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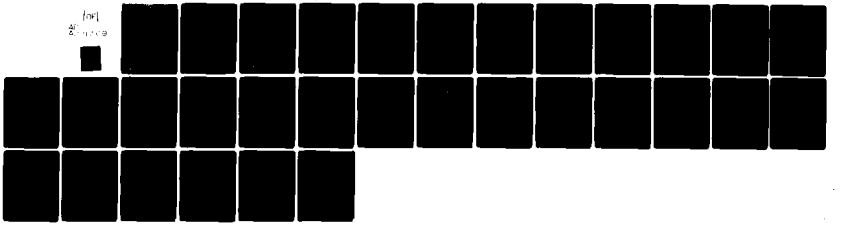

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by

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AN X-RAY PHOTOELECTRON SPECTROSCOPIC EXAMINATION OF SURFACES OF SOME THERMOSETTING RESINS AND CARBON FIBRE COMPOSITES

by

Brenda M. Parker

SUMMARY

The surfaces of a range of cast thermosetting resins and carbon fibre composites have been investigated by electron spectroscopy for chemical analysis (ESCA). The peaks recorded were assymmetrical and could be resolved to give minor peaks which were related to the chemical groups present in the resins. In particular, peaks due to the $-CF_2-$ group were deconvoluted from the carbon 1s and fluorine 1s peaks and related quantitatively. These groups arose from contamination of the resin and composite surfaces by polymeric fluorinated hydrocarbon release agents. Surface contamination was reduced to a low level by abrasion. Oxidative chemical treatment of composite surfaces caused an increase in the amount of oxygen bonded to carbon.

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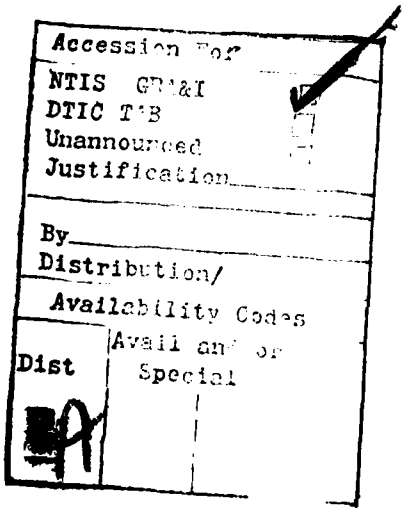


1 INTRODUCTION

A large number of spectroscopic methods are now available for the analysis of solid surfaces[1], one of the more commonly used being X-ray photoelectron spectroscopy (XPS) (also known as ESCA - electron spectroscopy for chemical analysis). In the work reported here ESCA was used to investigate the surfaces of some cast epoxy and polyester resins and carbon fibre reinforced epoxy resins.

The technique of ESCA was developed by Siegbahn and co-workers[2]. When a sample is bombarded with X-rays in the energy range 10-1500 eV, electrons are ejected with energies characteristic of the elements in the material, and of their chemical environment. The mean free paths of the electrons and hence the depth to which the material is sampled, are in the range 5-20 Å for metals, 15-40 Å for oxides and 40-100 Å for organic materials[1].

Although ESCA has been used extensively to characterise surfaces of linear polymers, notably by Clark[3], little has been published on the ESCA spectra of cross-linked thermoplastics[4-6] or thermosetting resins[7].

The study reported here was preliminary work for a programme to assess the effects of various surface treatments, immediately prior to bonding, on the strength and durability of adhesive bonds to CFRP. The aims were to identify and correlate peaks in the ESCA spectra with the structure of the cast resins before and after postcure, to study the effect of oxidative treatment on carbon fibre composite surfaces and to identify surface contamination.

2 MATERIALS AND METHODS

2.1 Cast resins

The basic epoxy resins and curing agents used to prepare the materials used in this work are listed in Table 1. The components of each of the resins are listed in Table 2. With the exceptions of resins B, C and H all materials were proprietary formulations. Polyesters K and L, which are not listed in Table 2, were of unknown composition.

The room temperature curing formulations H, K and L were cast in polyethylene beakers. Slices of resin about 2 mm thick, cut on a band saw, were surface abraded and washed with acetone to remove any debris before being dried at 90°C for 2½ days.

The remaining resins were all hot-setting systems. Where the initial mixture contained solvent this was removed under vacuum at 110°C. The resins were cured on glass dishes coated with fluorinated hydrocarbon release agent in

air at temperatures about 30°C below the temperature of 180°C normally used for these resins when reinforced with carbon fibre.

Sheets of cured resin were cut in half, one half being further heated in air for 5 hours at 180°C. (Resin D, exceptionally, was heated for 10 hours.) This was equivalent to a postcure normally applied to carbon fibre composites. Postcured resins are indicated in the text by 'P' after the resin identification. Samples were stored in polyester film or in corked glass tubes.

ESCA examination was carried out on surfaces which had not been in contact with either polyethylene or release agent coated glass during casting.

2.2 Carbon fibre reinforced composites

Composites of resins D and F were prepared by autoclave moulding. Preimpregnated film sheets were cured against a woven peel-ply cloth of glass fibre coated with polymeric fluorinated hydrocarbon. This was stripped off after cure to leave a textured resin-rich surface. These composites are designated CD and CF.

Composites of resin D were also prepared by compression moulding of preimpregnated sheets in a metal mould. In order to be able to remove the composite after cure, the mould was coated with a fluorinated hydrocarbon release agent. By partially curing a layer of matrix resin on to the mould before adding the preimpregnate, the laminates had one resin-rich surface. Seven different surface pretreatments, described in Table 3, were intended first to remove the release agent transferred from the mould and then to alter the resin surface chemically.

2.3 ESCA spectra acquisition

Photoelectron spectra of the samples were acquired on a Vacuum Generators ESCA 2 at the Department of Metallurgy and Materials Technology, University of Surrey, and recorded and processed by a VG Data System 3000. The anode was AlKα giving radiation at 1486.6 eV. Spectra were recorded in terms of the electron binding energy E_b where

$$E_b = h\nu - KE + \phi_S$$

and

$h\nu$ = 1486.6 eV

KE = kinetic energy of emitted electrons

ϕ_S = 4.5 eV and is the spectrometer work function.

Wide scan spectra of binding energy 0-1000 eV covered the range of peaks expected on the basis of resin composition. A normalised wide scan spectrum for a resin D composite is shown in Fig 1. Since this resin did not contain sulphur the position of the sulphur 2p peak is indicated.

A wide scan spectrum was run manually for each sample to identify the peaks present and to determine their approximate relative intensities. Narrow scans for each peak, of width ±10 eV about the expected maximum, were then acquired by the data system. At least two scans were made of each peak, but for the weak peaks up to seven scans were accumulated. The printout for each peak gave the binding energy and the cumulative number of counts at the peak maximum. From this data, the peak intensities could then be calculated relative to carbon 1s = 1.00. Narrow scan peaks reproduced in the figures were normalised using the data system.

2.4 Deconvolution of peaks

The binding energy of an electron depends on the bonding of the atom from which the electron is expelled. Binding energies of electrons removed from carbon atoms bonded only to carbon or hydrogen atoms are less than those of carbon atoms bonded to oxygen or fluorine. In the latter case, the binding energy is 5-6 eV higher[8].

In the materials investigated in this work particular atoms are bonded in a number of different ways, each type of bonding producing a peak at a characteristic binding energy and of an intensity related to its frequency of occurrence. Because the peaks generally have a width at half maximum height of 1-2 eV, they will overlap to produce a broader peak. By taking a standard peak shape for a bond, the broad peak can be deconvoluted into its separate components. This was done using a Dupont 310 Curve Resolver on which up to ten peaks of predetermined shape could be combined to fit the experimental peak.

Of the elements in the resins, only nitrogen could be expected to give a reasonably 'pure' peak of high relative intensity (see Table 1) since, with the exception of resin D, it occurs bonded to either two or three carbon atoms which are themselves further bonded to only carbon or hydrogen. It was found that the shape of the nitrogen 1s peak was very close to Gaussian, and on the assumption that the peak shapes for the other elements would be of the same form, each channel of the Curve Resolver was set to the nitrogen 1s peak shape. Peak widths were slightly different for different atoms but were held constant within each atom.

Because of electrostatic charging of the sample in the X-ray beam, the whole spectrum for a compound can be shifted by several electron volts. To enable comparisons to be made, the line for carbon 1s $-(CH_2)_n-$ was set at 285.0 eV and all other binding energies were related to it. The position of the maximum of the total carbon 1s peak was taken as 285.0 eV except in the case of samples which were heavily contaminated with fluorinated hydrocarbon where the peak maximum related to $-(CF_2)_n-$ and not to $-(CH_2)_n-$. Deconvoluted peaks with an area of less than 5% of the total peak were disregarded.

3 ANALYSIS OF RESULTS

3.1 Structural correlation of ESCA peaks

Nominal binding energies associated with peaks expected in the ESCA spectra of the resins and composites are,

Carbon	1s	285 eV
Nitrogen	1s	400 eV
Oxygen	1s	532 eV
Fluorine	1s	690 eV
Sulphur	2p	165 eV

Actual peak positions, adjusted to carbon 1s at 285.0 eV to eliminate the shift in the peak positions due to sample charging, are given in Table 4. For carbon 1s only the positions of the deconvoluted peaks are given. For other elements the position of the major peak is given followed by the binding energies of the deconvoluted peaks, where this was possible.

3.1.1 Carbon 1s

The average positions of the deconvoluted minor peaks were, for resins, 287.1 ± 0.4 eV, 290.2 ± 0.4 eV, 292.4 ± 0.8 eV and for composites 286.5 ± 0.2 eV, 289.7 ± 0.6 eV, 292.2 ± 0.6 eV. Only the first peaks were significantly different between resins and composites; these peaks were found in the spectra of all samples. The peak at 290 eV was found in the spectra of polyester resins K and L, of epoxy-polyester H, two of the postcured resins and of all the samples containing resin D. The third peak at 292 eV was associated with samples which had high relative fluorine contents.

Deconvolution of the carbon 1s peak for several resin samples is illustrated in Figs 2 and 3. Fig 2 shows peaks for samples containing three different basic epoxy resins (numbered as in Table 1). The variation in the minor peak position with epoxy type is coincidental - in all samples containing R1 the variation was from 286.8 to 287.1 eV and for R2 from 286.5 to 287.5 eV. Only resin D

containing R3 with a high -NHCO- content, consistently gave a minor peak at 290 eV. Resin J which contained a high proportion of $-CO_2-$ groups showed a peak at 290 eV only in the postcured sample. Fig 3 shows resins D, H and K, all with high $-CO_2-$ or $\diagdown C{=}O$ contents. A peak at 290 eV could not be deconvoluted for any sample that did not contain carbonyl groups with the exception of postcured sample AP.

From their work on homopolymers Clark and Thomas[5,9] found that the average position for a carbon singly bound to oxygen was 286.6 ± 0.1 eV corresponding to the first of the deconvoluted peaks in this study. The carbon in ester groups $-C(=O)-O-$ gave a peak at 289.1 ± 0.2 eV which agrees with the second deconvoluted peak for the composites; however the corresponding peak for the resins was at least 0.5 eV higher.

The origin of the third deconvoluted peak at about 292 eV as being from a $-CF_2-$ groups is confirmed in Fig 4 where the carbon 1s peaks for two composite samples with high fluorine to carbon ratios are compared with resin B (no detectable fluorine) and the fluorinated hydrocarbon release agent. The peak binding energy of 292.3 eV overall may be compared with the values for the $-CF_2-$ group in polytetrafluoroethylene; Yasuda[10] found 292.6 eV, Clark[11] 291.2 ± 0.7 eV and Brecht[12] 292.8 eV.

3.1.2 Oxygen 1s

Using the nitrogen 1s as the basic shape, some of the oxygen 1s peaks could be deconvoluted as shown in Fig 5 giving minor peaks at 530.8 ± 0.6 eV and 534.4 ± 0.5 eV with the major peak at 532.8 ± 0.4 eV. The upper set of curves is for two resins E and F which were made from the non-ether containing epoxy compound and DDS. The third resin J contained an epoxy resin with a high proportion of carbonyl groups and gave a larger deconvoluted peak at 534 eV. The lower set of curves also compares three resins. Resin A contained the diether epoxy and DDS and gave a larger 534 eV peak than resin C which contained no DDS. However, resin D which had a higher oxygen content than the others gave an oxygen 1s peak which did not convolute despite having both carbonyl and ether oxygens in its structure.

Clark and Thomas[5], working with acrylate homopolymers, attributed deconvoluted oxygen 1s peaks at 532.9 eV and 534.3 eV to carbonyl and ether oxygens respectively. The shift between -O- and -NHCO- , at 1.5 eV [9], was almost identical. These attributions agreed with their theoretical calculations[5].

However, this implies that most of the oxygen in the epoxy resin surfaces is present in the form of carbonyl rather than ether, in contrast to the results of the carbon 1s deconvolution.

Waghorne[13] resolved oxygen 1s peaks from epoxy resin carbon fibre composites into peaks at 532.2 eV and 533.4 eV. Initially the former was the larger peak, but after soaking in water at 50°C for 14 days the relative intensities of the peaks were reversed. This implies that the 533.4 eV peak is associated with the presence of water. The proportion of -C-O- in the carbon 1s peak was either unchanged or reduced.

3.1.3 Fluorine 1s

The binding energies of the fluorine 1s peaks and, where possible, their deconvoluted minor peaks are given in Table 4. Fluorine 1s spectra were not acquired for resins B, BP, C, H or L. D, DP and J gave peaks of low intensity and high background which could not be deconvoluted. The major peak had a binding energy of 690.0 ± 0.4 eV which agreed well with the result of Clark, *et al*[11] for a fully fluorinated polymer.

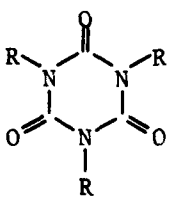
The minor peaks had binding energies of 686.9 ± 0.8 eV for resins and 687.3 ± 1.1 eV for composites. All the peaks that could be deconvoluted were for resins containing BF_3 adduct (H4).

Fig 6 compares the fluorine 1s peaks of two samples containing BF_3 and with some degree of surface contamination. The third peak was obtained[13] for a sample with very low surface contamination. The minor peak at about 686 eV compared well with the binding energy of 685.6 eV found for a BF_3:pyridine adduct[14].

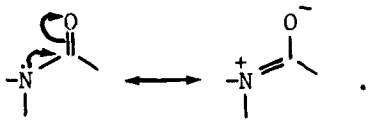
The peaks for samples of resins D and J, both of which contained BF_3 and had low surface contamination are shown in Fig 7.

3.1.4 Nitrogen 1s

The average binding energies of the nitrogen 1s peaks (Table 4) were 400.9 ± 0.3 eV for all the samples containing resin D and 399.7 ± 0.4 eV for the remainder. This difference of 1.2 eV is significant and can be attributed to the difference in electron density between the nitrogen in the cyanurate ring



and the nitrogens attached to $-CH_2-$ or to aromatic rings. No binding energies are yet available from the literature for $>CH-NH_2$, $-CH_2-NH-CH_2$, or $-C-N(CH_2-)(CH_2-)$ groups with the exception of Browning[7] who found 402.9 eV for an epoxy resin containing RI. He was able to resolve the nitrogen 1s into two peaks. One at 404.3 eV he attributed to oxidation of the R_3N to R_3NO^{2-}. The shift of +1.4 eV was attributed to the electron-withdrawing effect of the oxygen. A similar effect was observed on the formation of a BF_3:pyridine adduct[11] where the electron-withdrawing effect of the fluorine atoms led to an increase in binding energy of 2.5 eV. The shift of +1.2 eV observed here would not, therefore, be inconsistent with electron-withdrawal by the oxygen of the adjacent carbonyl group in the cyanurate ring



Literature values for nitrogen 1s binding energies for -NHCO- vary from 399.8 eV in nylon 6 [10] to 402.5 eV for a range of nylons[9].

3.1.5 Sulphur 2p

The expected position for the sulphur 2p peak in $-SO_2-$ was in the region of 164.7 eV [7] to 167.9 eV [9]. However, all the peaks recorded were of low intensity and rather uncertain position.

3.2 Quantitative analysis

In view of the low range of atomic percentages of oxygen and nitrogen in the samples and the scatter of the measured intensity ratios of the ESCA peaks for these elements, it was not possible to calculate meaningful values for the relative intensity factors which relate peak height, or peak area, to concentration.

However, as Fig 8 shows, a good linear relationship was obtained for fluorine, between the fluorine 1s peak and the deconvoluted part of the carbon 1s peak at 292 eV. The 292 eV peak has been identified with the carbon atom in the $-CF_2-$ group, while the fluorine 1s peak should be equal to twice the intensity of the carbon 1s (292 eV) peak multiplied by the relative intensity factor for fluorine 1s. All measurements here have been made relative to the carbon 1s (285 eV) peak.

From Fig 8 the intensity factor for fluorine 1s relative to carbon 1s (285 eV) is 4.06, which compares well with the values of 3.7, 3.8 and 4.17 found by Jørgensen[15], Carter[16] and Nefedov[17] respectively from inorganic fluorine and carbon compounds.

4 DISCUSSION

4.1 Effect of postcure and comparison of resins and composites

Resin samples were postcured at 180°C to match the postcure generally used for the composite. If postcure causes changes in the surface composition similar differences might be expected between the spectra of the composites and postcured resins on the one hand and the resins on the other.

For the six resin/postcured resin pairs, there was no systematic change in the oxygen 1s/carbon 1s ratio; surface oxidation and loss of absorbed water would be expected to increase and decrease respectively the oxygen content. There was a slight increase in the oxygen content after postcure as measured by changes in the shape of the carbon 1s peaks. Resins AP and JP gave peaks from which a $>C=O$ constituent could be deconvoluted, whereas this was not possible before postcure. Fig 9 shows that DP and FP peaks were also broadened although not to an extent where deconvolution was significantly altered. Compared with the resin carbon 1s peaks, the peak for composite CD was considerably broadened but that for composite CF was virtually unchanged.

On balance the evidence from the ESCA spectra is that postcure of an epoxy resin leads to a slight increase in $>C=O$ bonds on the surface.

4.2 Surface contamination

Contamination by fluorinated hydrocarbon release agents was easily detected by the appearance of an intense fluorine 1s peak at 690 eV. Where the resins contained fluorine originating from the BF_3 complex catalyst, the fluorine 1s peak had a binding energy of about 686 eV and was of very low intensity. Where the ratio of intensities of fluorine 1s to carbon 1s exceeded about 0.1 to 0.2 a minor peak at about 292 eV could be deconvoluted from the carbon 1s peak. This was attributed to the $-CF_2-$ group in the release agent as illustrated in Fig 4.

Composites CD and CF, which were cured against a peel cloth coated with release agent, had fluorine contents near the fluorine/carbon limit for deconvolution of the carbon 1s peak but in excess of what was expected from their BF_3 contents. Their fluorine 1s peaks are compared with those of the resins, which were only slightly contaminated by release agent, in Fig 10. There was little

difference between CF and FP but CD gave a more intense peak than D. Thus a small amount of the 'non-migratory' fluorinated hydrocarbon polymer on the peel cloth was transferred to the surface of the composite.

The surfaces of composite samples which were moulded against a metal surface coated with release agent were grossly contaminated. An initial abrasive treatment (CD2 and CD3) did not decrease the fluorine content, but a second (CD4 and CD5) reduced it to a level comparable with that found on the 'peeled' composites (Fig 11). Thus it is probable that all carbon fibre composite prepared in the presence of a fluorinated hydrocarbon release agent will have contamination on the surface, this may lead to lower wetting of the surface by an adhesive and hence to poorer bondability. Surface abrasion, if thorough enough, will remove the contamination.

4.3 Surface chemical treatment

The effect of two oxidative chemical treatments on the composite carbon 1s peak is shown in Fig 12. The increase in the oxygen 1s/carbon 1s ratio corresponded to the increase in the high binding energy shoulder on the carbon 1s peak, which deconvoluted to about 289 eV. CD6 which was soaked in water had an oxygen content equal to that of CD7 but did not show any increase in the 289 eV deconvoluted peak. From this it can be concluded that both chemical treatments increased the carbonyl functionality on the composite surfaces and that the cold chromic-sulphuric acid pickle was more effective than 50 v/v HNO_3.

5 CONCLUSIONS

The study by ESCA spectroscopy of cast resins, carbon fibre composites revealed some differences between the spectra of different resins that could be linked with the chemical structure of the components of the cured resin. Carbon 1s peaks could frequently be deconvoluted to give minor peaks attributable to -O- and to >C=O functionalities. ESCA is an excellent method for determining fluorine contamination of the surface as the fluorine 1s peak has a high intensity factor.

Such contamination arose from fluorinated hydrocarbon mould release agents on the resins and press-moulded composites or from coated peel ply release cloths on the autoclave cured composites. At high concentrations of fluorinated hydrocarbon it was possible to make a quantitative identification of a $-CF_2-$ component in the carbon 1s peak. At low fluorine concentrations further work is needed to distinguish positively between fluorocarbon contamination and BF_3 hardener in the resin.

It was possible to detect changes in the chemical nature of composite surfaces which had been given oxidative chemical pretreatments.

Work is in progress to relate surface contamination and surface oxidative effects to the strength, durability and mode of failure of adhesively-bonded CFRP joints.

Table 1

PRECURSOR RESINS AND CURING AGENTS

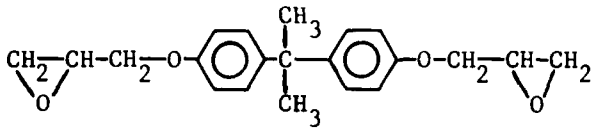
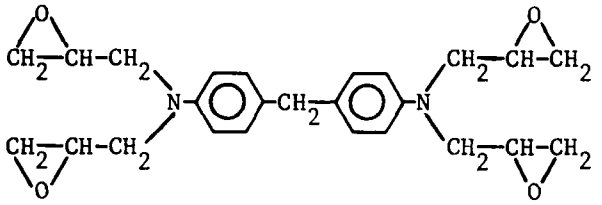
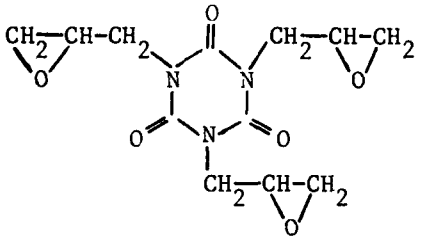
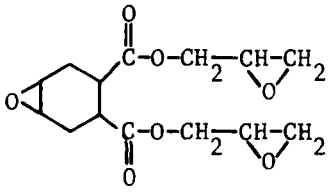
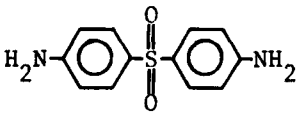
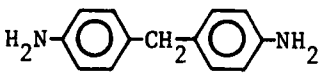
	Structure	Name
R1		2,2-diphenylpropane-p,p'-diglycidyl ether
R2		tetra-N-glycidyl-4,4'-diaminophenyl methane
R3		tri-N-glycidyl isocyanurate
R4		diglycidyl-4,5 epoxy-cyclohexyl(1,2-dicarboxylate)
H1		4,4'-diamino diphenyl sulphone
H2		4,4'-diamino diphenyl methane
H3	$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	triethylene tetramine

Table 1 (concluded)

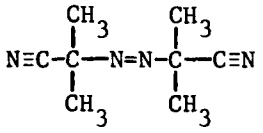
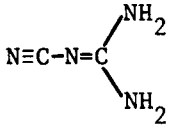
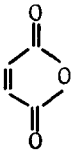
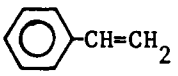
	Structure	Name
H4	$BF_3.NH_2CH_2CH_3$	boron trifluoride mono-ethylamine complex
H5		azobisisobutyronitrile
H6		dicyandiamide
H7		maleic anhydride
H8		styrene

Table 2

COMPONENTS OF CURED RESINS

Cured resin	Components
A	R1 H1 H4
B	R1 H2
C	R1 H3
D	R1 R3 H4
E	R2 H1 H4
F	R2 H1 H4
G	R2 H1 H6
H	R2 H5 H7 H8
J	R4 H1 H4

Table 3

SURFACE TREATMENT OF CARBON FIBRE COMPOSITES

Sample	Surface treatment
CD1	None, as prepared
CD2	Light abrasion with 400 grit paper + acetone wash
CD3	CD2 + 16 hours at 90°C in air
CD4	CD2 + further abrasion and wash
CD5	CD4 + 16 hours at 90°C in air
CD6	CD4 + further abrasion and wash + 24 hours in distilled water at room temperature + 16 hours at 90°C in air
CD7	CD4 + further abrasion and wash + 16 hours in 50 v/v HNO_3 at room temperature + 8 hours wash in distilled water + 16 hours at 90°C in air
CD8	CD4 + further abrasion and wash + 16 hours in chromic-sulphuric acid pickle solution (DEF 03/2 method D) at room temperature + 8 hours distilled water wash + 16 hours at 90°C in air

Table 4

DECONVOLUTION OF ESCA PEAKS

Peak binding energies are relative to carbon 1s major peak = 285.0 eV and have been shifted by the amount given in the second column. Peaks in brackets are of low intensity and uncertain position.

Sample	Charging shift (eV)	Carbon 1s			Oxygen 1s			Fluorine 1s				Nitrogen 1s	Sulphur 2p
		Minor peaks			Major peak	Minor peaks		Major peak	Minor peaks				
A	+0.7	286.8			533.6		534.8	690.3	687.6		691.9	399.7	(153.1)
AP	-0.5	286.7	290.8		533.1			689.8	687.6			(399.8)	165.7
B	+0.4	287.1			533.2							(400.0)	
BP	-0.4	287.7			532.9	530.2	534.9					(400.8)	
C	+0.1	287.0			533.3	531.9	534.1					399.5	
D	+0.1	287.7	290.3		532.6							401.2	
DP	+0.4	287.8	290.1		532.6							401.4	
E	-0.1	286.9			532.9			689.8	686.2			399.1	168.5
F	+0.8	286.7			532.8	530.4	535.0	689.7	686.3	684.4		(399.1)	168.8
FP	+1.0	286.5			533.3	530.9	535.1	690.5	686.6			400.3	168.6
G	0	287.3			532.5		534.7	689.9				399.7	
GP	-0.7	287.5		291.4	532.5		534.6	689.5				399.3	
H	-0.5	286.9	290.0	293.0	532.8		534.5					400.0	
J	+0.7	287.7			532.7	530.7	534.3	689.2	686.1	684.0	690.8	399.8	
JP	0	286.6	289.6		532.8	530.6	533.9					399.5	170.2
K	-0.8	287.3	290.6	292.9	532.9		534.7	690.5					
L	-1.0	286.8	290.1	292.4	532.2		534.2						
CF	-0.9	286.2	289.9		533.3	531.3	534.6	690.3	686.4			400.6	(154.1)
CD	-1.3	286.5	290.6		532.1	531.4	534.6	689.8	685.3			400.8	
CD1	+0.4	286.4	287.4 290.6	293.1	533.4	531.3	534.9	690.8	689.0		693.3		
CD2	-1.2	286.6	289.4	292.0	532.6	530.0	534.3	690.0	687.9		691.3	400.9	
CD3	-1.2	286.6	289.0	291.8	532.5	530.1	534.3	689.9	687.8		691.0	400.5	
CD4	+0.7	286.5	289.6		532.4	530.9	534.2	690.1	687.6			400.9	
CD5	+0.7	287.0	289.7		532.4	531.7	533.8	689.6	686.9	685.0		400.9	
CD6	+0.8	287.2	289.2	291.7	532.0	530.3	533.1	690.4	687.9		692.5	400.3	
CD7	+1.6	286.5	289.5		532.4	530.9	534.0	689.7				400.7	
CD8	+1.3	286.8	289.3	292.5	532.5	530.9	534.0	689.6				401.0	

REFERENCES

No.	Author	Title, etc
1	A.W. Czanderna (Ed)	Methods of surface analysis. Elsevier, Amsterdam (1975)
2	A. Fahlman K. Hamrin J. Hedman R. Norberg C. Nordling K. Siegbahn	Electron spectroscopy and chemical binding. *Nature*, 20 (5031), 4-8 (1966)
3	K. Larsson C. Nordling K. Siegbahn E. Stenhagen	Photoelectron spectroscopy of fatty acid monolayers. *Acta Chem. Scand.*, 20 (10), 2880-1 (1966)
4	D.T. Clark	ESCA applied to polymers. *Advances in Polymer Science*, 24, 126-188 (1977)
5	D.T. Clark H.R. Thomas	Applications of ESCA to polymer chemistry. X Core and valence energy levels of a series of polyacrylates. *J. Polym. Sci., Polym. Chem.*, 14, 1671-1700 (1976)
6	D.W. Dwight J.P. Wightman	A fundamental approach to adhesion; synthesis, surface analysis, thermodynamics and mechanics. NASA CR 152672 (1977)
7	C.E. Browning	The mechanics of elevated temperature property losses in high performance structural epoxy resin matrix materials after exposure to high humidity environments. AFML-TR-76-153 (1977)
8	M. Gettings A.J. Kinloch	Surface analysis of polysiloxane/metal oxide interfaces. *J. Mater. Sci.*, 12, 2511-2518 (1977)
9	D.T. Clark H.R. Thomas	Applications of ESCA to polymer chemistry. XVII Systematic investigation of the core levels of simple homopolymers. *J. Polym. Sci., Chem. Ed.*, 16, 791-820 (1978)
10	H. Yasuda H.C. Marsh S. Brandt C.N. Reilly	ESCA study of polymer surfaces treated by plasma. *J. Polym. Sci., Chem. Ed.*, 15, 991-1019 (1977)

REFERENCES (concluded)

No.	Author	Title, etc
11	D.T. Clark W.J. Feast D. Kilcast W.K.R. Musgrave	Application of ESCA to polymer chemistry. III Structures and bonding of ethylene and the fluoroethylenes and determination of the composites of fluoropolymers. *J. Polym. Sci., Chem. Ed.*, 11 (2), 389-411 (1973)
12	H. Brecht F. Mayce H. Binder	ESCA investigation of etched polytetrafluoroethylene film. *Angew. Makromol. Chem.*, 33, 89-100 (1973)
13	R.G. Waghorne	Private communication
14	H.J. Anderson	X-ray photoelectron spectra of poly (2-vinyl pyridine) and its adduct with boron trifluoride. *J. Adhesion*, 7, 347-349 (1976)
15	C.K. Jørgensen H. Berthou	Relative intensities and widths of X-ray induced photoelectron signals from different shells for 72 elements. *Farad. Disc.*, 54, 269-276 (1972)
16	W.J. Carter G.K. Schweitzer T.A. Carlson	Experimental evaluation of a simple model for quantitative analysis in X-ray photoelectron spectroscopy. *J. Elect. Spect. Rel. Phenom.*, 5, 827-835 (1974)
17	V.I. Nefedov N.P. Sergushin I.M. Band M.B. Trzhashov	Relative intensities in X-ray photoelectroscopy. *J. Elect. Spect. Rel. Phenom.*, 2, 383-403 (1973)

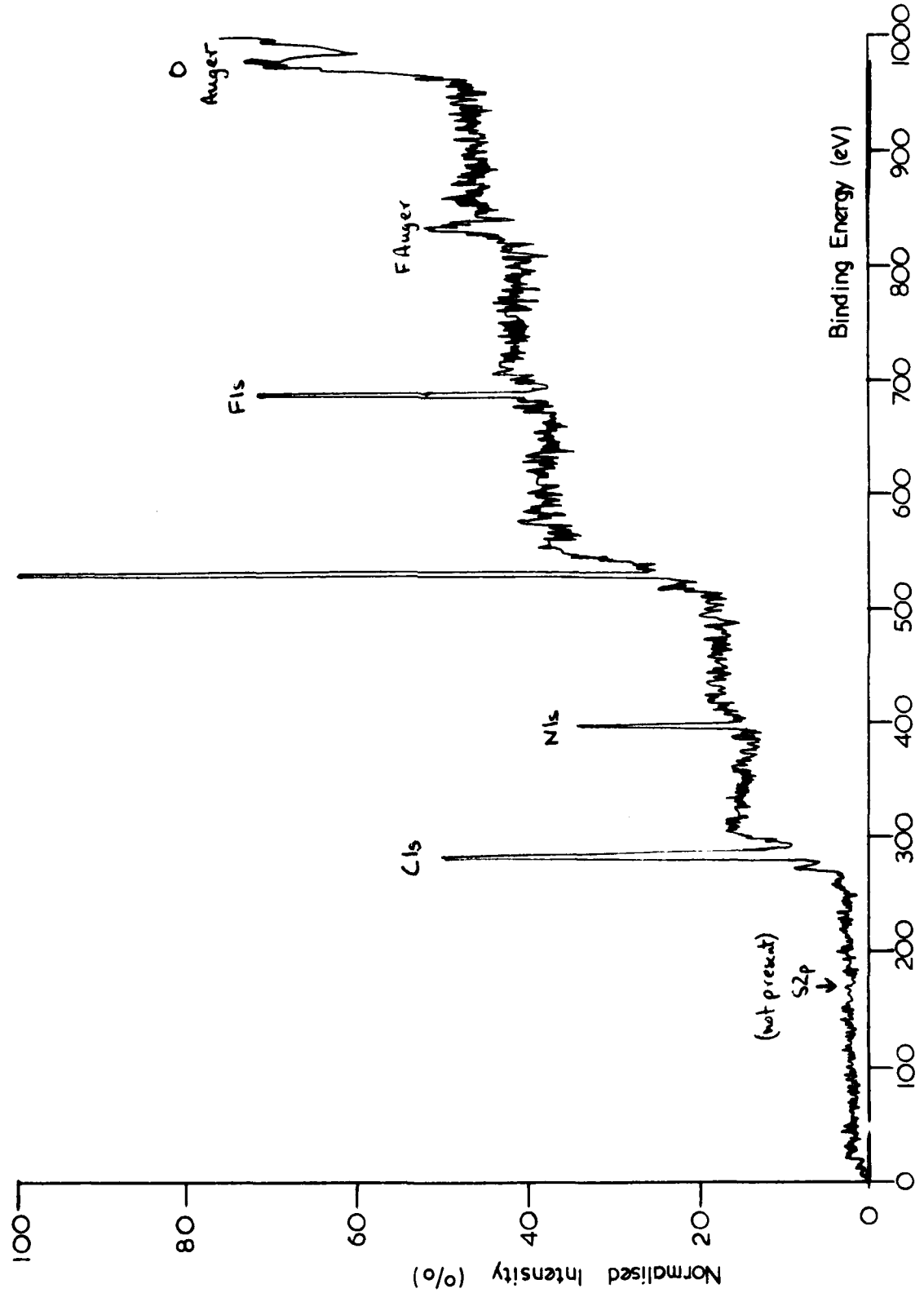


Fig 1 Typical ESCA spectrum for epoxy resin

Fig 2

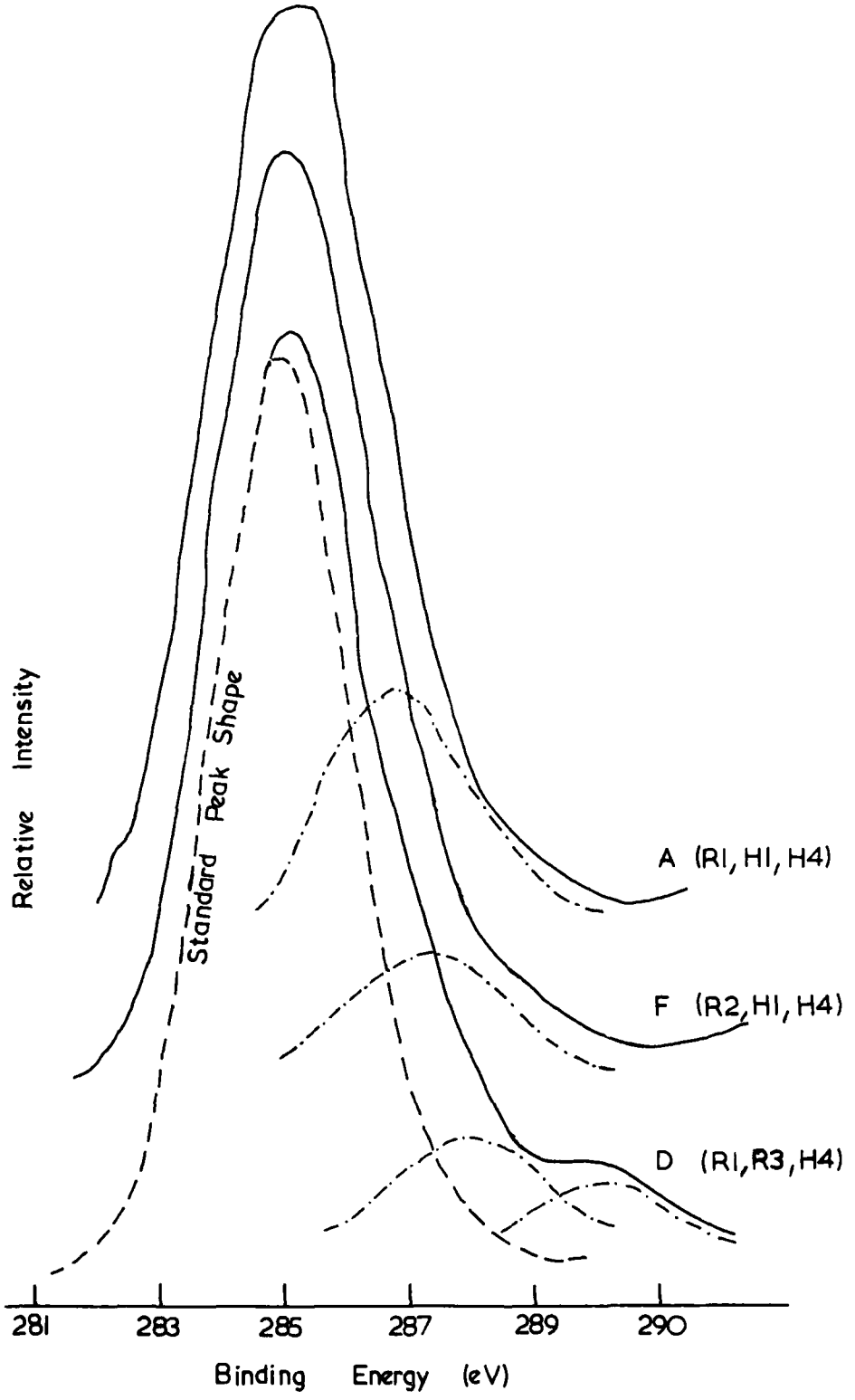


Fig 2 Carbon 1s peaks for different epoxy-based resins

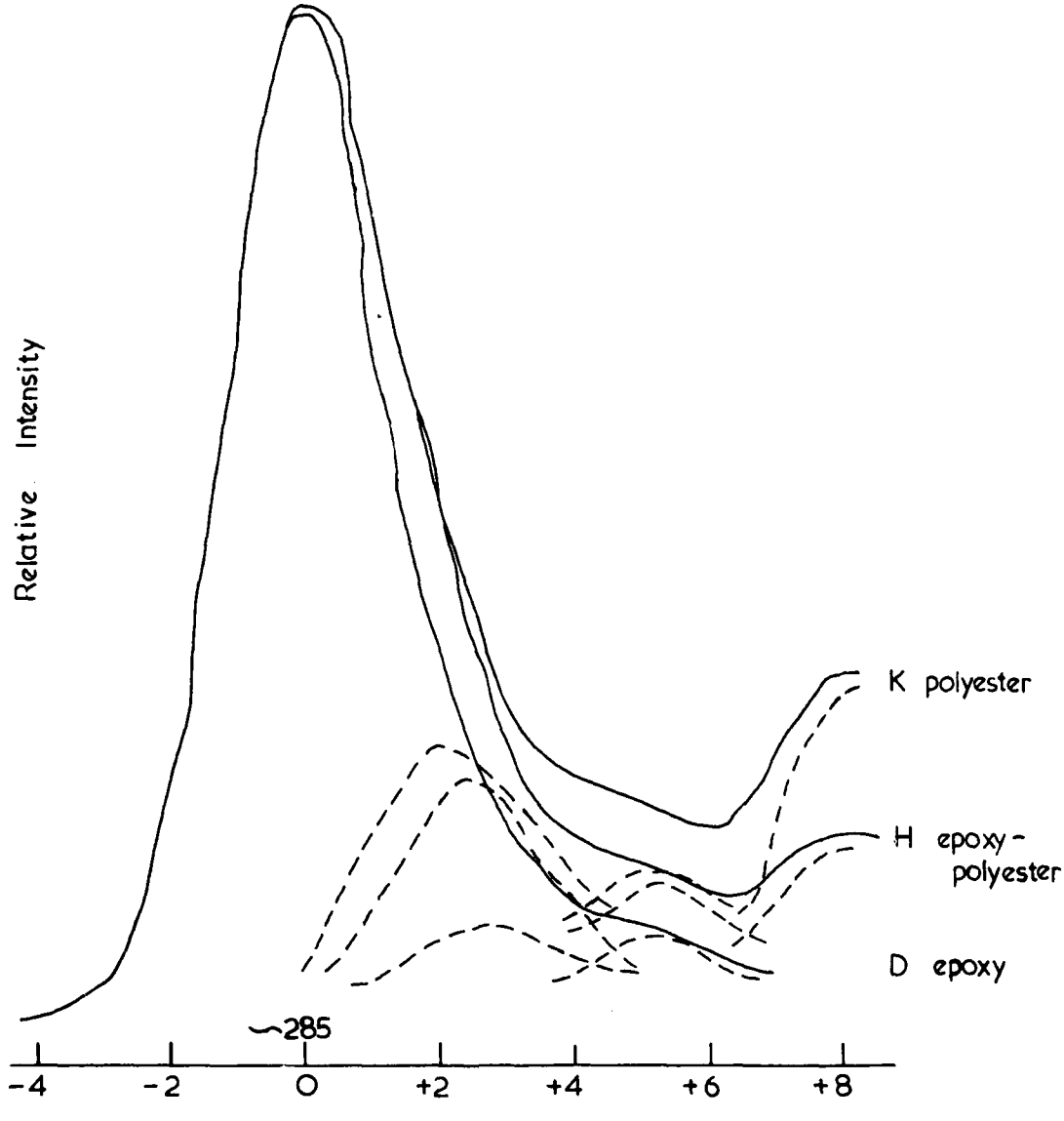


Fig 3 Carbon 1s peaks for resins of high oxygen content

Fig 4

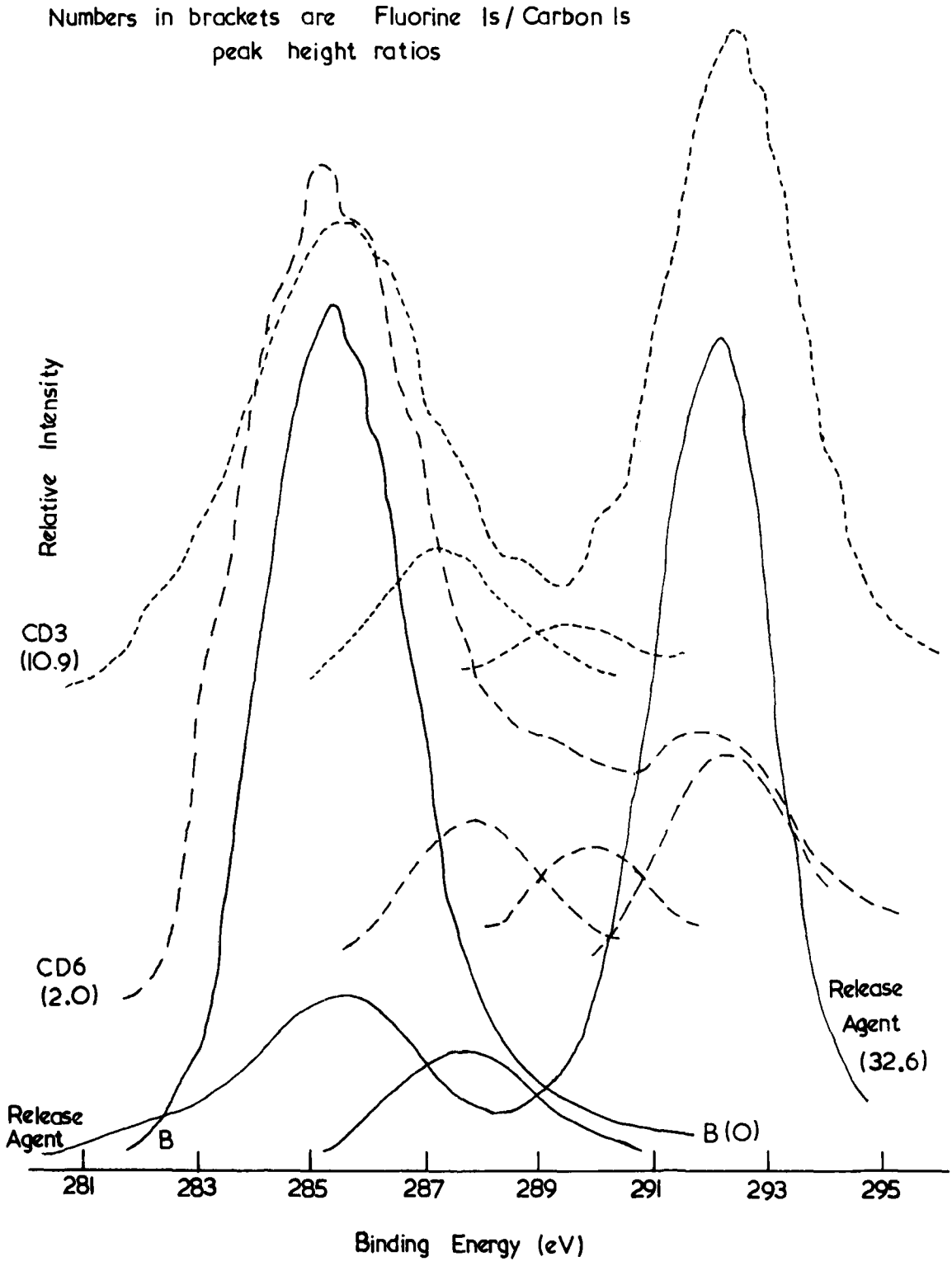


Fig 4 Carbon 1s peaks for fluorine-contaminated surfaces

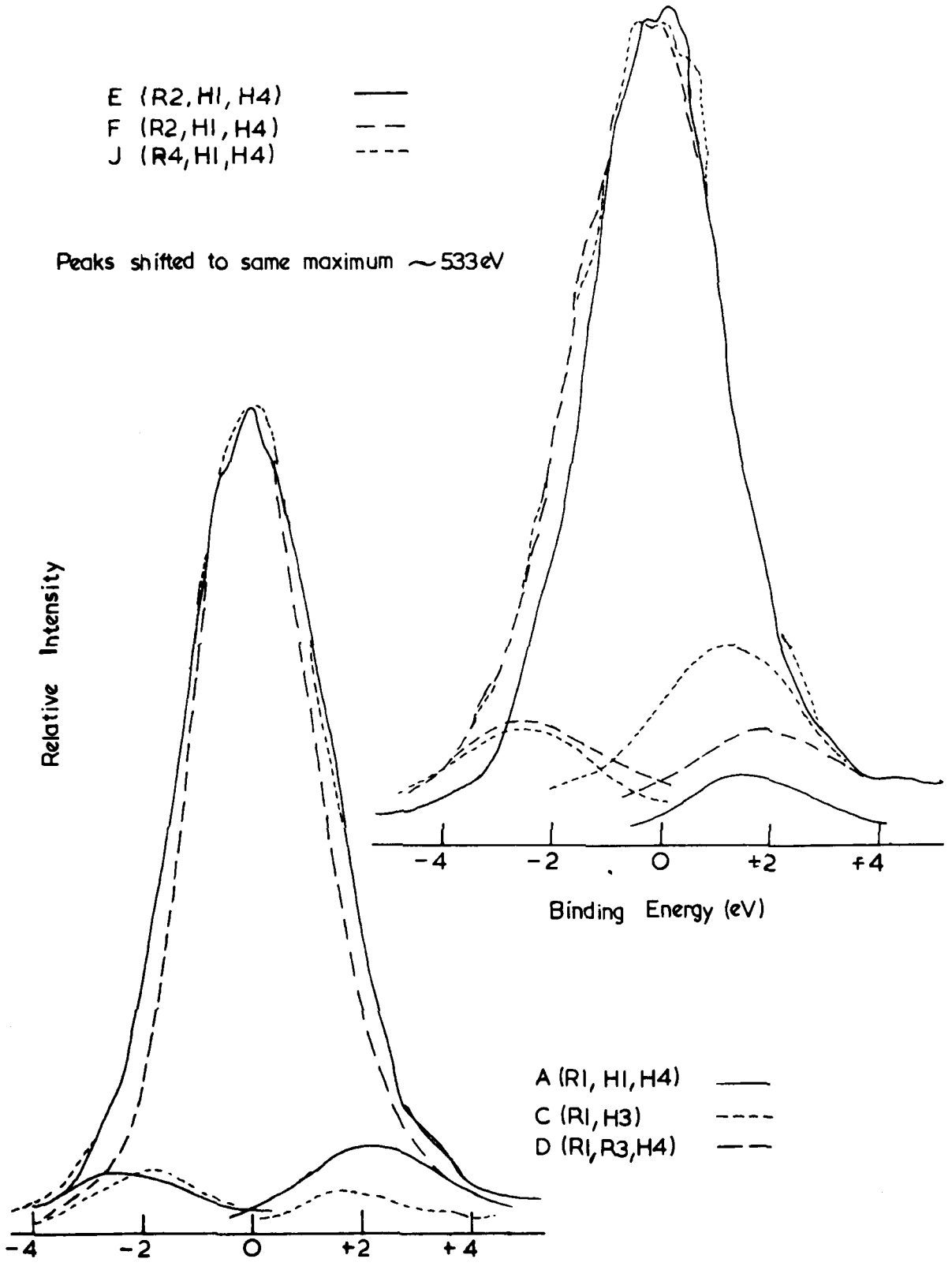


Fig 5 Oxygen 1s peaks for resins of different compositions

830136/7000/8-71/NM/1844

Fig 6

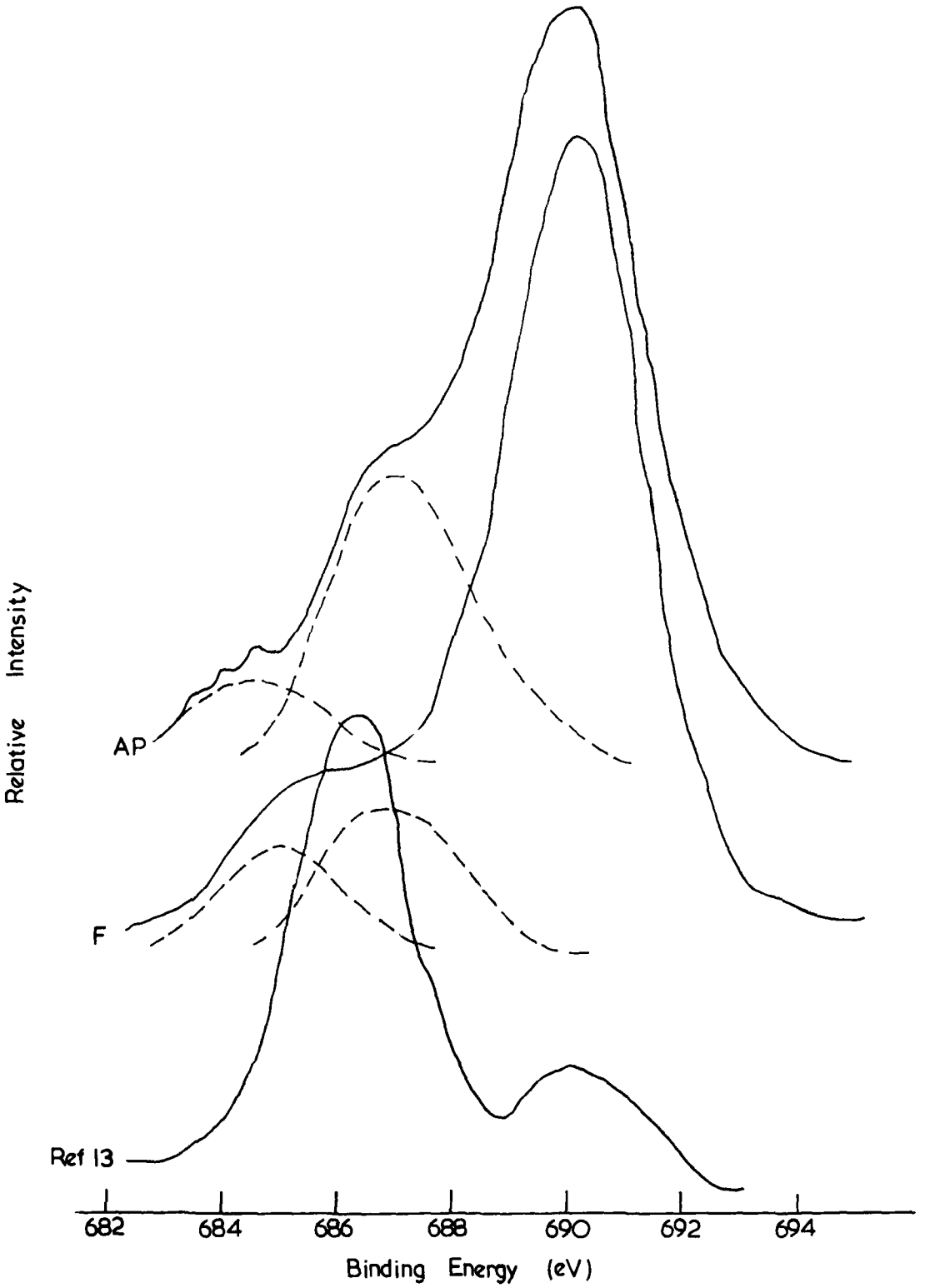


Fig 6 Fluorine 1s peaks at medium levels of contamination

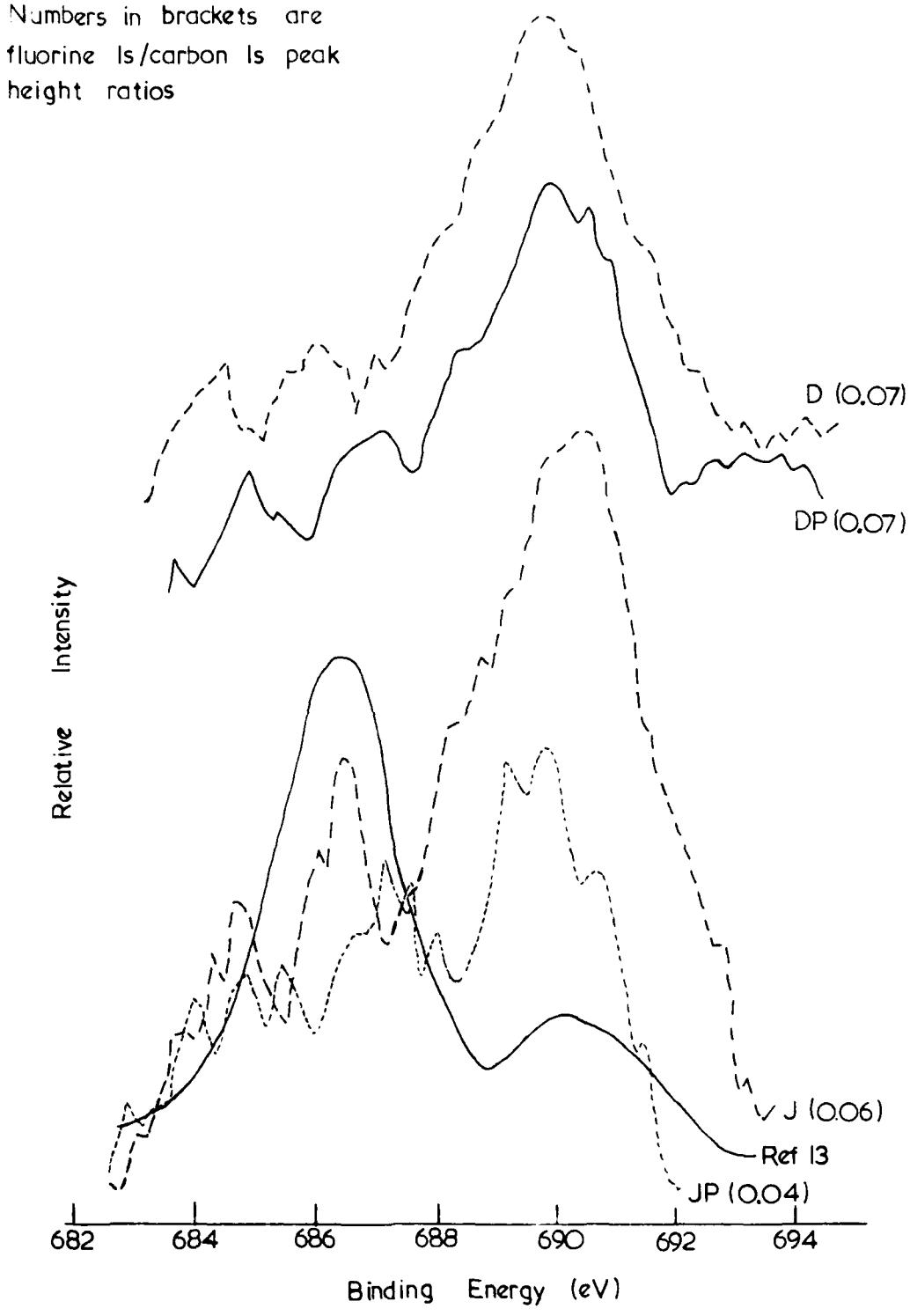


Fig 7 Fluorine 1s peaks at low fluorine levels

Fig 8

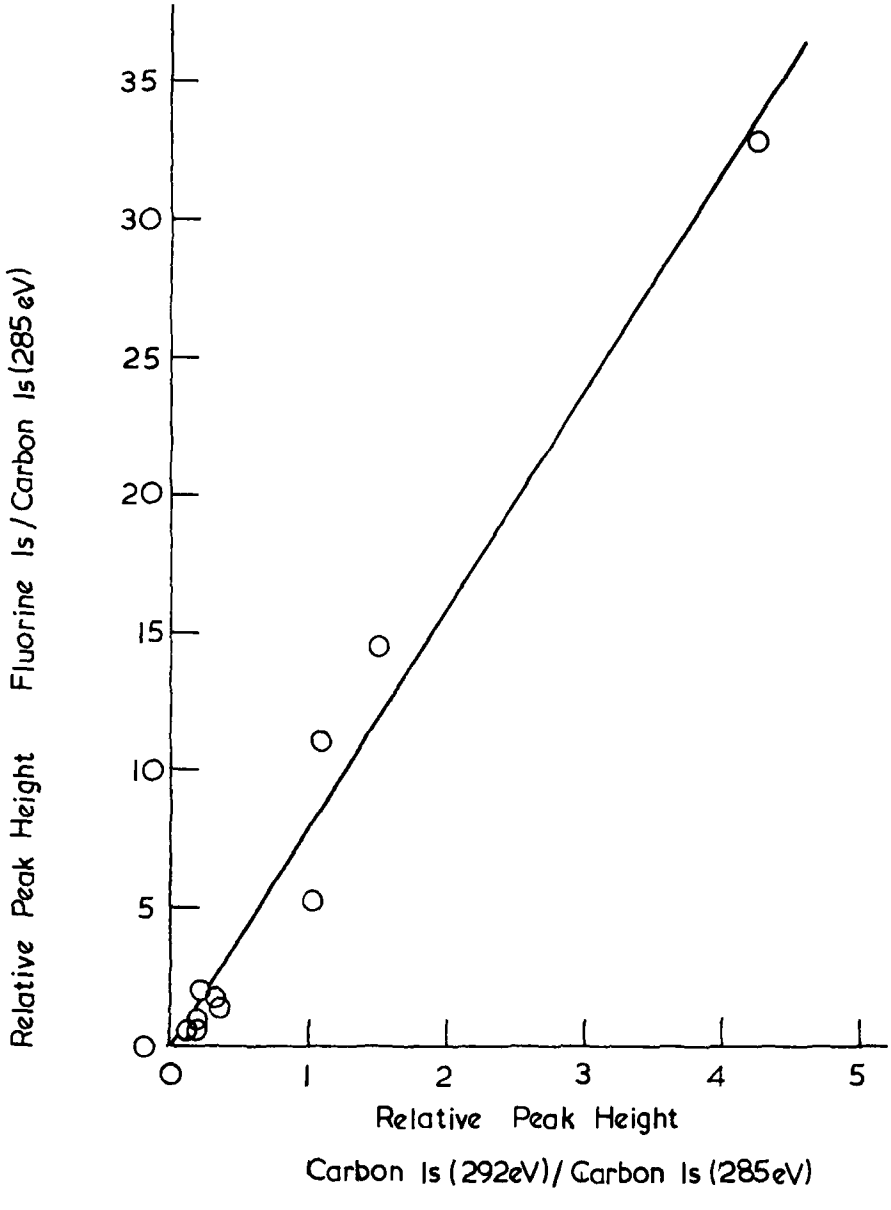


Fig 8 Calculation of fluorine 1s/carbon 1s intensity factor

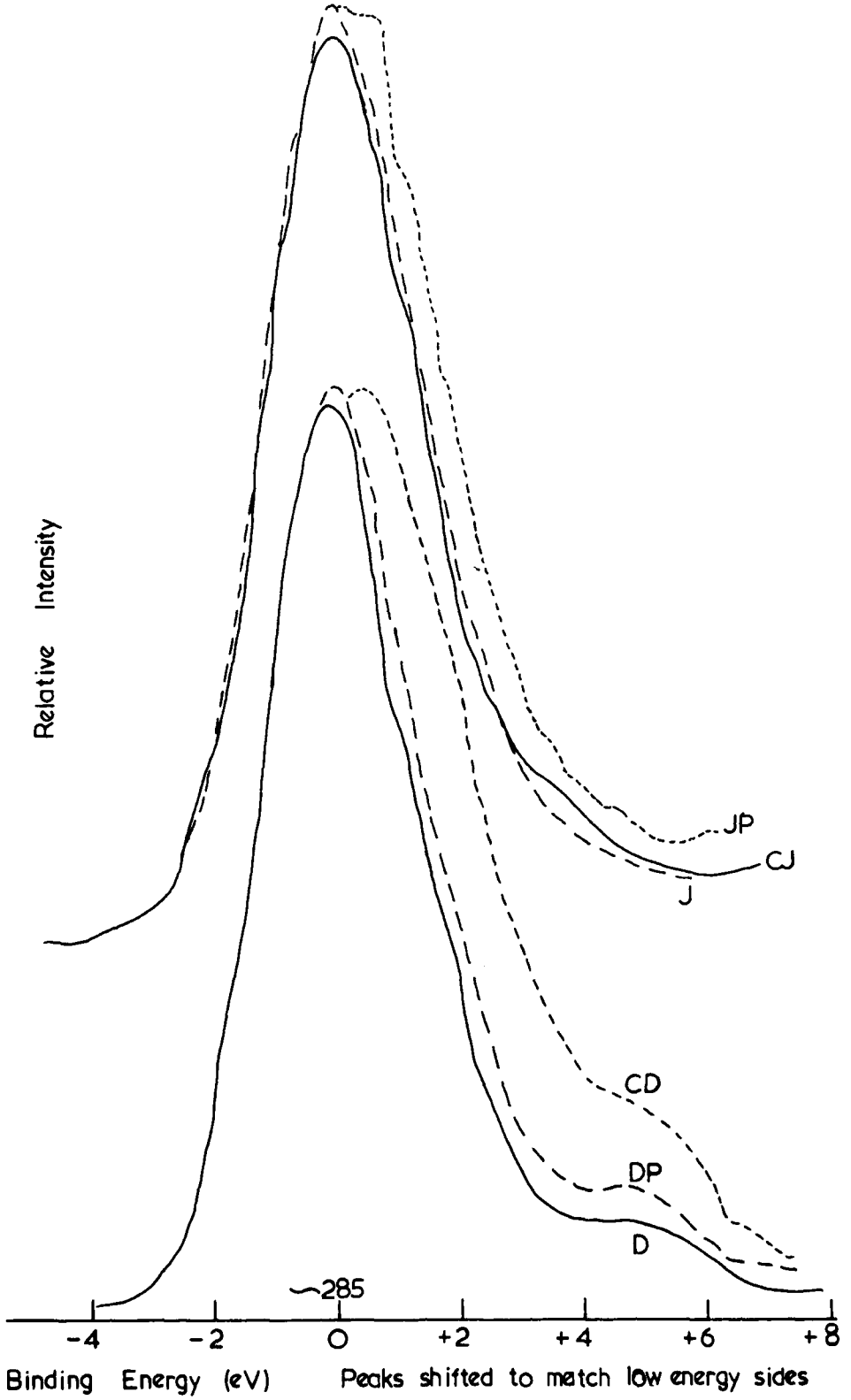


Fig 9 Comparison of carbon 1s peaks for composites and resins

Fig 10

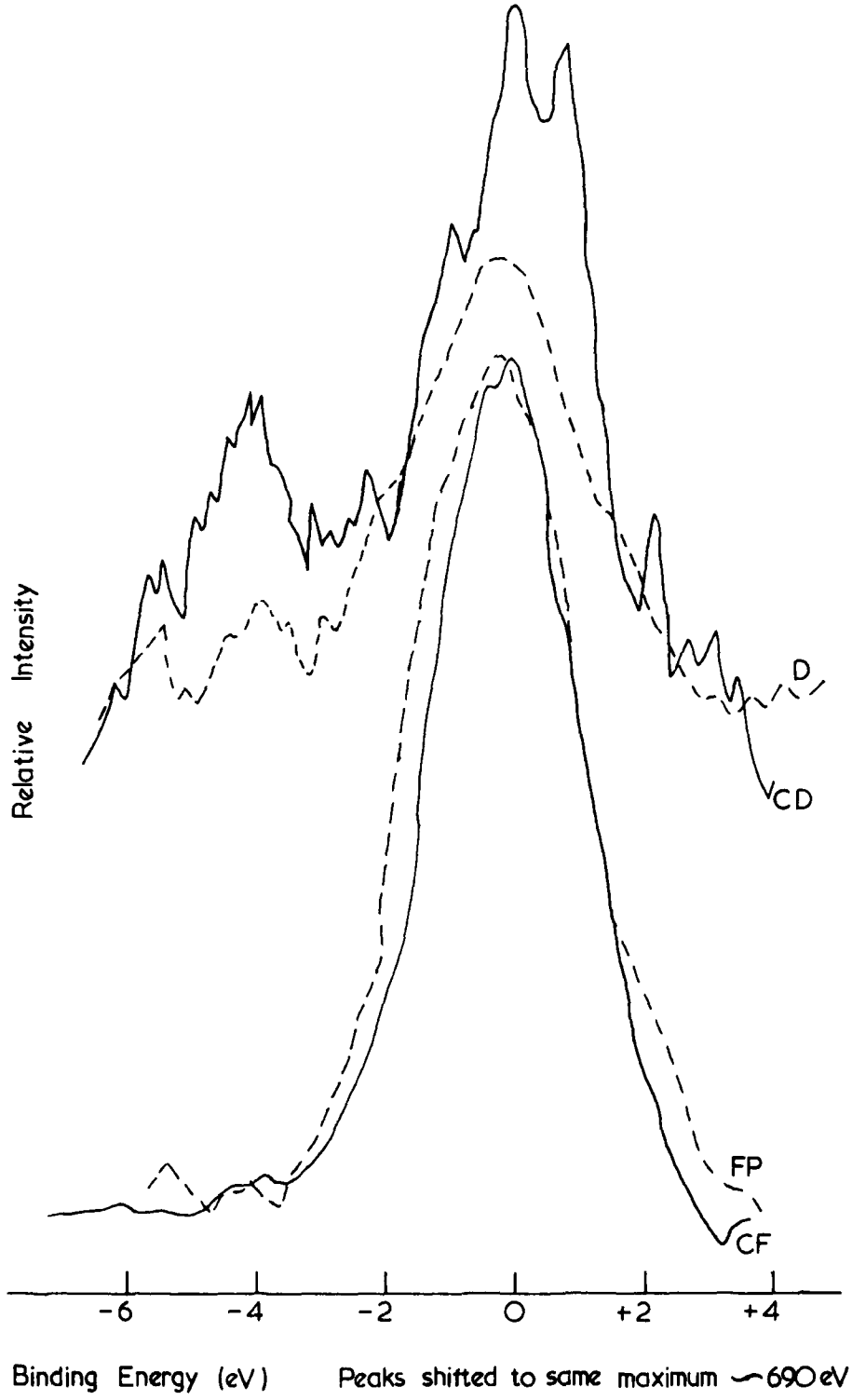


Fig 10 Comparison of fluorine 1s peaks for composites and resins

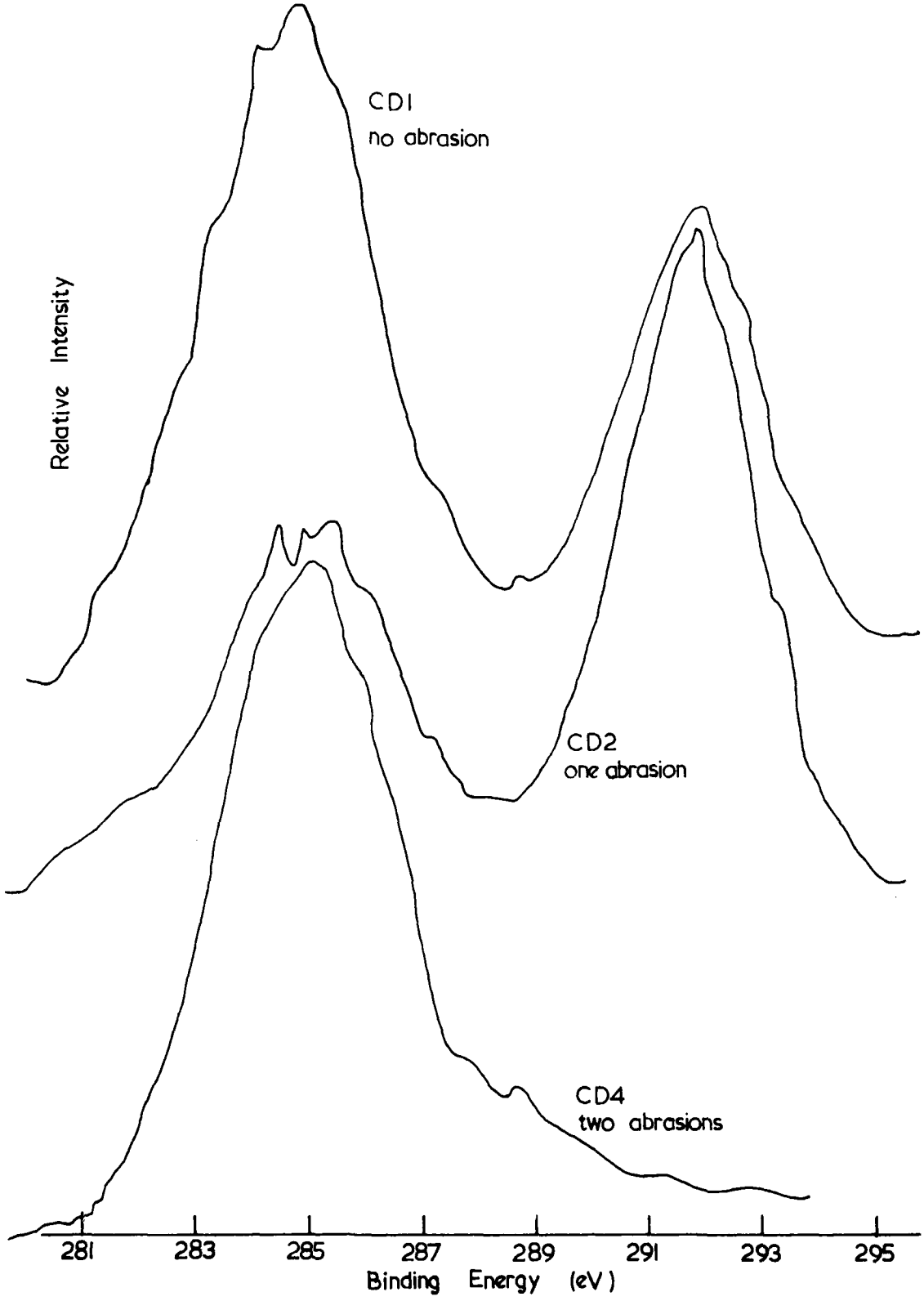


Fig 11 Effect of abrasion on composite carbon 1s peaks

Fig 12

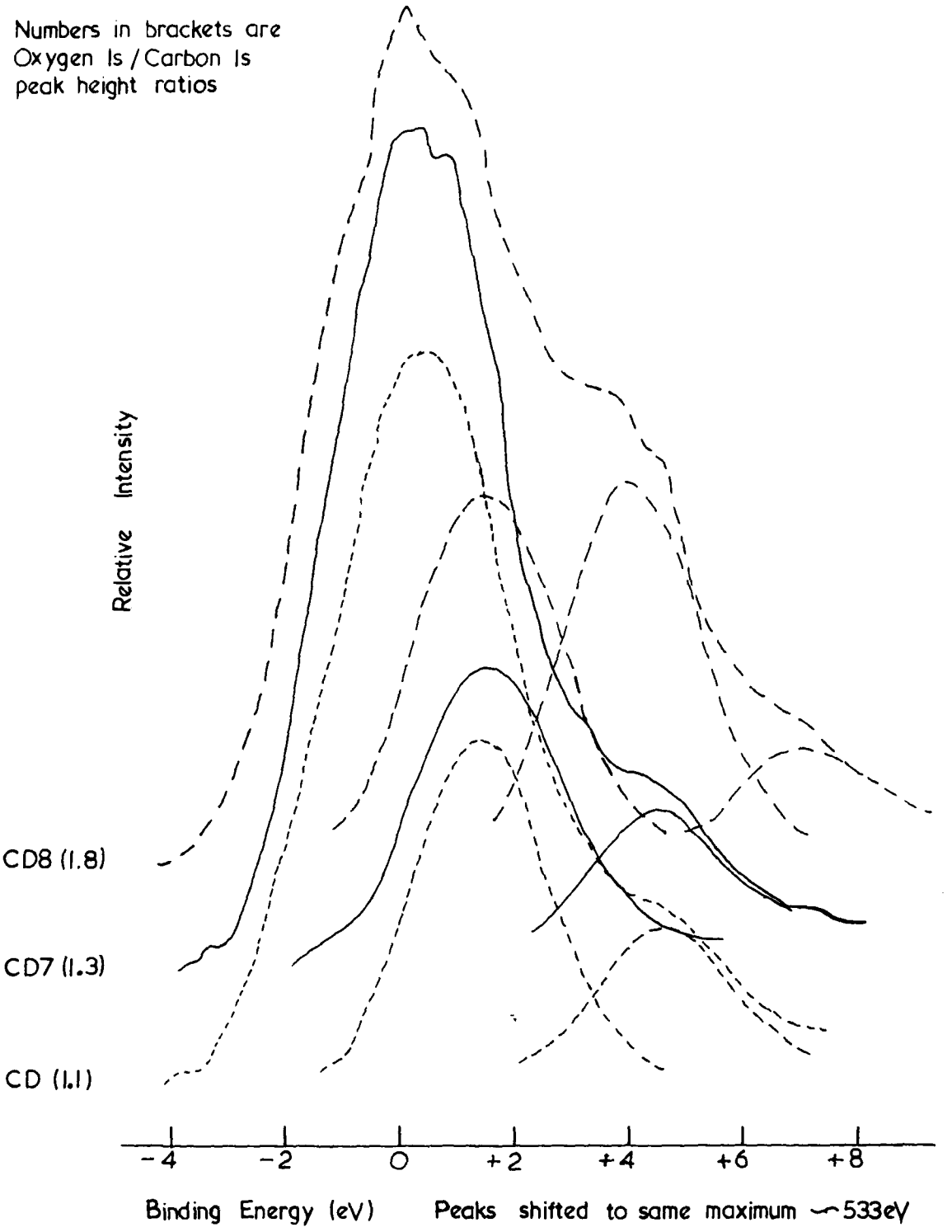


Fig 12 Effect of chemical treatment on oxygen 1s peaks

REPORT DOCUMENTATION PAGE

Overall security classification of this page

UNLIMITED

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17. Abstract

The surfaces of a range of cast thermosetting resins and carbon fibre composites have been investigated by electron spectroscopy for chemical analysis (ESCA). The peaks recorded were assymmetrical and could be resolved to give minor peaks which were related to the chemical groups present in the resins. In particular, peaks due to the $-CF_2-$ group were deconvoluted from the carbon 1s and fluorine 1s peaks and related quantitatively. These groups arose from contamination of the resin and composite surfaces by polymeric fluorinated hydrocarbon release agents. Surface contamination was reduced to a low level by abrasion. Oxidative chemical treatment of composite surfaces caused an increase in the amount of oxygen bonded to carbon.

FS910/1