2 NST					
	C	O	N	Ba	Cl	C	O	N	Ba	Cl	Change from UT	C	O	N	Ba	Cl	Change from UT
Control	95					89					−6	86					−9
		3.5					9.5				+6.0		13.0				+9.5
			1.3					1.0			−0.3			1.2			−0.1
				0					0						0		0
					0					0						0	0
Barium-labelled	92					84					−8	79					−13
		6.0					14				+8.0		16.7				+10.7
			1.9					1.1			−0.8			1.3			−0.6
				0.18					1.36		+1.18				2.14		+1.96
					0					0	0					0.5	+0.5
Change after barium labelling	−3	+2.5	+.6	+0.18	0	−5	+4.5	+0.1	+1.36	0		−7	+3.7	+0.1	+2.14	+0.5	

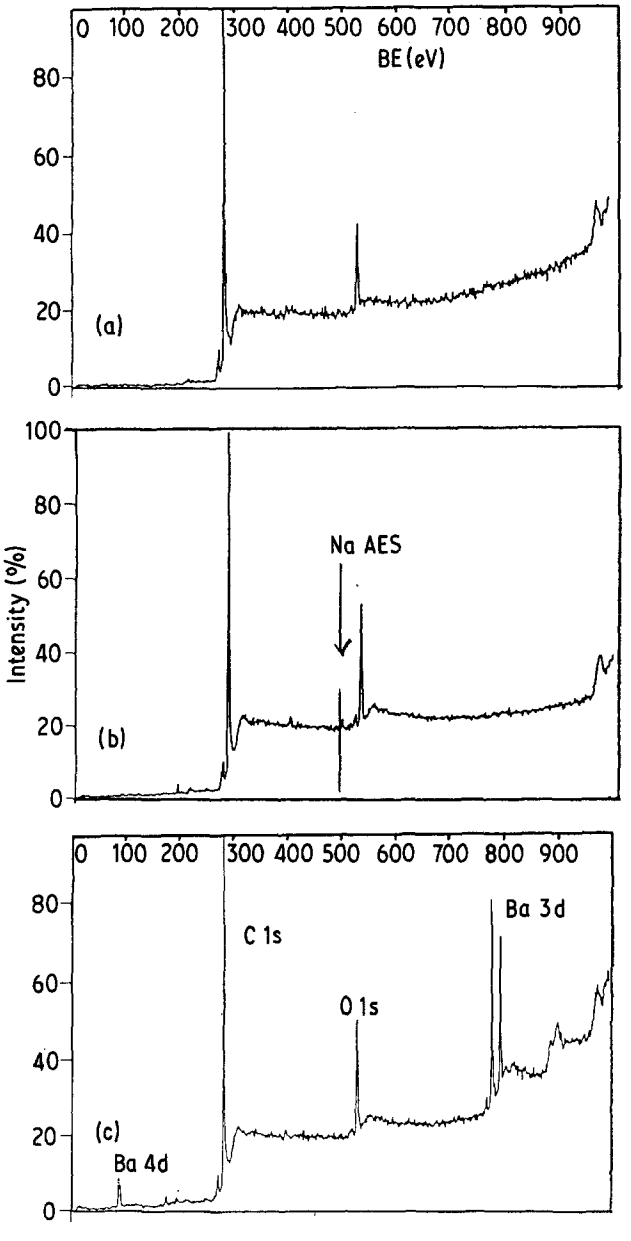


Figure 2 (a) 2 NST, control spectrom; (b) 2 NST after immersion in saturated NaCl containing 20 g l^{-1} NaOH, as a trial labelling solution, followed by rinsing in H_2O; (c) 2 NST, barium-labelled. Apart from confirming that monobasic labelling of acidic groups with Na^+ is unsatisfactory, as there is no sodium Auger peak on Spectrum (b), it is apparent that an uptake of oxygen, probably as water, occurs during immersion in an aqueous labelling medium, regardless of solution composition.

Virtually all of the chemisorbed barium is therefore bound to $(COOH)_2$ or (COOH–OH) pairs.

Table III shows the fraction of the oxygen on the control samples which could be present as COOH/OH or $(COOH)_2$, on the assumption that all the labelled barium binds to each type of acidic group pair respectively. In practice, the true situation probably lies between these two states, as a proportion of the labelled barium would bind to each type of acidic group pair. However, the trends presented in Table III show quite clearly that the commercial treatment of Type II fibres results in the formation of acidic groups on the fibre surface. This is in agreement with the conclusions of Rand and Robinson [10] who investigated carbon fibre surfaces by flow microcalorimetry and found that commercial treatments probably result in an increase in the surface concentration of acidic species.

From the surface atomic percentages, it is possible to evaluate approximately the degree of surface acidity of the fibres in terms of the concentration of surface acidic groups.

We consider a model graphitic segment of fibre at the surface, which has dimensions as

TABLE III Fraction of surface oxygen present in the form of labelled acidic groups

Fibre	Oxygen on control specimens (%)	Barium label (%)	Fraction of control oxygen as COOH–OH (= 3 Ba%/O%)	Fraction of control oxygen as $(COOH)_2$ (= 4Ba%/O%)
UT	3.5	0.18	0.15	0.21
1.25 NST	9.5	1.36	0.43	0.57
2 NST	13.0	1.89*	0.44	0.58

*Corrected for excess $BaCl_2$.

shown in Fig. 3a. An inelastic mean free path $\lambda \simeq 3.5$ nm for C 1s photoelectrons with 1200 eV kinetic energy is adopted [11]. The intensity of photoemission from atomic layers below the surface plane decays exponentially with depth according to the well known Beer–Lambert law.

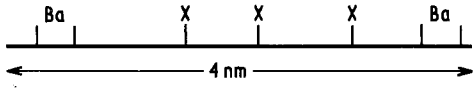
However, on the assumption of an approximately graphitic structure down to ~10 nm below the surface, integration of the exponential decay function gives a result which is equivalent to all the carbon atoms within the analysis area and approximately 3.5 nm of the surface plane contributing to the C 1s signal. Hence, an effective photoelectron analysis depth of 3.5 nm is used and it is assumed, initially, that virtually all of the oxygen-containing species present are on the surface plane. The segment contains ≃40 000 carbon atoms, and referring to Table II, the "surface" atomic percentages can be used to estimate the number of oxygen atoms on the segment, e.g. for the UT control specimen there are 3.5 oxygens per 95 carbon atoms, which implies the presence of ~(3.5/95) × 40 000 = 1500 oxygen atoms.

Similarly, after labelling, the Ba/C atomic percentage ratio can be used to estimate the number of acidic groups present, as 1 barium is equivalent to two monobasic groups. The results are presented in Table IV.

Since there are 4000 carbon atoms on the segment surface plane, our estimated number of acid groups on the most highly treated 2 NST specimen, 1900, suggests that ~50% of the surface carbon atoms have such groups attached. The corresponding "degree of coverage" with acid groups at the lower level of treatment, 1.25 NST, is ~30%.

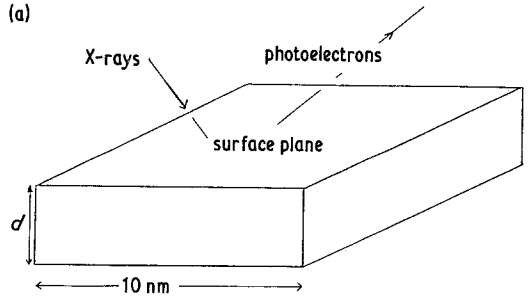
The relative close-packing of acid groups on the two treated samples implies that the majority of them are labelled pairwise by the Ba^{2+}. On statistical grounds, it is appreciated that a small proportion, ~$1/e^2$ (15%), may be left in single isolation; however, this is probably less than the percentage errors in the acid group numbers, arising from the assumptions made in their calculation.

With no surface treatment (UT), the average separation of labelled groups is ~0.8 nm. This implies that a significant proportion of the groups exist in single isolation and cannot be labelled by Ba^{2+}:



where the crosses represent unlabelled groups.

It is possible that during immersion in the labelling medium, isolated groups may react



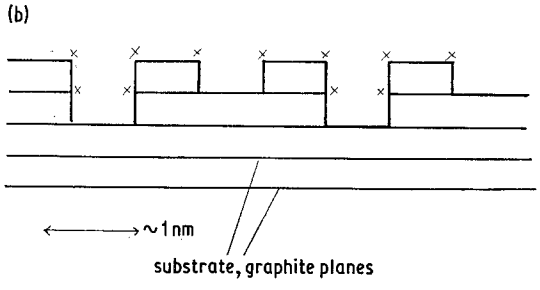


Figure 3 (a) Model surface segment for initial calculation purposes; photoelectron analysis depth $d = 3.5$ nm. (b) Possible structure of the surface at the atomic level; crosses mark possible sites at which C/O functional groups may attach.

TABLE IV Surface concentration of acidic groups labelled by barium*

Fibre sample	(1) O/C ratio on control specimens (Table II)	(2) No. of oxygen atoms per unit area on control specimens	(3) Ba/C ratio on labelled specimens (Table II)	(4) No. of barium atoms per unit area on labelled specimens	(5) No. of acid groups per unit area on control specimens which were labelled by barium	(6) Average separation scale of acid groups on control specimens (nm)
UT	3.05/95	1500	0.18/92	80	160 (320)†	0.79 (0.56)†
1.25 NST	9.05/89	4300	1.36/84	650	1300	0.28
2 NST	13.0/86	6000	1.89/79	960	1900	0.23

*(2) = (1) × 40 000; (3) corrected for $BaCl_2$; (4) = (3) × 40 000; (6) = [10 nm/$(5)^{1/2}$]; unit area = (10 nm × 10 nm).
†See text.

TABLE V Degree of surface acidity

XPS analysis			Ehrburger and Donnet [1]		
Fibre	Acid groups (μeq g^{-1})		Fibre	Acid groups neutralized by (μeq g^{-1})	
	R = 1.5	R = 2		NaOH	$NaOC_2H_5$
UT	2	3	AC, non-treated	7	10
1.25 NST	9	12	AC–HNO_3*	14	20
2 NST	13	17	AC–NaOH*	16	17

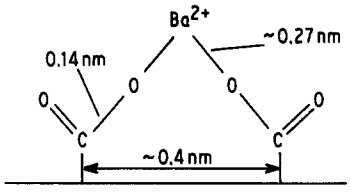
*Electrolytically treated in solution.

thus:

$$-COOH \xrightarrow{BaCl_2/BaOH} -COO-Ba-OH \text{ or } COO-Ba-Cl$$

However, barium-containing species which bind to only one acid group are likely to be removed during post-labelling rinsing, bearing in mind the earlier discussion regarding monobasic labels such as Ag^+.

The maximum separation between two monobasic groups for dibasic labelling to occur can be estimated from molecular geometry and bond lengths, and is probably ~0.4 nm:



Bond lengths and ionic radii are taken from Weast [12].

With an average separation of barium-labelled groups of ~0.8 nm (Table IV), approximately 4/8 or 50% of the monobasic group present exist in single isolation. Hence, a better estimate of the number of such groups on the surface segment is twice the number labelled by barium, ~320, and this result is also given in Table IV.

The fibre diameter as measured by scanning electron microscopy is 8.5 μm, which using a density for Type II fibres of 1.7 g cm^{-3} gives a geometrical area, assuming a smooth cylindrical surface, of 0.27 m^2 g^{-1}. Introducing a surface roughness factor R which has a likely range of 1.5 to 2, the number of (10 nm)^2 surface segments per gram of fibre is $0.27R/(10 + 10^{-9})^2 = 2.7 \times 10^{15}R$. Hence with a acidic groups per surface segment, the degree of acidity, in units of μeq g^{-1}, is $(a \times 2.7 \times 10^{15}R \times 10^6)/6.02 \times 10^{23} = aR/220$, as presented in Table V.

Obviously, exact correlations between the two sets of results could not be expected owing to differences in the fibres, surface treatments and experimental techniques. However, some generalized comparisons can be made. The electrolytic treatments of Ehrburger and Donnet [1] result in an increase in acidity by a factor of ~2, which compares with corresponding factors of ~4 (UT → 1.25 NST) and ~6 (UT → 2 NST) for our commercial fibres. It may be deduced, therefore, that the commercial treatment is relatively efficient at increasing the degree of fibre surface acidity.

This is an important result, as it has already been pointed out that the ILSS of epoxy–fibre composites may depend on the degree of fibre acidity (e.g. [1]), and a relatively high shear strength is required of composite components as used in aircraft, for example, which are fabricated from commercially treated fibres.

Consider now the non-acidic groups, as it is apparent from Table IV that a significant proportion of the oxygen present on a given fibre is not in a form that could be labelled by Ba^{2+}, and may therefore exist as carbonyl or quinone groups, containing C=O. In particular, our model surface segment of the 2 NST control specimen contains 6000 oxygen atoms, of which ~3000 are present in non-acidic form, since each of the 1900 acid groups contain one or two oxygen atoms. As the segment has 4000 carbon atoms on the surface, this high level of treatment appears to give effectively complete coverage by oxygen-containing groups. The surface may therefore be considered to be covered completely with an oxide layer.

The corresponding degrees of coverage at the lower level of treatment, 1.25 NST, and on the untreated UT specimens, are 90% and 60% respectively.

In our model surface segment, we have

assumed the existence of a substrate of graphite planes which effectively run parallel to the fibre axis, based upon the structure of fibres as elucidated by Bennett *et al.* [13]. However, it is apparent that the carbon at the surface of the substrate cannot be a continuous graphite sheet, as functional groups could not bind to it chemically. This substrate surface may undulate and contain lattice vacancies, discontinuities and defects to which chemical bonding of functional groups could occur. A possible structure is presented schematically in Fig. 3b.

The two main advantages of XPS and labelling over titration, in assessing fibre surface acidity, are that a relatively small quantity (< 50 mg) of fibre tow is required for analysis, and the high XPS sensitivity of barium provides a relatively accurate result, with an error of $\sim \pm 0.3\,\mu\text{eq}\,\text{g}^{-1}$, for a given surface roughness factor R. However, it is agreed that evaluating fibre acidity in $\mu\text{eq}\,\text{g}^{-1}$ from XPS data requires a number of assumptions regarding, for example, electron escape depths and surface structure.

Hence, the effective uncertainty in our calculated acidity values in Table V is probably ± 1 to $2\,\mu\text{eq}\,\text{g}^{-1}$, which is similar to the value of $\pm 2\,\mu\text{eq}\,\text{g}^{-1}$ quoted by Ehrburger and Donnet [1].

4. Conclusion

It is accepted that both the chemical and physical state of a fibre surface are complex, and probably dependent upon a number of factors, including the mechanism of the oxidation treatment process. A given experimental technique, therefore, cannot alone fully elucidate the nature of the surface.

However, it has been demonstrated that a barium labelling and XPS technique can be used to evaluate the degree of fibre surface acidity, to a degree of accuracy which is at least comparable to that obtainable from titration methods.

Generally, the technique of labelling groups, e.g. with heavy metals, opens up the possibility of investigating the distribution of groups, using high resolution techniques such as scanning Auger electron spectroscopy with a low beam energy.

Acknowledgements

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