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FT–IR ATR spectroscopy of the edge surface of pyrolytic graphite and its surface/PVC interface

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The edge surface of pyrolytic graphite (PG) has been oxidized by electrochemical and oxygen plasma treatments. The structure of the oxidized edge surfaces of PG and the interaction between the oxidized surface and poly(vinyl chloride) (PVC) have been studied by means of Fourier transform – infrared attenuated total reflection (FT–IR ATR) spectroscopy. Phenolic hydroxyl groups and functional groups with a carbonyl group are present on the untreated and all oxidized edge surfaces. For all the surfaces, some of the phenolic hydroxyl groups are linked by hydrogen bonds to each other or functional groups with a carbonyl group, part of the carboxyl groups also being linked by hydrogen bonds to each other. Lactone, carboxyl, and quinone structure moieties are formed on the edge surface by the electrochemical treatment. Among the moieties, quinones are mainly introduced to the edge surface by the severe electrochemical treatment. Quinones are not present on the untreated and the plasma-treated edge surfaces. FT–IR ATR spectra provide evidence for the existence of hydrogen bonds between the $> C = O$ groups present on the edge surface and PVC.

1. Introduction

Carbon fibre (CF)-reinforced composites have been used in aerospace and sporting goods industries. Most of the materials being used as the matrix of the composites are thermosetting resins such as epoxy resin. Thermoplastic resin is also used for improving composite toughness. A variety of methods for CF surface modification have been studied in order to achieve desirable mechanical properties of the composites. The mechanical properties of the composites can be controlled by tailoring the structure of the CF surface and the interface between the CF and the matrix. Tailoring by electrochemical and oxygen plasma treatments is particularly effective for the improvement of the mechanical properties [1–4].

In order to tailor CF surface structure and the interfacial structure of the composites, it is necessary to clarify the relationship between the degree of disorder of the graphitic surface structure, the type and concentration of chemical species located at the surface, and the manner and extent of the surface treatments. Studies using the basal and edge surfaces of pyrolytic graphite (PG) as a model of a CF surface make possible a comprehensive understanding of the effect of surface treatments on CF surface structure and the interfacial structure of the composites [5–9].

Because the structure of the edge surface would be essential for the achievement of strong interfacial adhesion for the epoxy resin matrix [7], it is necessary to obtain more detailed information on the edge surface structure. For a thermoplastic resin with no reactive groups, non-covalent bonding will be dominant in the interface between the resin and the CF surface. However, no detailed study has been reported on the bonding and the structure of the interface.

In this work, the edge surface of PG has been used as a model of a CF surface, and poly(vinyl chloride) (PVC) as thermoplastic resin. We have utilized Fourier transform – infrared attenuated total reflection (FT–IR ATR) spectroscopy to characterize the chemical structure of the edge surface and the interface between the edge surface and PVC.

2. Experimental procedure

The PG used in this study was supplied by Tomoe Engineering Company. Edge surfaces of PG, which are parallel to the *c*-axes of graphitic crystallites, were cut to dimensions of approximately 25 mm × 2.5 mm and then polished according to the method given by Katagiri *et al.* [10]. The surfaces were ultrasonically rinsed in acetone and distilled water successively, and then dried at 100° C for 20 min in an oven before surface treatments.

Electrochemical treatment in 5% ammonium bicarbonate aqueous solution and oxygen radio-frequency plasma treatment were carried out as described in our previous paper [8].

To facilitate the characterization of the interfacial structure, PVC with no oxygen-containing functional

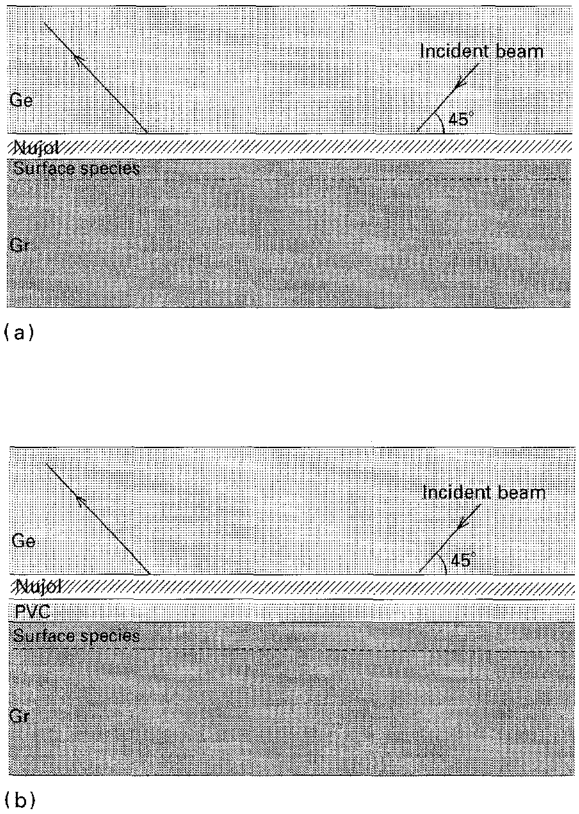

Figure 1 Schematic diagram of the FT–IR ATR assembly.

groups was used as thermoplastic resin. The degree of polymerization of PVC used in this study was 430 ± 30. A solution of PVC in tetrahydrofuran (THF), 0.1% by weight, was prepared. PVC coating on the oxidized edge surface was performed by soaking the edge surface in the solution for about 1 s. Then the specimen was dried at 100° C for 20 min in the oven. The X-ray photoelectron spectroscopy (XPS) wide-scan spectrum of the PVC-coated sample showed C 1 s, O 1 s, and C 12 p peaks. The thickness of the PVC coating layer was estimated to be of the order of nanometres, judging from the XPS data. Moreover, a chemically shifted signal due to carboxyl or ester groups on the oxidized edge surface [8] was observed at about 4 eV from the main carbon–carbon signal in the C 1 s peak. The existence of a thin PVC layer on the oxidized edge surface was confirmed by these XPS data.

FT–IR ATR spectroscopy was used for characterization of the edge surfaces treated or coated as mentioned above. The measurement of FT–IR ATR spectra was carried out in the same manner as described in our previous paper [9]. FT–IR ATR configuration utilized in the characterization of the structure of the edge surface and PVC in this study can be approximated as the four-layer system of Ge/Nujol/surface species/Graphite(Gr) and the five-layer system of Ge/Nujol/PVC/surface species/Gr (Fig. 1). The "surface species" layer means an oxidized layer having oxygen-containing functional groups near the edge surface, the "Gr" layer is an unoxidized bulk inside the oxidized surface layer.

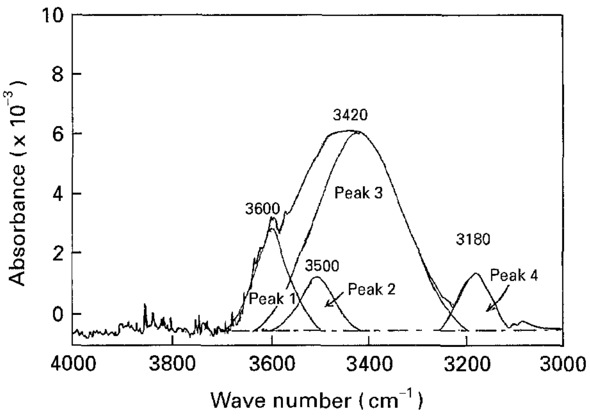

Figure 2 FT–IR ATR spectrum in the region 4000–3000 cm^{-1} for the untreated edge surface.

3. Results and discussion

3.1. FT–IR ATR spectra of the edge surface of PG

3.1.1. FT–IR ATR spectra in the region 4000–3000 cm^{-1}

The FT–IR ATR spectrum of the untreated edge surface in the region 4000–3000 cm^{-1} is shown in Fig. 2. A broad and asymmetric absorption band is observed in the region 4000–3000 cm^{-1}. The band can be deconvoluted into four peaks suggesting four types of O–H stretching vibration mode; that is, Peak 1 ($\sim$3600 cm^{-1}), Peak 2 ($\sim$3500 cm^{-1}), Peak 3 ($\sim$3400 cm^{-1}), and Peak 4 ($\sim$3200 cm^{-1}), respectively. The deconvoluted peaks are associated with the stretching mode of free OH of alcohols or phenols (Peak 1), the stretching mode of free OH of carboxyl groups (Peak 2), the stretching mode of hydrogen-bonded OH between hydroxyl groups (Peak 3), and the stretching mode of "strong" hydrogen-bonded OH between a hydroxyl group and a carbonyl group (Peak 4), respectively [11].

These peaks can be regarded as being mainly due to the OH of phenols rather than that of alcohols. The untreated and treated edge surfaces investigated in this paper would be primarily composed of sp^2-bonded edge carbon atoms taking account of the data of laser Raman spectroscopy [8]. It seems, therefore, that a hydroxyl group is covalently bonded to the sp^2-bonded edge carbon atom.

In addition, a band at 3045 cm^{-1} due to the stretching vibrations of aromatic hydrocarbons [11] was not observed for any of the samples. This fact suggests that no hydrogen atoms are covalently bonded to the sp^2 carbon atoms of surface aromatic rings.

Because a change in sample surface morphology would affect the change of the value of absorbance, the value itself cannot be used for comparison purposes. We can discuss the area percentage of each peak. The area percentage of each peak for the untreated and treated edge surfaces are given in Table I. For the untreated surface, peak 4 is observed at about 3180 cm^{-1} in isolation. Functional groups with a carbonyl group present on the edge surface are assumed to be linked by hydrogen bonds to phenolic hydroxyl groups or carboxyl groups. Taking into account the

TABLE I Area percentage of each peak in the region 4000–3000 cm^{-1}

Treatment	Area (%)			
	Peak 1[a]	Peak 2[b]	Peak 3[c]	Peak 4[d]
Untreated	15	7	71	7
Electrochemical, 5000 $C m^{-2}$	4	7	58	31
Electrochemical, 50 000 $C m^{-2}$	6	7	56	31
Plasma, 50 W/240 min	5	5	65	24

[a] Free OH of phenols.
[b] Free OH of carboxyl groups.
[c] Hydrogen-bonded OH between hydroxyl groups.
[d] "Strong" hydrogen-bonded OH between a hydroxyl group and a carbonyl group.

large percentage of peak 3, phenolic hydroxyl groups are found to be present close to each other even in the untreated surface. The area percentage of peak 1 in the untreated surface is greater than for the other treated surfaces, indicating that more isolated phenolic hydroxyl groups are present on the untreated surface in comparison with the other treated surfaces.

The area percentage of peak 1 is reduced by the electrochemical treatment. This suggests that phenolic hydroxyl groups and/or functional groups with a carbonyl group are introduced in the vicinity of isolated phenolic hydroxyl groups by the treatment. Moreover, the area percentage of peak 4 is significantly increased by both the electrochemical and plasma treatments, indicating that functional groups with carbonyl groups linked by hydrogen bonds to phenolic hydroxyl groups have increased by their treatments. Part of phenolic hydroxyl groups would be present close to functional groups with a carbonyl group for the oxidized edge surfaces.

3.1.2. FT-IR ATR spectra in the region 1800–1100 cm^{-1}

The FT-IR ATR spectrum for the untreated edge surface in the wave number region 1800–1100 cm^{-1} is shown in Fig. 3a. The presence of peaks around 1460 and 1380 cm^{-1} is due to Nujol.

For only the untreated surface, the inversion of the absorbance appears to occur at about 1200 cm^{-1} (Fig. 3a). According to ATR spectral simulations by Sellitti *et al.* [12], the inversion phenomenon occurs with decreasing thickness of the oxidized layer. The inversion seems to be due to the presence of the thin oxidized layer of the untreated surface; the thickness of the oxidized layer for the untreated surface would be 5 nm or below and the thickness of the oxidized layer for the oxidized surfaces would be more than 5 nm [6].

In Fig. 4, the FT–IR ATR difference spectrum of the 5000 $C m^{-2}$ treated surface has been magnified over the region 1800–1500 cm^{-1}. We have already reported an assignment of each peak in the region 1800–1500 cm^{-1} [9]. A large absorption band at 1737 cm^{-1} for the 50 000 $C m^{-2}$ treatment seems to be overlapped by two peaks at 1737 and 1716 cm^{-1} as shown in Fig. 4. The two peaks would be assigned to lactone groups and isolated carboxyl groups, respectively [9]. The peaks occurring in the region about 1704–1680 cm^{-1} are probably due to the $C=O$ stretching vibration of hydrogen-bonded carboxyl groups [11]. In the following paragraphs we regard a peak in the region about 1720–1680 cm^{-1} as due to the $C=O$ stretching vibrations of carboxyl groups.

In the case of the electrochemical treatment, a broad and asymmetric absorption band is observed in the region about 1640–1500 cm^{-1} as shown in Fig. 4. The band is not present for the untreated and the plasma-treated surfaces. A strong absorption band and a weak band can be recognized at about 1580 cm^{-1} and in the region about 1610 cm^{-1}, respectively. According to the literature [11], when a substituent, $C=O$, is directly conjugated to aromatic rings, a doublet is observed at 1625–1575 cm^{-1}. In addition, the substituent resulting in conjugation increases the intensity of the doublet [11]. We have shown, using XPS, that carbonyl groups are introduced to the edge surface after the electrochemical treatment [8]. The carbon–carbon stretching vibrations of aromatic rings conjugated with carbonyl groups would contribute to the appearance of the bands. Therefore, peak 8 shown in Fig. 4 can be assigned to aromatic rings conjugated with carbonyl groups, that is, quinones.

A broad absorption band is recognized in the region about 1550–1500 cm^{-1} for the electrochemical treatment (Fig. 4). According to the literature [11], naphthalenes have bands in the regions 1620–1580 and 1550–1505 cm^{-1} due to carbon–carbon stretching vibrations, anthracenes absorbing near 1630 and 1550 cm^{-1}. Thus the broad bands seen in Fig. 4 would be due to the aromatic carbon–carbon stretching vibrations such as naphthalene- and anthracene-like structures, which are probably linked by covalent bonds and/or hydrogen bonds to the edge surface. The formation of the structures is possible through the electrochemical treatment process, which has been found to destroy the graphitic structure of the edge surface at the treatment level of 5000–50 000 $C m^{-2}$ [8]. It may be concluded that the bands in the region about 1550–1500 cm^{-1} are due to the aromatic $C=C$ stretching vibrations such as naphthalene- and anthracene-like structures.

No quinones are recognized on the untreated edge surface. Quinones are formed by the electrochemical treatment and are not formed by the oxygen plasma treatment. The electrochemical treatment increases the disorder of surface graphitic structure, the oxygen

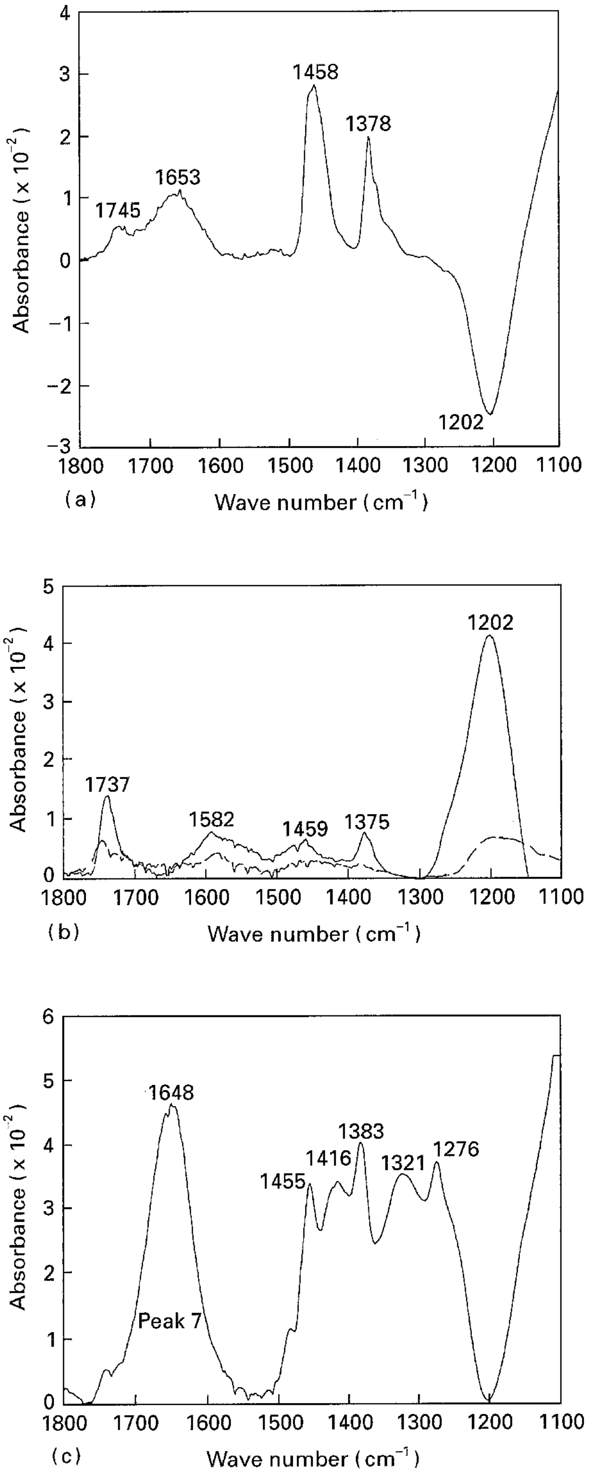

Figure 3 (a) FT–IR ATR spectrum and (b, c) FT–IR ATR difference spectra in the region 1800–1100 cm^{-1}; (a) untreated, (b) electrochemically treated at (---) 5000 C cm^{-2} and (—) 50 000 C cm^{-2}, and (c) plasma treated at 50 W/240 min.

plasma treatment minimizing it [8]. Therefore, the disorder of the surface graphitic structure would result in the increase of quinones on the edge surface.

The difference between the plasma treatment and the electrochemical treatment can be clarified by the comparison of the ratio of oxygen-containing functional groups newly introduced. The ratio can be represented by the area percentage of each peak (peaks 5–8) in the difference spectra (Fig. 4) as shown in Table II. The ratio can be regarded as characterizing the chemical structural change of the edge surface.

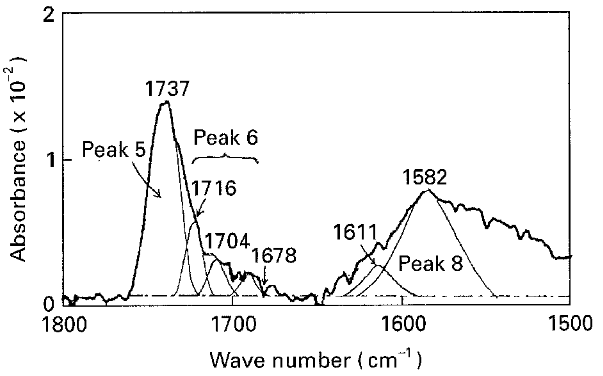

Figure 4 FT–IR ATR difference spectrum in the region 1800–1500 cm^{-1} for the 50 000 C m^{-2} treated edge surface.

By using the area percentage, we can approximately estimate the ratio of surface functional groups effective for interfacial adhesion in composite materials. For example, functional groups effective for an epoxy resin matrix are phenolic hydroxyl, carboxyl, and enol groups [1, 7, 13–16]. As can be seen from Table II, many useless functional groups are found to be introduced to the edge surface for the electrochemical treatment; at this point, the plasma treatment may be superior to the electrochemical treatment for the epoxy resin matrix. As such, the area percentage obtained from FT–IR ATR spectra may be applicable to the characterization of the carbon surface and the estimation of interfacial adhesion in carbon-reinforced materials.

A broad absorption band in the region about 1300–1100 cm^{-1} is observed for the electrochemical treatment (Fig. 3b). For esters G–CO·OG′, where G and G′ are aromatic groups, the band due to the C–O–C asymmetric stretching vibration occurs at 1310–1250 cm^{-1} and that due to the C–O–C symmetric stretching vibration at 1150–1080 cm^{-1} [11]. The broad band in the region about 1300–1100 cm^{-1} is considered to be overlapping of their bands and is possibly due to the lactone C–O–C stretching vibrations. The assignment is consistent with the assumption that lactone groups are present on the electrochemically treated surfaces, as described above.

Absorption bands at 1455, 1416, 1383, 1321 and 1276 cm^{-1} are observed for the plasma treatment (Fig. 3c). Because enol groups are introduced for the plasma treatment [9], the strong absorption bands at 1455 and 1416 cm^{-1} could be correlated to the carbon–carbon stretching vibrations of aromatic rings with enol groups. The bands at 1383, 1321 and 1276 cm^{-1} are possibly due to the C–O stretching and in-plane O–H deformation vibrations of phenols [11].

The basic structures of the untreated and treated edge surfaces are summarized in Fig. 5. For the untreated edge surface, lactone, carboxyl, phenolic hydroxyl, and enol groups are present; part of the phenolic hydroxyl groups are linked by hydrogen bonds to each other and functional groups with carbonyl groups, part of the carboxyl groups also being linked by hydrogen bonds to each other. The hydrogen bonds would be present on the all treated edge surfaces. Following the electrochemical treatment,

TABLE II Area percentage of each peak in the region 1800–1500 cm^{-1}

Treatment	Area (%)			
	Peak 5[a]	Peak 6[b]	Peak 7[c]	Peak 8[d]
Untreated	18	5	77	0
Electrochemical, 5000 C m^{-2}	48	28	0	24
Electrochemical, 50 000 C m^{-2}	37	13	4	46
Plasma, 50 W/240 min	2	7	91	0

[a] Lactone groups.
[b] Carboxyl groups.
[c] Enol groups.
[d] Quinones.

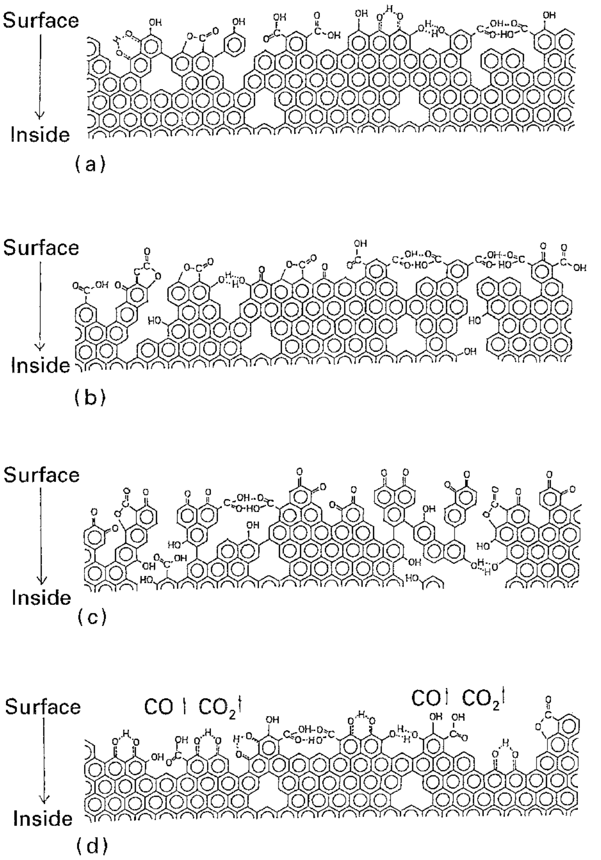

Figure 5 Basic structure of edge surfaces; (a) untreated, (b) electrochemically treated at 5000 C m^{-2}, (c) electrochemically treated at 50 000 C m^{-2}, and (d) plasma treated at 50 W/240 min.

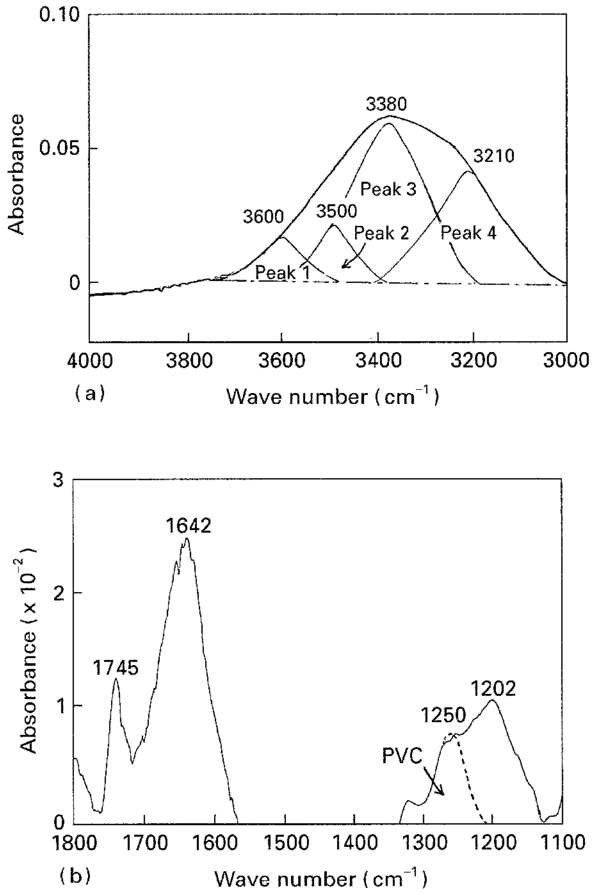

Figure 6 FT–IR ATR spectrum of 50 000 C m^{-2} treated edge surface/PVC in the regions (a) 4000–3000 cm^{-1} and (b) 1800–1100 cm^{-1}.

lactone, carboxyl and quinone structure moieties are further formed on the disordered edge surface. Among the entities, quinones are mainly introduced to the edge surface by the severe electrochemical treatment. Therefore, quinones would be present on the outermost edge surface for the severe electrochemical treatment. On the other hand, for the plasma treatment, enol groups are mainly introduced to the edge surface as described in the previous paper [9].

3.2. Edge surface/PVC interface

The FT–IR ATR spectrum of the 50 000 C m^{-2} treated edge surface coated with PVC is shown in Fig. 6. The area percentage of each peak (Peaks 1–4) is shown in Table III, compared with the case for 50 000 C m^{-2} treatment.

Absorption bands due to PVC are absent in the region 4000–3000 cm^{-1}. Little change in the area percentage of each peak as shown in Table III is seen

TABLE III Change in area percentage of each peak in the region 4000–3000 cm^{-1} by PVC coating

Sample	Area (%)			
	Peak 1	Peak 2	Peak 3	Peak 4
50 000 C m^{-2}	6	7	56	31
50 000 C m^{-2}/PVC	8	9	51	32

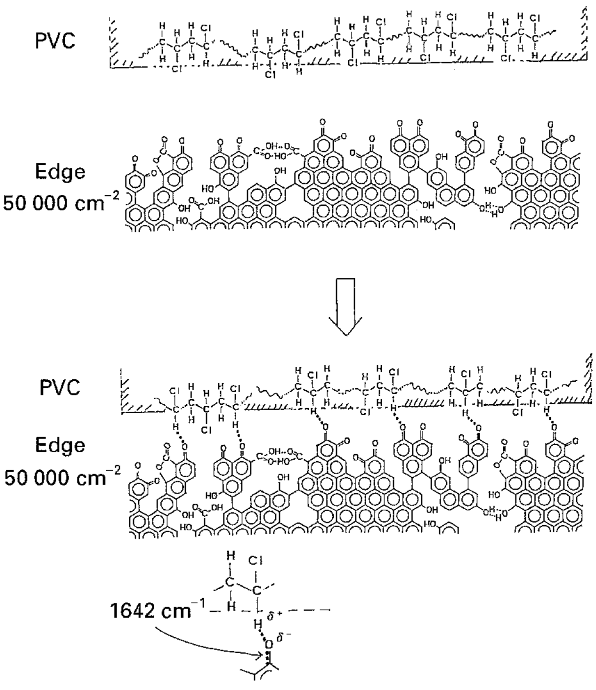

Figure 7 Interaction between the oxidized edge surface and PVC.

when PVC is coated on the edge surface, suggesting that the interaction by hydrogen bonds scarcely occurs between PVC and –OH on the oxidized surface. Functional groups with –OH such as carboxyl groups and phenolic hydroxyl groups, would be present inside the oxidized edge surface in comparison with lactone groups and quinones (Fig. 5). Therefore, the functional groups with –OH are considered to be little affected by the polar structure, H–C–Cl, of PVC.

Absorption bands at 1745 and 1202 cm^{-1} characteristic of the edge surface treated at 50 000 C m^{-2} are observed (Fig. 6b). An absorption at about 1250 cm^{-1} would be due to PVC. The characteristics of both layers of treated edge surface and PVC have been detected. Because a significant absorption band at 1642 cm^{-1} is due to neither the edge surface nor PVC, its band can be assigned to an interaction between the edge surface and PVC. In addition, the appearance of the 1642 cm^{-1} band is unlikely to be due to THF, which could remain in the thin PVC layer, and the interaction between THF, PVC, and the oxidized layer of the edge surface. For the 50 000 C m^{-2} treated edge surface, quinones are mainly present on the outermost surface (Fig. 5). The 1642 cm^{-1} band would occur when carbonyl groups on the edge surface are linked by hydrogen bonds to C–H groups of PVC, and can be assigned to carbon–oxygen stretching vibrations, as shown in Fig. 7.

As such, FT–IR ATR spectra provide evidence for the existence of the interaction between the treated edge surface and PVC. It is proposed that hydrogen bonding is present in the interfacial region between the oxidized edge surface and PVC.

4. Conclusions

Phenolic hydroxyl groups and functional groups with a carbonyl group are present on the untreated, the electrochemically treated, and the oxygen-plasma treated edge surfaces; some phenolic hydroxyl groups are linked by hydrogen bonds to each other or functional groups with a carbonyl group, some carboxyl groups being also linked by hydrogen bonds to each other. Lactone, carboxyl and quinone structural entities are introduced to the edge surface for the electrochemical treatment. Among the entities, quinones are mainly introduced by the severe treatment. Hydrogen bonding between $> C = O$ groups on the edge surface and PVC is present in the edge surface/PVC interface.

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