

# Modification of oxidized graphite edge surface with poly(vinyl chloride)

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An oxidized edge surface of pyrolytic graphite (PG) has been prepared by electrochemical treatment. A thin layer of poly(vinyl chloride) (PVC) was coated on the oxidized edge surface, and the PVC-coated sample heat treated at 300, 400, and 500 °C, respectively. The influence of the PVC coating on the structural change of the oxidized edge surface of PG caused by the heat treatment was studied by laser Raman and Fourier transform-infrared attenuated total reflection spectroscopies. For the electrochemical treatment, the formation of oxygen-containing functional groups proceeds over the edge surface of PG. With increasing degree of oxidation, the functional groups are formed in the following order; hydroxyl groups, carboxyl groups, lactone groups, quinones, and acid anhydrides. Acid anhydrides are formed on the outermost surface and completely eliminated by heat treatment up to 300 °C. The other functional groups remain even after heat treatment up to 500 °C. However, the functional groups are eliminated by the PVC coating, the elimination temperature depending on the type of functional groups: quinones, lactone groups, and carboxyl groups are eliminated at 300, 400, and 500 °C, respectively. PVC coated on the edge surface is found to play an important role in the complete elimination of oxygen-containing functional groups with  $>C=O$  through heat treatment at 500 °C.

## 1. Introduction

Carbon fibre-reinforced carbon (C/C) composite has been developed for high-temperature resistant and light structural material and has potential for application to space vehicles. In application, an appropriate protection system against high-temperature oxidation is required for the C/C composite. Silicone carbide (SiC) coating is well known as a modification technique for the composite surface [1, 2]. However, the structural non-uniformity of the composite surface disturbs the uniform coating of the SiC film.

Ueda *et al.* [3] found a novel protection system: an additional carbon layer, which bonds tightly to the surface of the C/C composite, is introduced to the composite system. They demonstrated that a strong bonding between the carbon layer introduced and the composite can be obtained by thermal decomposition of poly(vinyl chloride) (PVC) as an interlayer material between the carbon layer and the composite. However, the strong bonding mechanism of the carbon layer over the composite surface is unknown.

In order to clarify the phenomena occurring in the interface, the oxidized edge surface of pyrolytic graphite (PG) is used as the composite model surface. In

this work, the effect of PVC coating on the composite model surface was investigated by spectroscopic analyses.

## 2. Experimental procedure

Mirror-polished edge surfaces of PG (Tomoe Engineering) [4], which are parallel to the *c*-axes of graphitic crystallites, were prepared for use as a model of active surfaces of C/C composites. The surfaces were ultrasonically rinsed in acetone and distilled water, successively, and then dried at 100 °C for 20 min in an oven.

In order to introduce oxygen-containing functional groups to the edge surface, electrochemical treatment was carried out with 0.1 M ammonium hydrogen carbonate solution; the specific electric charge (electric charge, C, per unit area  $m^2$ ) was  $4 \times 10^5 C m^{-2}$ . After surface treatment, the surfaces were rinsed in distilled water and dried at 100 °C for 20 min in the oven.

The electrochemically treated edge surfaces were coated with PVC by the following procedure. The surfaces were soaked in a tetrahydrofuran (THF) solution containing 2.5% PVC by weight for 30 min. After

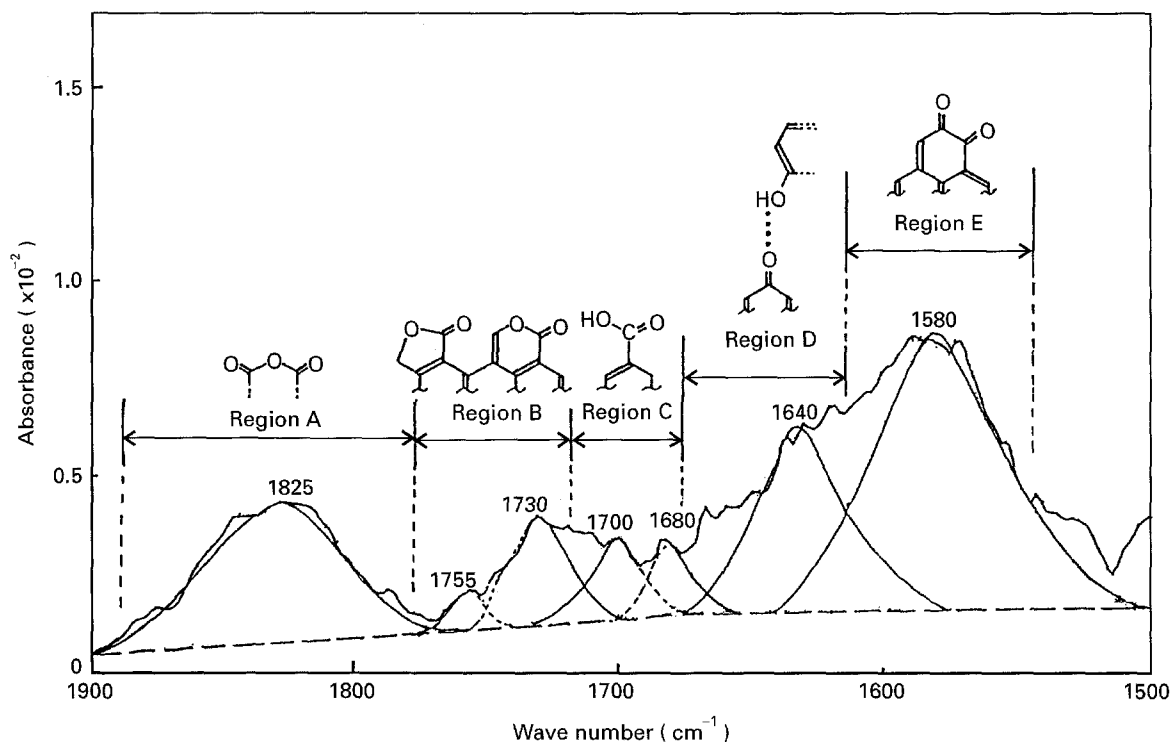


Figure 1 ATR spectrum of an edge surface electrochemically treated at  $4 \times 10^5 \text{ C m}^{-2}$ .

soaking, the surfaces were again dried at  $100^\circ\text{C}$  for 20 min in the oven.

PVC-coated and uncoated samples were heat treated under an argon gas stream at the following temperatures; 300, 400, and  $500^\circ\text{C}$ . After attainment of the given temperatures, the samples were allowed to cool immediately.

The samples thus prepared were analysed by using Fourier transform infrared-attenuated total reflection (FTIR-ATR) technique [5] with respect to surface functional groups and interfacial interaction between the thin layer of PVC and the edge surface of PG. An FT-IR system 800 (Nicolet Japan) with a model-9 ATR attachment (Wilks Scientific) was used to measure FTIR-ATR spectra. The resolution of absorption spectra was  $4 \text{ cm}^{-1}$ , signals of 200 scans being collected. The change of graphitic structure of the edge surfaces after heat treatment was estimated by laser Raman spectroscopy. Raman spectra of the surfaces were measured by using the RAMALOG-10 system (SPEX). The  $514.5 \text{ nm}$  of an argon-ion laser (200 mW) was used to induce the Raman spectra. The details of the measurements are described elsewhere [4].

### 3. Results and discussion

Fig. 1 shows the ATR spectrum of an edge surface electrochemically treated at  $4 \times 10^5 \text{ C m}^{-2}$ . Absorption of oxygen-containing functional groups is clearly marked in the range  $1900\text{--}1500 \text{ cm}^{-1}$ . The range can be divided into five regions, A-E, as shown in Fig. 1. Absorption bands in Regions B, C, and E can be assigned to the C=O stretching vibrations of lactone and carboxyl groups, and C=C stretching vibrations of aromatic rings conjugated with a carbonyl group, respectively [6]. We have already reported that the

main absorption bands appear in Regions B, C, and E for the specimens electrochemically treated over the range  $5000\text{--}50\,000 \text{ C m}^{-2}$  [6].

On increasing the specific electric charge from  $5 \times 10^4 \text{ C m}^{-2}$  to  $4 \times 10^5 \text{ C m}^{-2}$ , new absorption bands appear clearly in the Regions A and D. An absorption band in Region A can be assigned to acid anhydrides [7]. On the other hand, an absorption band in Region D can be assigned to carbon-oxygen stretching vibrations induced by hydrogen bonds, as shown in Fig. 1 [7].

Fig. 2a shows the relation between the *R*-value and the extent of electrochemical oxidation for the edge surface of PG. The *R*-value is the intensity ratio of the G band ( $1585 \text{ cm}^{-1}$  band) to the D band ( $1360 \text{ cm}^{-1}$  band) [8] and is a function of the crystallite size,  $L_a$  [9]. Taking account of the *R*-values for the pristine specimen ( $L_a = 10 \text{ nm}$ ) and for the oxidized one ( $L_a = 2.6 \text{ nm}$ ), surface graphitic structure treated at  $4 \times 10^5 \text{ C m}^{-2}$  undoubtedly becomes disordered.

It seems that acid anhydrides are introduced to the edge surface, when the edge surface structure is dramatically destroyed. In this case, because absorption in Region D also occurs at the same time, oxygen-containing functional groups present on the edge surface would form hydrogen bonds to acid anhydrides. From previous studies, the following facts are clarified. (i) Mild treatment, which does not induce the destruction of edge surface structure, introduces hydroxyl groups to the edge surface [4]. (ii) When the surface structure is destroyed, carboxyl groups are introduced to the surface [4]. (iii) The ratio of lactone groups to carboxyl groups increases with the electrochemical treatment level [5]. In addition, absorption due to quinones increases markedly on severe treatment,  $5 \times 10^4 \text{ C m}^{-2}$  [6]. Judging from these facts, the oxidation of the edge surface would result in the

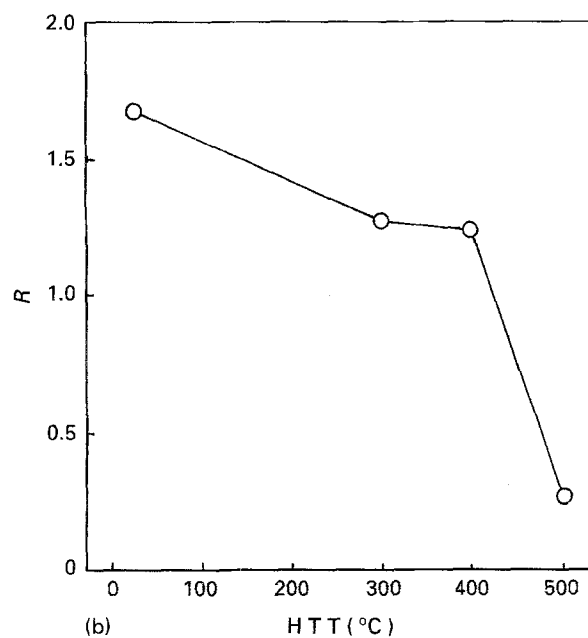
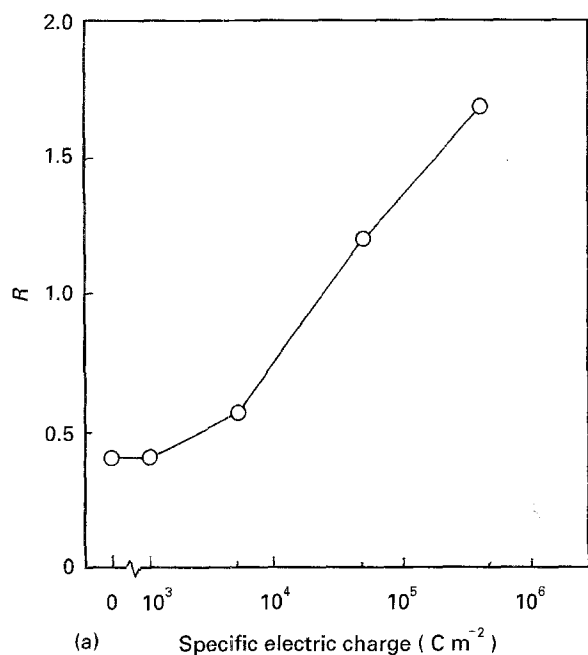


Figure 2 R obtained from Raman spectra. (a) Electrochemical treatment. (b) Electrochemical treatment at  $4 \times 10^5 \text{ C m}^{-2}$  and heat treatment.

formation of oxygen-containing functional groups in the following order: hydroxyl groups, carboxyl groups, lactone groups, quinones, and acid anhydrides. Therefore, for the sample treated at  $4 \times 10^5 \text{ C m}^{-2}$ , various types of oxygen-containing functional groups can be assumed to be widespread from the surface to the inside in the following order: acid anhydrides, quinones, lactone groups, carboxyl groups, and hydroxyl groups, as shown in Fig. 3. In addition, the appearance of absorption in Region D suggests that acid anhydrides form mostly hydrogen bonding to carbonyl groups in quinones. We have confirmed that acid anhydrides as well as hydroxyl groups [4], lactone groups [5], carboxyl groups [4], and quinones [6] can also be introduced to the edge surface by the electrochemical treatment in separate experimental runs.

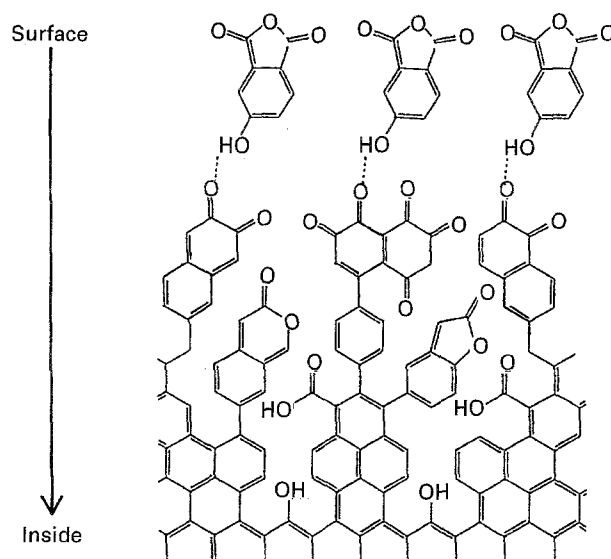


Figure 3 A schematic diagram of an oxidized edge surface.

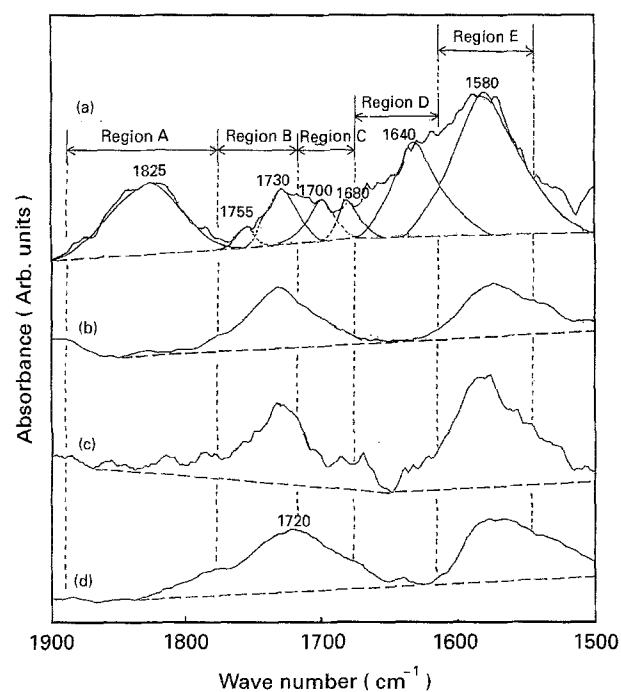


Figure 4 ATR spectra of a heat-treated edge surface: (a) unheated, and heat treated at (b) 300 °C, (c) 400 °C, and (d) 500 °C.

The effect of heat treatment on the oxidized edge surface can be calibrated by FTIR-ATR spectra. The ATR spectra of the heat-treated edge surfaces are shown in Fig. 4. When the edge surface oxidized at  $4 \times 10^5 \text{ C m}^{-2}$  is heat treated at 300 °C, the disappearance of absorption bands in both Regions A and D is clearly marked. This indicates that acid anhydrides are eliminated from the edge surface and hydrogen bonds are already broken by the heat treatment up to 300 °C. These facts lend support to the fact that acid anhydrides are linked by hydrogen bonds to the edge surface. From the above consideration, quinones appear on the outermost surface in comparison with the other groups when acid anhydrides are eliminated. Therefore, acid anhydrides seem to be linked by hydrogen bonds to mainly carbonyl groups in quinones.

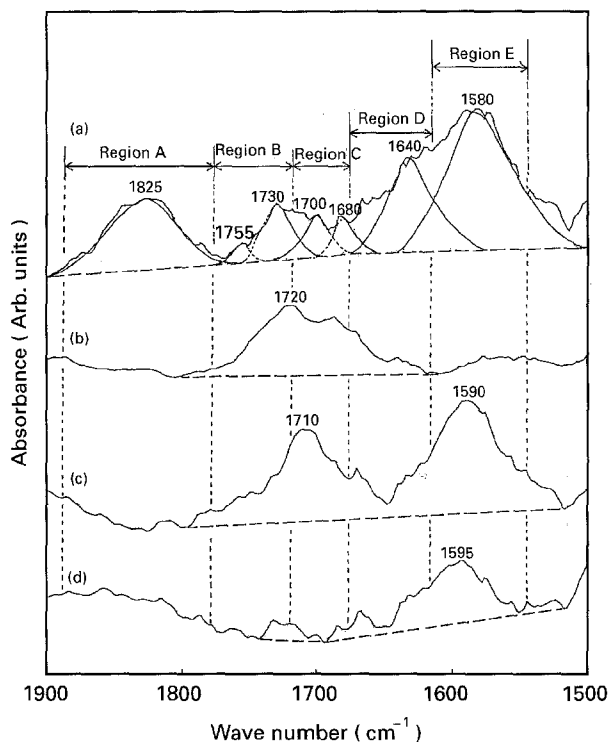


Figure 5 ATR spectral change of PVC/oxidized edge surface caused by heat treatment: (a) unheated, and heat treated at (b) 300 °C, (c) 400 °C, and (d) 500 °C.

This suggests that the structure with acid anhydrides also includes hydroxyl groups, as shown in Fig. 3.

No marked difference in the ATR spectra between heat treatment 300 and 400 °C is recognized. After heat treatment up to 500 °C, an absorption band centred at 1730  $\text{cm}^{-1}$  is shifted to smaller wave number, that is, 1720  $\text{cm}^{-1}$ . This implies that the ratio of carboxyl groups to lactone groups increases after heat treatment at 500 °C. Because  $R$  decreases from 1.70 to 0.27 by the treatment (Fig. 2), the disordered surface structure is restored to a more ordered structure. It can be assumed that the ratio of carboxyl groups to lactone groups relates to the degree of disorder of the surface structure. The absorption band in Region E is present in the vicinity of 1580  $\text{cm}^{-1}$  and is little altered by the heat treatment. Oxygen-containing functional groups, other than acid anhydrides, remain on the edge surface even after heat treatment up to 500 °C. Thus lactone groups, carboxyl groups, and quinones cannot be completely eliminated by the heat treatment up to 500 °C.

PVC coating on the oxidized edge surface induced no marked spectral change in the region 1900–1500  $\text{cm}^{-1}$  (compare the spectra of Figs 4a and 5a). This means that the thickness of the PVC layer is less than about 500 nm [10]. Fig. 5 shows the ATR spectral change of the PVC/oxidized edge surface caused by the heat treatment. When the PVC/oxidized edge surface is heat treated at 300 °C, absorption bands in Regions A, D, and E disappear. This indicates that acidic anhydrides and quinones are eliminated by heat treatment up to 300 °C. As mentioned above, acidic anhydrides are eliminated without the coating of PVC. This means that PVC assists the

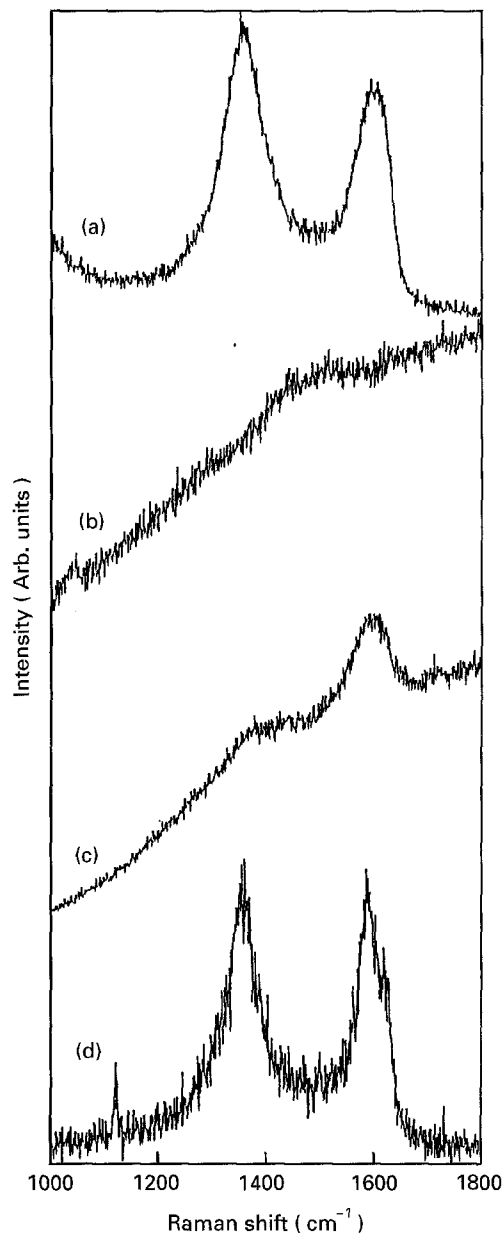


Figure 6 Raman spectral change of PVC/oxidized edge surface caused by heat treatment: (a) unheated, and heat-treated at (b) 300 °C, (c) 400 °C, and (d) 500 °C.

elimination of quinones during heat treatment. It is well known that PVC decomposes above about 190 °C. Furthermore, we have demonstrated that PVC is linked by hydrogen bonds to  $>C=O$  of quinones [6]. Thus both the decomposition of PVC and the hydrogen bonds could permit the elimination of quinones on the edge surface at 300 °C.

For a heat-treatment temperature (HTT) of 400–500 °C, an absorption band in Region E again appears. The appearance of the absorption band would be due to the carbonization product of PVC. Fig. 6 shows the Raman spectral change of PVC-coated samples caused by the heat treatment. Uncoated and PVC-coated samples without heat treatment showed the same Raman spectrum. Distinct G- and D-bands occur when the HTT is raised from 400 °C to 500 °C. The Raman spectra of samples heat treated at 300–500 °C, illustrated in Fig. 6, apparently show only the carbonization process of PVC. This

means that the thickness of the carbonized PVC layer is above about 20 nm [11]. ATR spectra of samples heat treated at 400–500 °C show an absorption band located at 1590–1595  $\text{cm}^{-1}$ , which is different from the position of the absorption band due to quinones, that is, 1580  $\text{cm}^{-1}$ . These Raman and ATR spectral data confirm that the carbonized structure of PVC is formed on the edge surface during heat treatment and the thickness of the structure is in the range from 20–500 nm.

When the HTT is raised up to 400 °C, the position of maximum absorbance in the Region B–C shifts from 1730  $\text{cm}^{-1}$  to 1710  $\text{cm}^{-1}$ . This indicates that the ratio of lactone groups to carboxyl groups decreases during heat treatment. Lactone groups are suggested to be mainly eliminated by the heat treatment at 400 °C. Furthermore, when the HTT is raised from 400 °C to 500 °C, the absorption band in Region C almost disappears. This disappearance means that most of carboxyl groups are eliminated by heat treatment at 500 °C. PVC coated on the edge surface would promote the elimination of lactone and carboxyl groups.

In summary, without doubt, the PVC coated on the oxidized edge surface has a function of reducing the elimination temperature of oxygen-containing functional groups. That is, lactone, quinone, and carboxyl groups are all removed by heat treatment up to 500 °C. The elimination temperature depends on the type of the functional groups. Quinones, lactone groups, and carboxyl groups are mainly eliminated at 300, 400, and 500 °C, respectively.

The elimination mechanism of functional groups for PVC coating is then discussed. We have proposed that PVC coated on the edge surface is linked by hydrogen bonds to  $> \text{C}=\text{O}$  of quinones [6]. At 300 °C, hydrogen bonds between  $> \text{C}=\text{O}$  of quinones and PVC could be formed and assist the elimination of quinones during the PVC thermal decomposition process. After the elimination of quinones, lactone groups would be mainly exposed to the outermost edge surface. At 400 °C, interaction between lactone groups and PVC-decomposition products, such as HCl, could facilitate the elimination of lactone groups. After the elimination of lactones, carboxyl groups would be present mainly on the outermost edge surface, that is, the interface between PG and the carbonized PVC layer. At 500 °C, interaction between carboxyl groups and PVC-decomposition products could enable the elimination of carboxyl groups. The detailed interaction cannot be revealed in this study.

When the elimination of oxygen-containing functional groups and the thermal decomposition of PVC occurs at the same time, radicals are formed and react with each other to form strong bonds in the interfacial region [3]. Thus, the coating of PVC leads to almost perfect elimination of oxygen-containing functional groups and, as a result, strong carbon–carbon bonds are formed in the interface. Thermoplastic resin, which is easy to decompose thermally and has many polar groups, such as PVC, is assumed to be effective to promote the elimination and the formation of strong interfacial bonding.

#### 4. Conclusion

Electrochemical treatment can introduce a variety of oxygen-containing functional groups with  $> \text{C}=\text{O}$  to the edge surface. The functional groups are carboxyl groups, lactone groups, quinones, and acid anhydrides. All of the functional groups, except for acid anhydrides, remain even after heat treatment up to 500 °C. PVC coating enables the functional groups to be completely eliminated by heat treatment up to 500 °C. The elimination temperature depends on the type of functional groups. Quinones, lactone groups, and carboxyl groups are mainly eliminated at 300, 400, and 500 °C, respectively. PVC coated on the edge surface is found to play an important role in the elimination of oxygen-containing functional groups with  $> \text{C}=\text{O}$  present on the edge surface.

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