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Structural changes of a pyrolytic graphite surface oxidized by electrochemical and plasma treatment

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Pyrolytic graphite (PG) surfaces have been oxidized by electrochemical and oxygen plasma treatment. The oxidized PG surfaces have been studied by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared attenuated total reflection spectroscopy (FT-IR–ATR). Oxidation caused by the plasma treatment results in a small increment of the oxygen:carbon (O/C) ratio, compared to electrochemical treatment. Moreover, the increment of the O/C ratio for the plasma treated edge surface is smaller than that for the plasma treated basal surface. A steep gradient in oxygen concentration exists within the edge subsurface of PG for samples subjected to severe electrochemical treatment, as compared to those samples subjected to plasma treatment. For the electrochemical treatment, carbonyl, carboxyl, ester and lactone groups are introduced to the edge surface following relatively severe treatment. The ratio of ester and lactone groups to carboxyl groups increases with the extent of electrochemical treatment. For plasma treated samples, other types of oxygen-containing groups, which are probably keto–enol groups, are added to the edge surface, unlike during electrochemical treatment.

1. Introduction

Studies using the basal and edge surfaces of pyrolytic graphite (PG) as a model for carbon fibre (CF) surfaces have been carried out with respect to the factors affecting interfacial adhesion in CF reinforced composite materials [1–4].

Surface treatment of the CF is essential in order to achieve desirable mechanical properties of the material, such as shear and impact strengths [5]. A variety of methods have been used for CF surface treatment [6–9]. Electrochemical and plasma methods have especially been studied by many investigators [10–11], who have investigated the surface chemistry of several types of CFs by mainly using X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA).

Takahagi and Ishitani [12] have shown, using Fourier transform infrared reflection absorption spectroscopy (FT-IR–RAS), that oxidized CFs have carboxyl groups directly combined to an aromatic ring. Sellitti *et al.* [13] have also proved that FT-IR attenuated total reflection spectroscopy (FT-IR–ATR) is a useful technique in characterizing surface functional groups in CFs. They detected the presence of carboxylic, ester, lactone, enol and quinone structural moieties, as well as a product due to nitration of the aromatic ring, on the oxidized CFs [13].

Recent work [4] has demonstrated, using XPS and laser Raman spectroscopy, that oxidation by oxygen plasma treatment is restricted to the vicinities of the basal and edge surfaces of PG. However, oxygen functional groups formed on the oxidized surfaces could not clearly be assigned using XPS [4].

In this paper FT-IR–ATR has been chosen as an investigating technique for analysis of the oxidized PG surface. The oxidation chemistry of PG surfaces treated by electrochemical and plasma methods is discussed on the basis of FT-IR–ATR spectra, together with XPS spectra.

2. Experimental procedure

The PG sample used in this study was supplied from Tomoe Engineering Company. Basal and mirror-polished edge surfaces of PG were prepared in the same manner as described previously [4]. Basal surfaces were perpendicular to the *c*-axes of graphitic crystallites, and edge surfaces were parallel to the *c*-axes. These surfaces were ultrasonically rinsed in acetone and distilled water, successively, and then dried at 100 °C for 20 min in an oven before surface treatment.

Since structural changes caused by electrochemical treatment were investigated in detail for both the basal and edge surfaces, using XPS and laser Raman spectroscopy [1–3], only the edge surface was electrochemically treated for comparison with plasma treated surfaces. Modification by plasma treatment was carried out for both the basal and edge surfaces. Electrochemical treatment, in 5 vol % ammonium bicarbonate solution, and oxygen radio-frequency

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plasma treatment were similar to those described previously [4].

The functional groups introduced to the basal and edge surfaces, and the O/C ratios of their surfaces, were examined by XPS. An ESCALAB MK II instrument (VG) with a monochromatized MgK_α X-ray anode, operating at a power of 300 W and 15 keV, was used for XPS measurement in a vacuum of about 13.33×10^{-8} Pa. Photoemitted electrons were measured at angles of 30 and 75° to the basal and edge surfaces of PG, respectively. Curve deconvolution with mixed Gaussian–Lorentzian functions for the oxygen 1s electron (O 1s) peak was carried out on data following background subtraction. Relative sensitivity factors determined with standard reagent, i.e. 9-anthracenecarboxylic acid, were used for estimation of atomic ratios (O/C ratios) from O 1s/C 1s peak area ratios. When the intensity of the carbon 1s peak was assumed to be unity, the relative sensitivity factor of O 1s was 2.19.

The functional groups present on the untreated and treated edge surfaces were also examined by FT-IR–ATR measurement. An FT-IR system 800 (Nicolet Japan) with a mercury cadmium telluride detector (MCT–A) was used to measure FT-IR–ATR spectra. Absorbance spectra were collected using FT-IR–ATR at a resolution of 4 cm^{-1} and signals of 1000 scans were collected. A Model 9 ATR attachment (Wilks Scientific) was used. A germanium internal reflection element, with dimensions of $50 \times 20 \times 2$ mm^3 and with an endface angle of 45°, was used. Nujol was used to increase the optical contact between the PG surfaces and the ATR element.

3. Results and discussion

3.1. XPS studies

Fig. 1 shows a plot of XPS O/C ratios obtained from the untreated and treated samples versus electron emitting angle measurements at angles of 30 and 75°, respectively. The O/C ratio in each sample can be characterized by the electron emitting angle. As can be seen from Fig. 1, the O/C ratios for all the samples increase with decreasing electron emitting angle. This confirms that more oxygen functionalities are present around the surface of rather than inside, each sample.

In the case of the untreated samples, the slope of the straight line for the edge surface in Fig. 1 is about twice that for the basal surface. This implies that the distribution of oxygen concentration versus sin θ is influenced by the graphitic surface structure, namely the direction of the c-axes of graphitic crystallites. A marked change in the slope did not arise during plasma treatment of the edge surface, unlike for the basal surface. A change in the O/C ratio for the edge surface caused by the plasma treatment is restricted to a small region at both photoelectron emitting angles, compared to other cases. On the other hand, electrochemical treatment of the edge surface results in a steep slope; the slope for the electrochemically treated edge surface is about three times that for the untreated edge surface. A steep gradient in oxygen concentration exists within the edge subsurface of PG for samples subjected to severe electrochemical treatment, compared with those subjected to treatment.

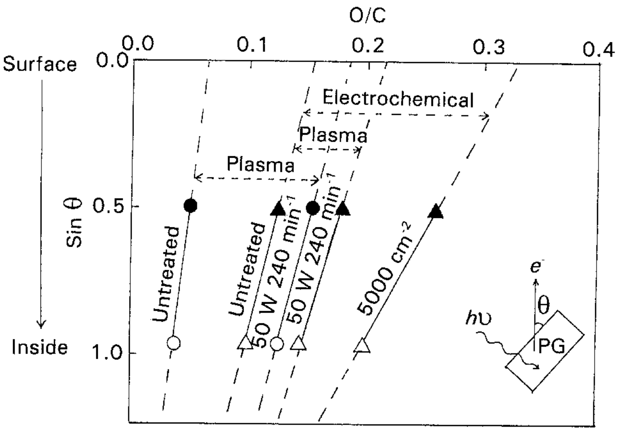

Figure 1 Variation of XPS O/C ratio with sinθ for surfaces having various R [4] determined by Raman spectra: (●, ○) basal, and (▲, △) edge surface.

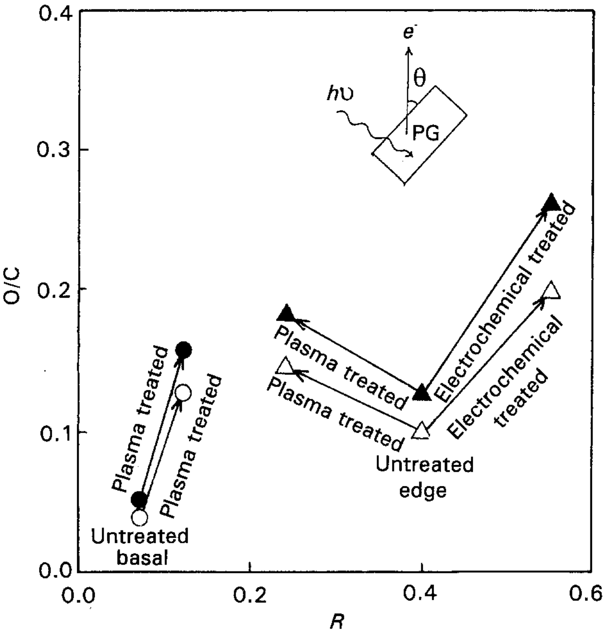

Figure 2 Change in O/C ratio as a function of R: For $\theta = 75°$; (○) basal surface, (△) edge surface, For $\theta = 30°$: (●) basal surface, and (▲) edge surface.

In Fig. 2, O/C ratios are plotted against the values of R, obtained by laser Raman spectroscopy, presented previously [4]. R indicates the degree of disorder in the graphitic surface structure [4]. The values of R for the carbon material are considered to be influenced by the change of graphitic structure in a region within a few tens of nanometers of the surface [14]. An increase in R in the surfaces of PG, implies an increase of active surface sites. Since oxygen atoms would be liable to bond to active surface sites, it is expected that the O/C ratio will increase with R. This is the case for the plasma treated basal and electrochemically treated edge surfaces. A decrease in R implies a decrease of active surface sites. In such a case, it is expected that the O/C ratio does not appreciably increase even after oxidation treatment since the amount of active surface site decreases. Actually,

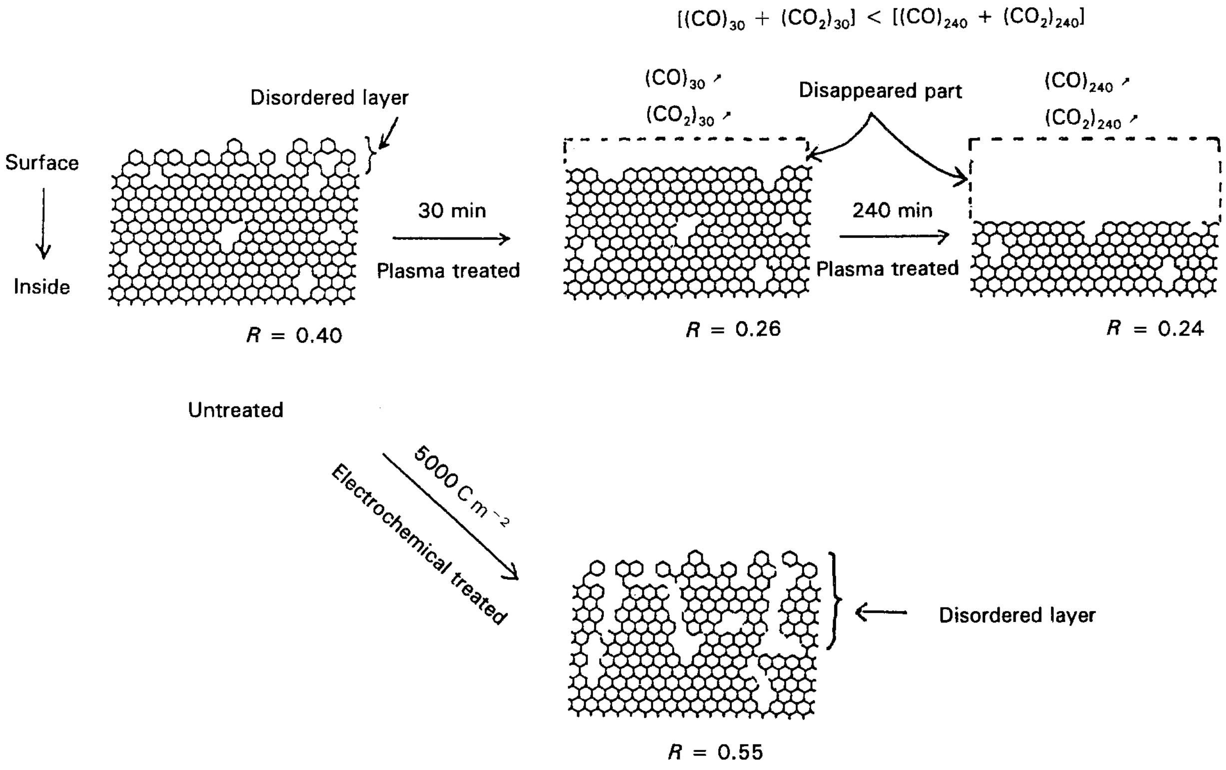

Figure 3 Schematic diagrams of edge surface structural changes caused by plasma [4] and electrochemical treatment.

the value of *R* for the plasma treated edge surface decreases compared with that for the untreated surface, and as a result the O/C ratio slightly increases according to expectation. That is, a change in the O/C ratio for the edge surface caused by plasma treatment is restricted to a small region, as compared to other cases. This indicates that the increment of the XPS O/C ratio, caused by oxidation treatment, is governed by variation of *R*.

Based on the evidence described above, schematic diagrams of the structural changes of the edge surface are shown in Fig. 3. Concerning the plasma treated basal surface, the schematic diagram has been reported previously [4]. As can be seen from Fig. 3, the number of possible active surface sites able to bond to oxygen atoms during electrochemical treatment, is more than that caused by plasma treatment. The concentration gradient of active sites is generated within the subsurface by an increase in *R*, and as a result the oxygen atom concentration gradient is considered to be generated. For the edge surface, *R* decreases after plasma treatment, and as a result active surface sites decrease. Therefore, the magnitude of change in the O/C ratio for the plasma treated samples will be smaller than that for the electrochemical treated samples. These facts may be applicable to surface modification of CFs.

As reported previously [4], by comparison of untreated and 240 min treated O ls peaks, carbonyl-type groups appear to dominate in the plasma treated basal and edge surfaces over –O– type groups. Further details of these O ls peaks have been studied for various plasma treatment time. XPS O ls spectra for the plasma treated samples are shown in Fig. 4. The spectra can be fitted to four peaks. Peak 1 (~ 531.5 eV) and peak 2 (~ 532.5 eV) correspond to $>C=O$ type groups and –O– type groups, respectively [15]. Peak 3 (~ 534 eV) and peak 4 (~ 535.5 eV) are probably due to chemisorbed oxygen [15]. Table I summarizes the binding energy (BE) and area percentage derived from curve deconvolution of the O ls spectra of samples, which represent the changes caused by various plasma treatment time.

Peak 1 cannot be detected for the untreated basal surface. The relative area of peak 1 increases with treatment time for the basal surface. At 240 min treatment, the area percentage of peak 1 is apparently larger than that of peak 2. Plasma treatment for the basal surface is found to cause an increase in $>C=O$ type groups. Moreover, plasma treatment causes structural disorder of the basal surface [4]. Therefore, this disorder is responsible for the increase in $>C=O$ type groups.

On the other hand, in the case of the untreated edge surface, the area percentage of peak 2 is much larger than that of peak 1. The area percentage of peak 1 is almost comparable to that of peak 2 in the 10–240 min range, unlike in the case of the basal surface. This indicates that $>C=O$ and –O– type groups are added to the edge surface in equal probability, and the proportion of $>C=O$ to –O– type groups is held almost constant in the 10–240 min range; in which no defects are introduced to the edge surface by oxygen plasma treatment [4].

3.2. FT-IR–ATR studies

The ATR spectrum of the untreated edge surface is shown in Fig. 5. The presence of peaks around 1460 and 1380 cm^{-1} is due to Nujol. Two main peaks occur at about 1740 and 1650 cm^{-1}; the intensity of peak around 1650 cm^{-1} is stronger than that at 1740 cm^{-1}. The peak around 1740 cm^{-1} is assigned to the $C=O$

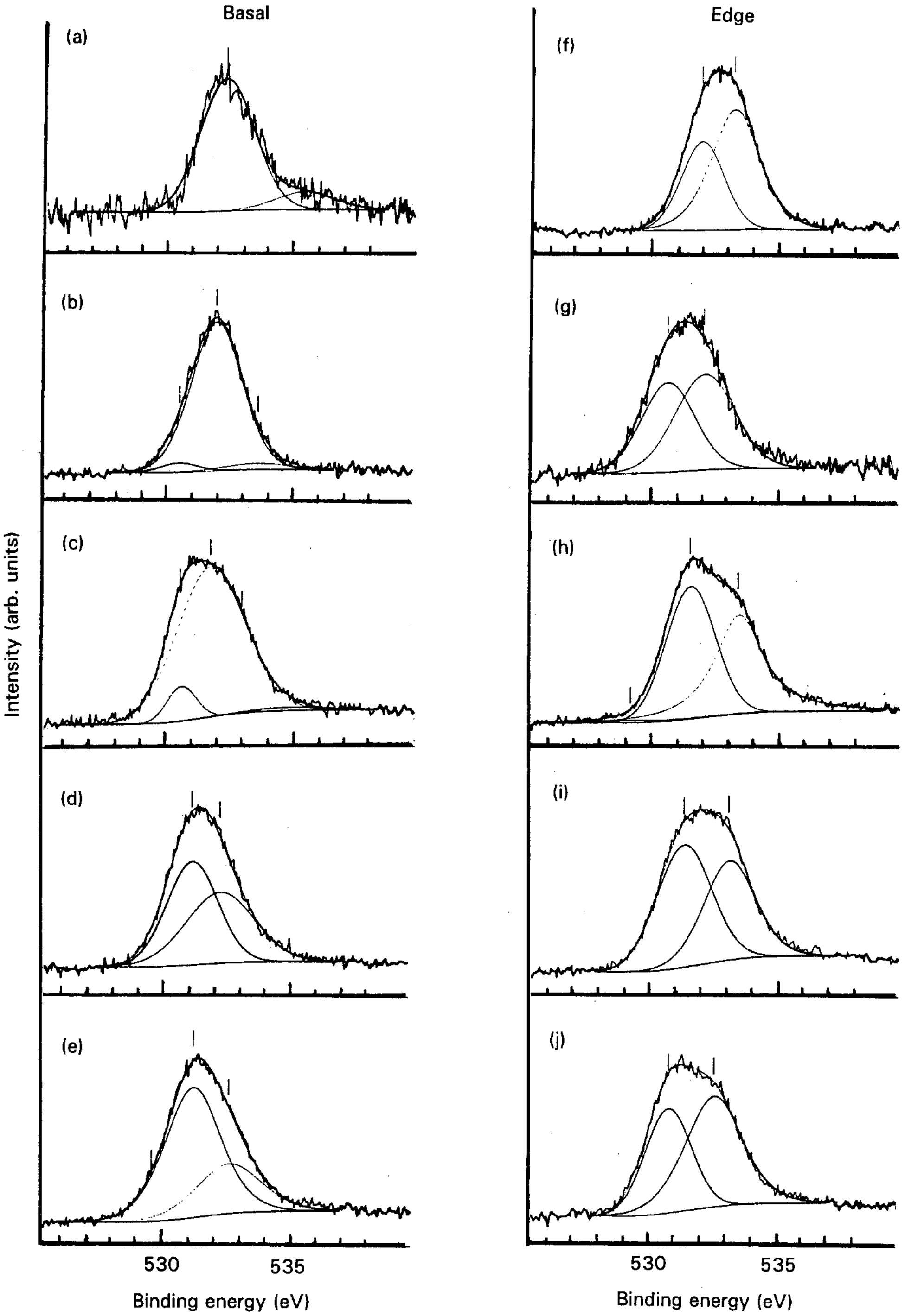

Figure 4 Curve fitted oxygen ls spectra (electron emitting angle, 75°) of plasma treated basal and edge surfaces. Basal surfaces: (a) untreated, (b) 10 min, (c) 60 min, (d) 120 min, (e) 240 min. Edge surfaces: (f) untreated, (g) 10 min, (h) 30 min, (i) 120 min, (j) 240 min.

stretching mode of ester and/or lactone groups [13]. Taking into account data on oxygen-containing groups reported previously [3], the possibility that ester and lactone groups are present on the untreated edge surface cannot be derived. However, the peak around 1650 cm^{-1} cannot be assigned to any groups, e.g. hydroxyl, ether, carbonyl, carboxyl and ester, as well as lactone groups. Sellitti *et al.* [13] have shown that the peak arising at 1640 cm^{-1} is due to enol groups. The peak around 1650 cm^{-1} can be interpreted as keto–enol tautomerism as shown in Fig. 5.

Fig. 6 shows the spectra of edge surfaces electrochemically oxidized for different treatment levels. These spectra are obtained from subtraction of the spectrum of the untreated edge surface. As can be seen from these ATR spectra differences, after electrochemical treatment two main peaks occur at about 1740 and 1580 cm^{-1}. Since the absorption peak of Nujol is absent in the region of $\sim$ 1500–1800 cm^{-1}, the intensity of the two main peaks is due to electrochemical treatment. Referring to the reports by Sellitti *et al.* [13], the peak around 1580 cm^{-1} can be assigned to $C=C$ stretching of the aromatic ring conjugated with a carbonyl group. Electrochemical treatment leads to the addition of ester, lactone and carbonyl groups to the edge surface.

A band assigned to carboxyl groups is clearly recognized around 1710 cm^{-1} in both specimens treated at

TABLE I O 1s peaks and relative peak areas for the basal and edge surfaces of PG with oxygen plasma (input power: 50 W)

Sample		O 1s peaks for various chemical types of oxygen							
Basal or edge	Treatment time (min)	Peak 1		Peak 2		Peak 3		Peak 4	
		BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)
Basal	0	–	0	532.6	87	–	0	535.6	13
Basal	10	531.0	4	532.4	91	534.1	5	–	0
Basal	60	531.0	9	532.2	89	–	0	535.2	2
Basal	120	531.7	52	532.8	48	–	0	–	0
Basal	240	531.6	69	533.0	31	–	0	–	0
Edge	0	531.8	38	533.0	62	–	0	–	0
Edge	10	531.6	46	533.0	54	–	0	–	0
Edge	30	531.3	54	533.2	46	–	0	–	0
Edge	120	531.4	56	533.2	44	–	0	–	0
Edge	240	531.1	42	532.8	58	–	0	–	0

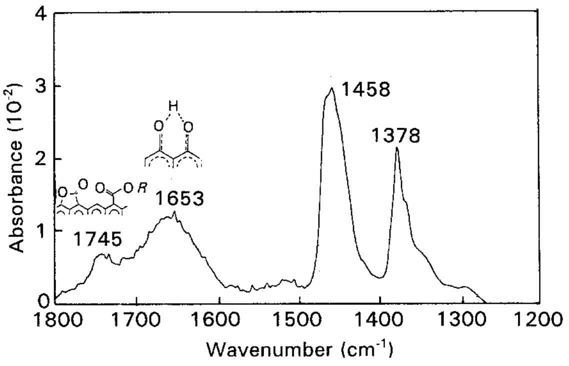

Figure 5 ATR spectrum of the untreated edge surface.

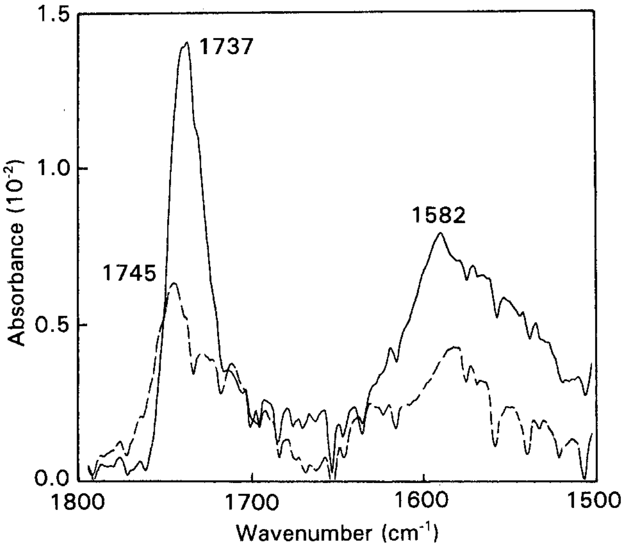

Figure 6 ATR difference spectra of the edge surface treated electrochemically: (- - -) at 5000 C m^{-2}, and (——) at 50 000 C m^{-2}.

5000 and 50 000 C m^{-2} as shown in Fig. 7. Deconvolution of the peak curve at ~1740 cm^{-1} has been attempted in order to obtain details. The peak was deconvoluted into two bands, arising from carboxyl and from ester and lactone groups according to Sellitti *et al.* [13]. The ratio of the area of the 1710 cm^{-1} band (carboxyl group) to that of 1740 cm^{-1} total peak (carboxyl, ester and lactone groups) is represented by

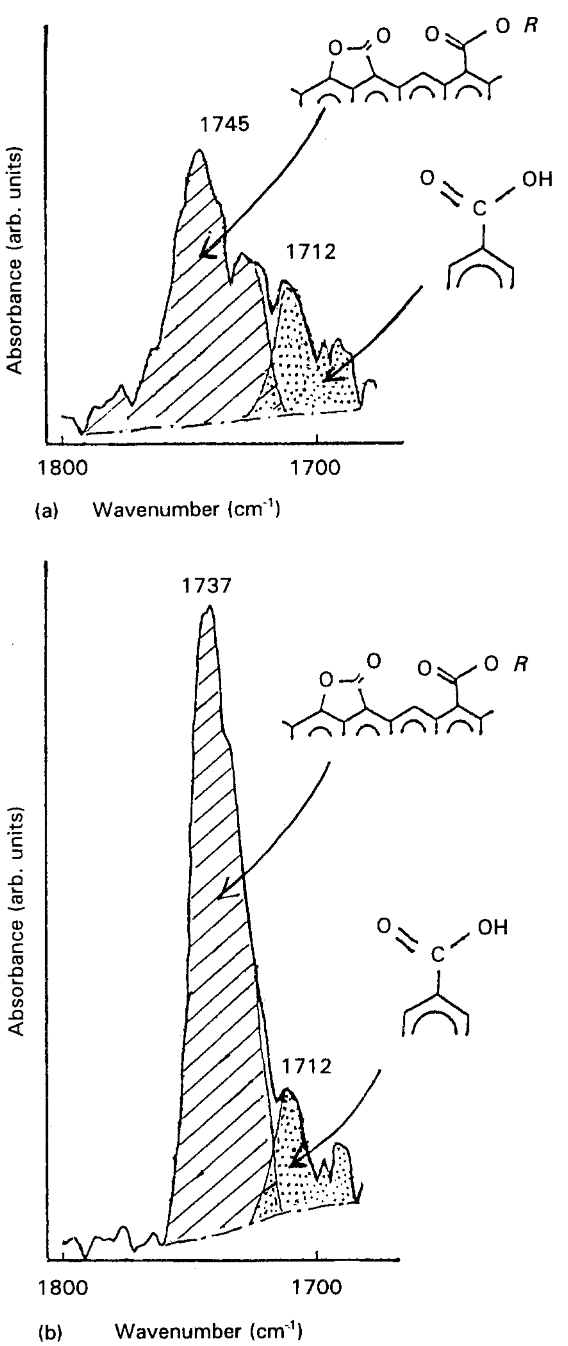

Figure 7 ATR 1740 cm^{-1} peak: (a) at 5000 C m^{-2}, and (b) at 50 000 C m^{-2}.

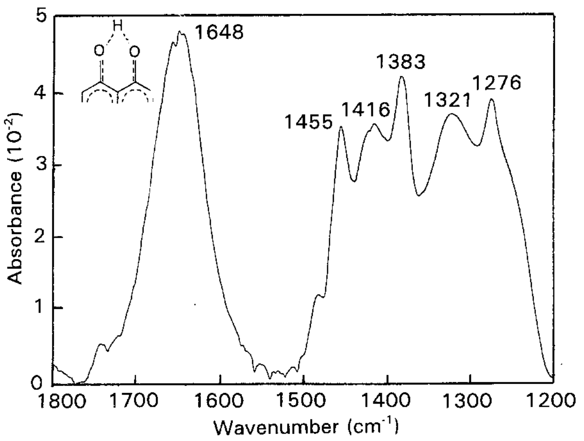

Figure 8 ATR difference spectra of the plasma treated edge surface.

the symbol CR. CR varies from 0.25 for 5000 C m^{-2} to 0.14 for 50 000 C m^{-2}. Thus, the amount of ester and lactone groups increases relative to the amount of carboxyl group with an increase in treatment level. This is of practical importance, i.e. only the carboxyl group among these groups can react with epoxy resins and diamine curing agents used in CF reinforced epoxy composites [16–17]. In addition, an increase in other groups, excluding carboxyl, may inhibit the reaction of carboxyl groups with epoxy resins and diamine curing agents. Taking into account these matters and the results on CR, 50 000 C m^{-2} treatment may be not appreciably effective for the reactions compared with 5000 C m^{-2} treatment, in terms of interfacial chemical bonding in the composites.

The difference in the ATR spectrum of the 240 min plasma treated edge surface is shown in Fig. 8. The presence of peaks around 1455 and 1383 cm^{-1} seems to be due to Nujol. Unlike electrochemical treated samples, distinct peaks around 1740 and 1580 cm^{-1} are not observed, only a main peak at ~ 1650 cm^{-1} being recognized in the range 1500–1800 cm^{-1}. The peak around 1650 cm^{-1} is probably due to keto–enol groups, as described previously. Oxygen plasma treatment would mainly cause the addition of keto–enol groups, as oxygen-containing groups, to the edge surface. Further, three peaks are observed at 1276, 1321 and 1416 cm^{-1}, respectively. Assignment of these three peaks is obscure at the moment. Anyway, ATR spectra have proved to give clear information concerning addition of oxygen-containing groups to the edge surface by plasma treatment, compared with XPS C 1s and O 1s spectra. It is emphasized that FT-IR–ATR has excellent sensitivity for the surface chemistry of well-graphitized carbon materials.

The peak around 1650 cm^{-1} is not observed for the electrochemical treated samples, in which the graphitic surface structure is disordered [4]. On the other hand, in the case of plasma treatment, the graphitic structure of the surface edge becomes more ordered [4]. Moreover, the presence of oxygen-containing groups is restricted to the vicinity of the surface on the basis of XPS data [4]. The oxygen-containing groups are keto–enol groups, on the basis of ATR data. Thus, keto–enol groups are assumed to be added to the graphitic edge surface. Sellitti *et al.* [18] have indicated, by using optical theory, that in the graphitic structure, stacking carbon layers in parallel enhances the infrared bands of the functional layer groups. Enhancement of the spectra results in the detection of small amounts of functional groups restricted to the vicinity of the edge surface.

Furthermore, taking into account the relationship between keto–enol groups and the disorder of the graphitic surface structure mentioned above, electrochemical treatment in an alkaline solution, in which destruction of the graphite surface structure does not occur even at a high treatment level of 5000 C m^{-2} [2], can be expected to add keto–enol groups to the edge surface. It has been demonstrated, by evaluating the XPS C 1s chemical shift, that keto–enol groups are introduced to electrochemically treated CF surfaces [19–20]. However, in the case of the plasma treated PG edge surface, an XPS C 1s spectral change showing the addition of keto–enol groups was not observed, as described previously [4]. It seems that observation of XPS spectral changes caused by the addition of keto–enol groups is difficult for well-graphitized carbon material surfaces such as PG surfaces.

4. Conclusions

Structural changes caused by plasma and electrochemical treatment have been investigated using XPS and FT-IR–ATR.

For the edge surface, the variation of the XPS O/C ratio caused by plasma treatment is very small, compared with that caused by electrochemical treatment. Following plasma treatment, the edge surface is less altered in terms of the XPS O/C ratio, compared with the basal surface. From XPS, a steep concentration gradient is found for oxygen within the edge subsurface of PG for samples subjected to severe electrochemical treatment, unlike the plasma treated samples.

For the plasma treated edge surface, a main peak in the FT-IR–ATR difference spectrum is observed at about 1650 cm^{-1}, which is probably due to keto–enol groups. On the other hand, two main peaks following severe electrochemical treatment, in which the graphitic surface structure is significantly disordered, occur at about 1740 and 1580 cm^{-1} for the edge surface. Electrochemical treatment introduces carboxyl, ester, lactone and carbonyl groups to the edge surface. The band at 1710 cm^{-1} (carboxyl group) is resolved from the 1740 cm^{-1} peak. The ratio of ester and lactone groups to carboxyl groups increases with the electrochemical treatment level.

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