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Interfacial debonding strength between the edge surfaces of pyrolytic graphite and epoxy resins

K. SHIMIZU, M. NAKAHARA*, K. NOGUCHI
Toray Industries, Inc., 3-2-1, Sonoyama Otsu, Shiga 520, Japan

The edge surfaces of pyrolytic graphite have been treated by anodic oxidation and the interfacial debonding strength (IFDS) between the oxidized edge surfaces and epoxy resin measured. The unoxidized and oxidized edge surfaces were examined by X-ray photoelectron spectroscopy. The edge and epoxy resin surfaces after debonding test were examined by a field-emission scanning electron microscope. Carboxyl groups were expected to be added in great quantities by breaking the carbon–carbon bonds at the edge surface. On the other hand, hydroxyl groups could be added to edge carbon atoms at the edge surface without breaking the carbon–carbon bonds. The rise in IFDS with anodic oxidation does not correspond directly to the O/C ratios or the amount of carboxyl groups present on the edge surface. Hydroxyl groups added to the edge surface are considered to play an important role in improving the adhesion between the edge surface and epoxy resin through covalent bonds between hydroxyl and epoxy groups. In the case of epoxy resin used in this study, IFDS initially increased to 9 MPa with increasing –OH/C ratio up to about 0.02; thereafter it remains constant at this value. This strength is lower than those of PG and epoxy resin.

1. Introduction

Anodic oxidation of carbon fibres (CFs) improves the interlaminar shear strength (ILSS) of CF–epoxy matrix composites [1–3]. Fitzer and Rensch [4] have reported that the behaviour of ILSS varies considerably depending upon the kind of electrolyte. Namely, NaOH electrolyte improves the adhesion much better than sulphuric acid electrolyte. Moreover, at a higher treatment level with sulphuric acid electrolyte, a marked decline of the ILSS occurs for high modulus CFs.

It is well known that anodic oxidation induces the increase in O_{1s}/C_{1s} ratio on the CF surface, judging from the data obtained by X-ray photoelectron spectroscopy (XPS). Harvey *et al.* [3] have concluded that the rise in ILSS is not dependent upon the O_{1s}/C_{1s} ratios or the number of carboxyl functional groups present on the surfaces. On the other hand, Ehrburger and Donnet [2] have suggested that the presence of stronger acidic groups (COOH and OH) results in an increased adhesion between CFs and epoxy matrices.

Both the functional groups and the graphitized structure of the CF surface are important for the interfacial adhesion. The elemental structure of CFs consists of graphitic crystallites, which have not only graphitic basal planes but also corners and edges of the crystallites [5]. Therefore, studies on anodic oxidation were carried out using the basal and edge surface of pyrolytic graphite (PG) as a model of the CF surface [6, 7].

In this paper, the results obtained by the edge surface–epoxy resin debonding tests are reported and discussed in relation to the structure of the edge surface before and after anodic oxidation.

2. Experimental procedure

Cleaved basal plane and mirror-polished edge surfaces of PG were prepared in the same manner as described in our preceding paper [6]. Basal surfaces are perpendicular to the *c*-axes of graphite crystallites, and edge surfaces are parallel to the *c*-axes.

Anodic oxidation of the edge surfaces was also carried out following the method described in our previous paper [6].

Sulphuric acid and tetraethylammoniumhydroxide solution (0.1N) were used as an example of acid and alkaline electrolyte, respectively. The specific electric charge (electric charge, C/unit area, m^2) applied to the surfaces was in six steps: 50, 100, 500, 1000, 5000, and $50\,000\ C\,m^{-2}$ in the sulphuric acid solution; 50, 500, 1000, 5000, 10 000, and $50\,000\ C\,m^{-2}$ in the tetraethylammoniumhydroxide solution.

The O/C ratios of the basal and edge surfaces were examined by XPS measurement. A spectrometer (SSI, SSX-100-206) with a monochromatized $AlK_{\alpha_{1,2}}$ X-ray anode ($h\nu = 1486.6$ eV) was used for XPS measurement in a vacuum of 1×10^{-8} torr (1 torr = 133.322 Pa). Photoemitted electrons were measured at an angle of 35° to the basal and edge surfaces

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* *Present address*: Hokkaido University, Kitakee Sapporo, Hokkaido 060, Japan.

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of PG. The graphitic peak corresponding to the C_{1s} binding energy (284.6 eV) was adopted for calibration purposes.

A specimen used for measuring the interfacial debonding strength (IFDS) of the edge surface–epoxy resin composite was made in the following way. An epoxy resin mixture was prepared, consisting of 2,2-diphenyl propane-p,p′-diglycidine ether (Epoxy Ep 828), 100 parts by weight; boron trifluoride monoethylamine complex catalyst ($BF_3 \cdot MEA$), at 80 °C for 10 min. The epoxy resin and catalyst mixture was degassed and then poured into a mould with 2 mm spacers. PG was inserted into the mould so that only the edge surface of PG was in contact with the epoxy resin mixture. The epoxy resin mixture was cured in a forced air oven at 170 °C for 1 h and post-cured at 170 °C for 2 h and allowed to cool down slowly. Then the PG–epoxy resin cured plate was taken out of the mould. The plate was cut into five specimens (about 100 mm long and about 5 mm wide) for the interfacial debonding test (Fig. 1).

IFDS was measured using an Autograph testing machine (Shimadzu Seisakusho, AG-500B). The load was applied on the specimens along their longitudinal direction. The gauge length was 30 mm and the tensile speed was 1 mm min^{-1}.

The surfaces of the specimens debonded after the interfacial debonding tests were examined by a field-emission scanning electron microscope (FE-SEM) (Hitachi, Model S-800). Before the observation, platinum was evaporated on to the surfaces under the pressure below 0.05 torr.

3. Results and discussion

3.1. Oxygen-containing groups

The O/C ratios obtained by XPS as a function of the specific electric charge are shown in Fig. 2. In the case of the sulphuric acid electrolyte, some of the oxygen-containing groups are considered to be present as SO_4^{2-} or HSO_4^-. The O/C ratios in Fig. 2 are the corrected value reducing the oxygen quantity in the S–O bonds. The O/C ratios in the basal and edge surfaces rise as the specific electric charge increases. The number of edge carbon atoms in the edge surface is larger than that in the basal surface. As a result, the edge surface has higher O/C ratios in the range 0–500 C m^{-2} than the basal surface as seen in Fig. 2. In both basal and edge surfaces, there is no significant difference in O/C ratio between the acid electrolyte and the alkaline electrolyte in the range 0–500 C m^{-2}. In this treatment range, destruction of the surface structure has not yet occurred, as described previously [7]. When the basal and edge surfaces are anodically oxidized in the acid solution at as much as 5000 C m^{-2}, O/C ratios in their surfaces rise rapidly. At this treatment level, the destruction of the surface structures begins to occur [6]. Because of the destruction of the surface structures, a large number of edge carbon atoms are newly produced in the surfaces. By anodic oxidation many oxygen-containing groups are added to the newly produced edge carbon atoms. Consequently, O/C ratios in the basal and edge surfaces rise rapidly at 5000 C m^{-2}. The same phenomenon occurs at 50 000 C m^{-2} for the alkaline electrolyte. These results indicate that the edge surface can have

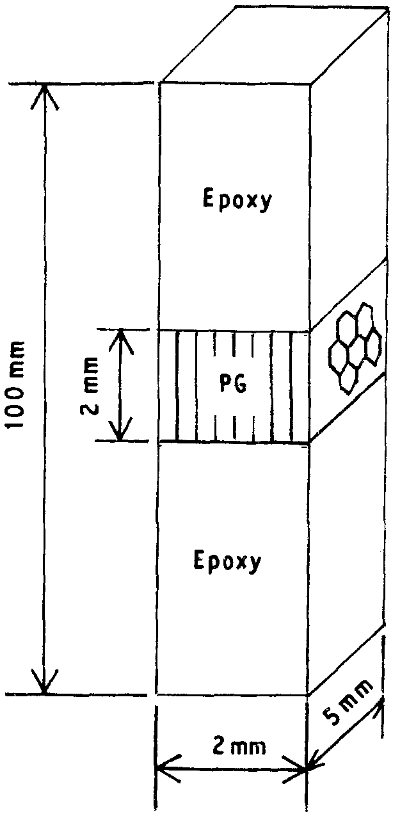

Figure 1 Specimen for interfacial debonding test.

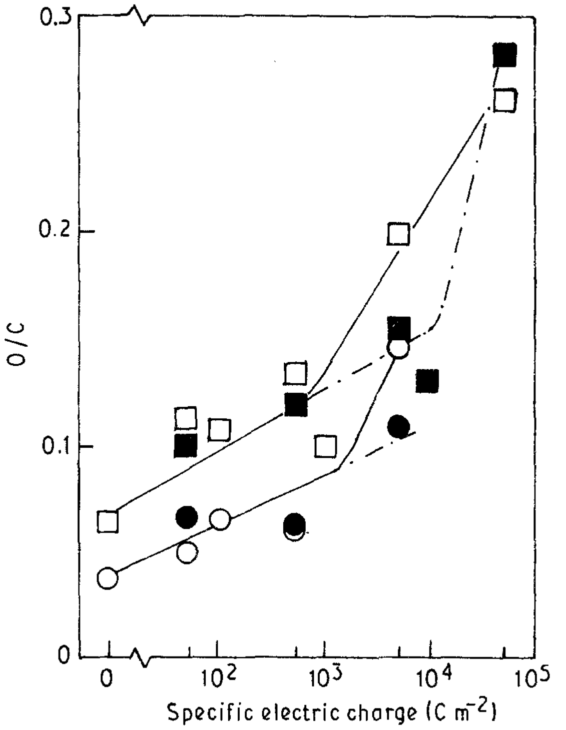

Figure 2 O/C ratios obtained by XPS as a function of the specific electric charge for (○) the basal surface in the acid electrolyte, (●) the basal surface in the alkaline electrolyte, (□) the edge surface in the acid electrolyte, and (■) the edge surface in the alkaline electrolyte.

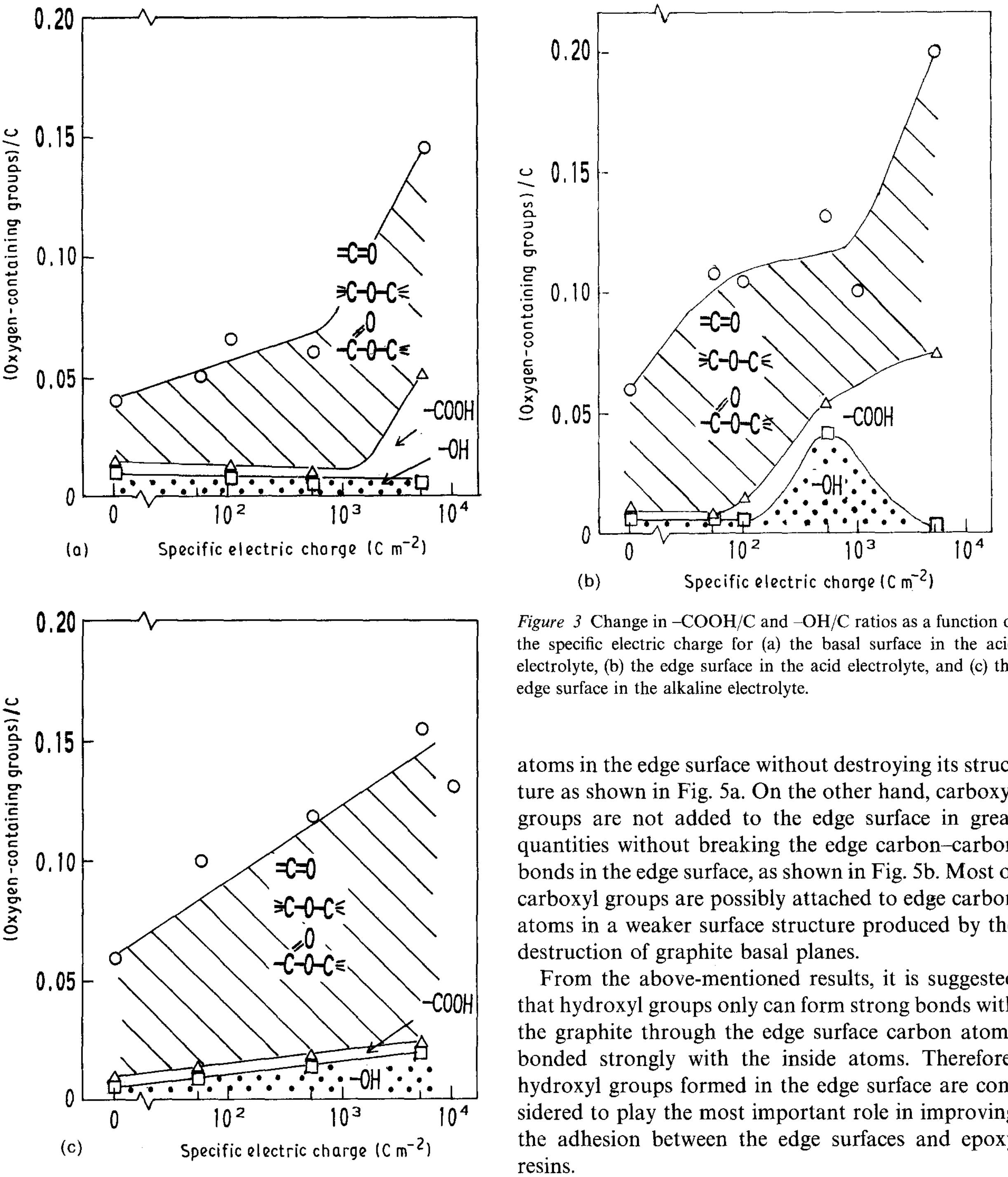

Figure 3 Change in –COOH/C and –OH/C ratios as a function of the specific electric charge for (a) the basal surface in the acid electrolyte, (b) the edge surface in the acid electrolyte, and (c) the edge surface in the alkaline electrolyte.

more oxygen-containing groups without destroying the surface structure, than the basal surface.

The change in –COOH/C and –OH/C ratios as a function of the specific electric charge [6] is shown in Fig. 3 together with the change in O/C ratio. Other oxygen-containing groups are expected to be carbonyl, ether, and ester groups. In these oxygen-containing groups, only hydroxyl and carboxyl groups can form covalent bonds with epoxy groups [1]. Which kind of effective functional group (–COOH or –OH) is added to the edge surface is closely related to the structure of the oxidized surface [6]. The relationship between the kind of functional groups and R (I_{1355}/I_{1580}) obtained by laser Raman spectroscopy [6] is shown in Fig. 4. Where no growth in R occurs, no marked increase in carboxyl groups is recognized. Hydroxyl groups can be added to the edge carbon atoms in the edge surface without destroying its structure as shown in Fig. 5a. On the other hand, carboxyl groups are not added to the edge surface in great quantities without breaking the edge carbon–carbon bonds in the edge surface, as shown in Fig. 5b. Most of carboxyl groups are possibly attached to edge carbon atoms in a weaker surface structure produced by the destruction of graphite basal planes.

From the above-mentioned results, it is suggested that hydroxyl groups only can form strong bonds with the graphite through the edge surface carbon atoms bonded strongly with the inside atoms. Therefore, hydroxyl groups formed in the edge surface are considered to play the most important role in improving the adhesion between the edge surfaces and epoxy resins.

3.2. The relationship between IFDS and surface structure

IFDS of the edge surface–epoxy resin composite as a function of the specific electric charge is shown in Fig. 6. In the case of acid electrolyte, IFDS has a maximum value at 1000 C m^{-2} of specific electric charge. On the other hand, IFDS with the alkaline electrolyte has a maximum value at 10 000 C m^{-2}, one order higher, of specific electric charge. At 50 000 C m^{-2}, IFDS falls to almost 0 MPa for both electrolytes. At this treatment level, debonding has already occurred in the specimen before the debonding test. The maximum IFDS is about 9 MPa for both acid and alkaline electrolytes. This strength is low enough compared with the tensile strength of PG (60 MPa) and epoxy resin (50 MPa), for it to be admitted as IFDS without any confusion.

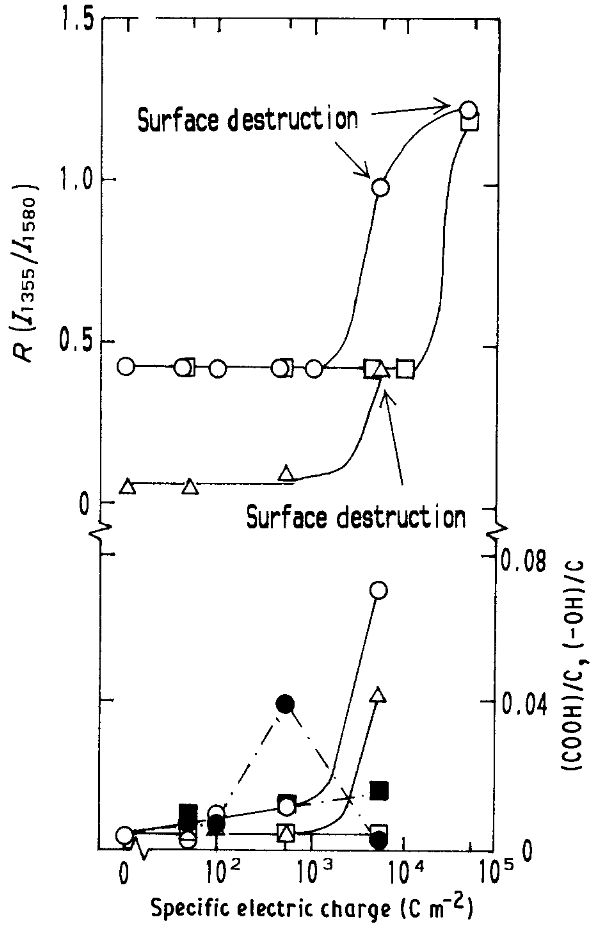

Figure 4 Relationship between the kind of functional groups and R (I_{1355}/I_{1580}) for (○, ●) the edge surface in the acid electrolyte, (□, ■) the edge surface in the alkaline electrolyte, and (△) the basal surface in the acid electrolyte. (○, △, □)–COOH, (●, ■)–OH.

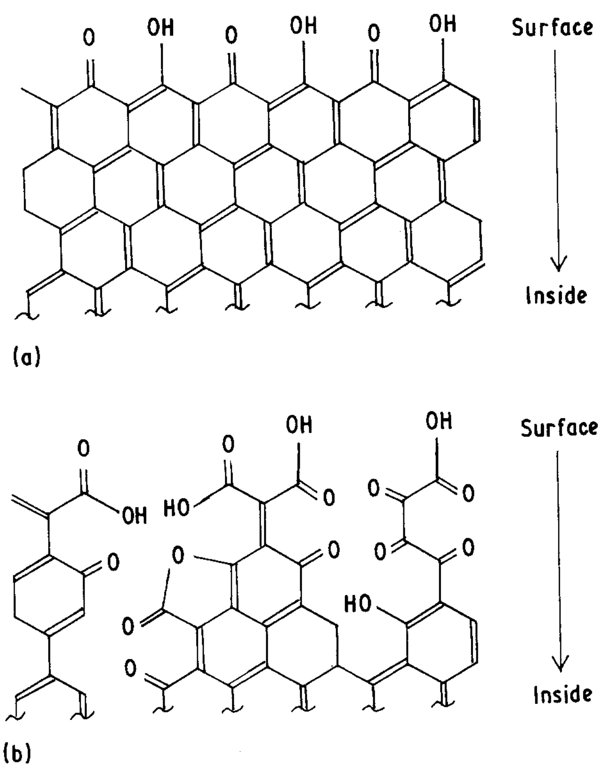

Figure 5 Functional groups added to the edge surface: (a) –OH; (b) –COOH.

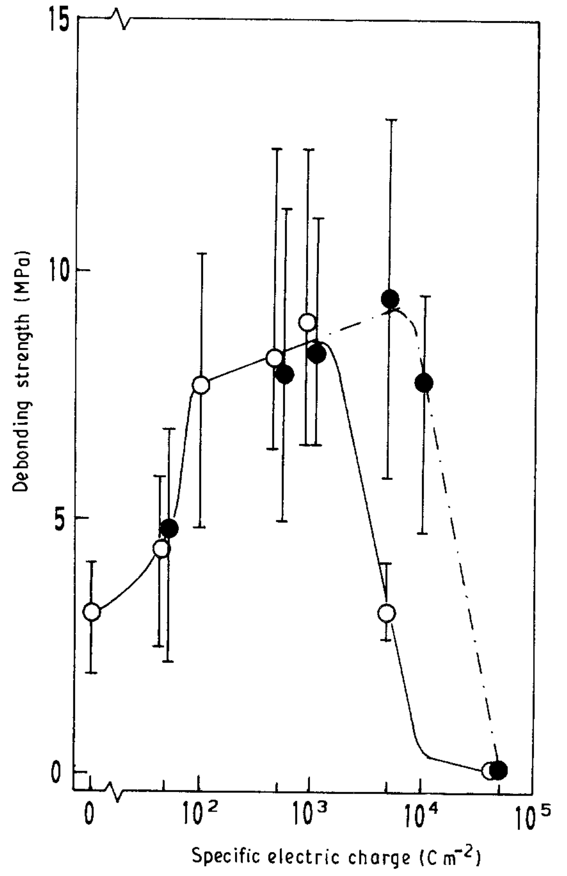

Figure 6 IFDS of the edge surface–epoxy resin combination as a function of the specific electric charge for (○) the acid electrolyte, and (●) the alkaline electrolyte.

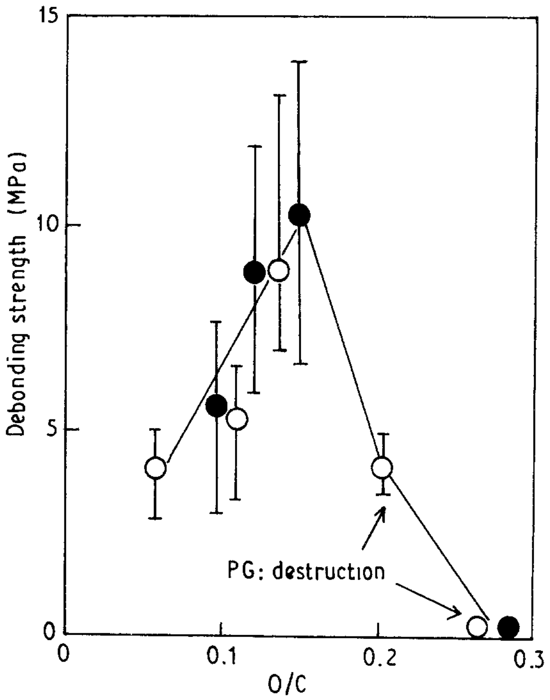

Figure 7 Relationship between IFDS and O/C ratio for (○) the acid electrolyte and (●) the alkaline electrolyte.

The relationship between IFDS and O/C ratio is shown in Fig. 7. IFDS has a maximum value at the O/C ratio of 0.15. It can be seen that IFDS initially increases linearly with O/C ratio up to a maximum value, and falls into the same line for both electrolytes.

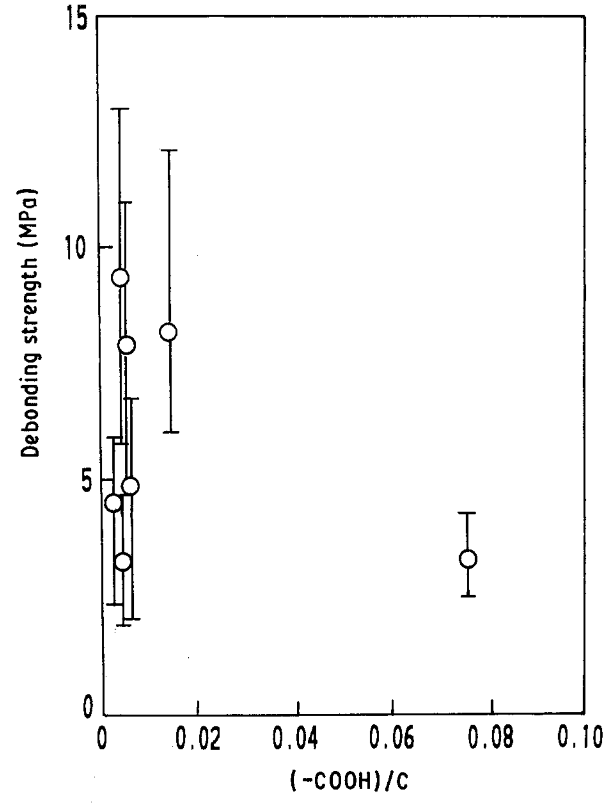

Figure 8 IFDS as a function of -COOH/C ratio.

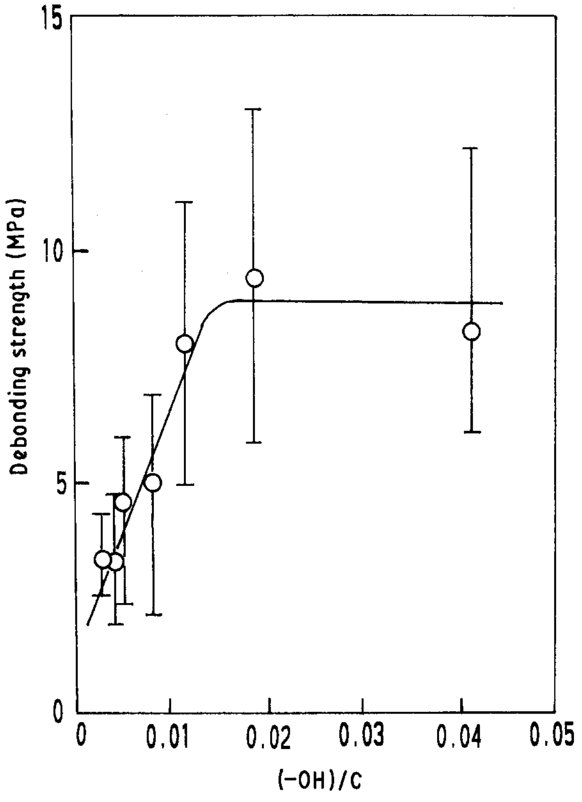

Figure 9 IFDS as a function of -OH/C ratio.

IFDS as a function of -COOH/C ratio is shown in Fig. 8. It is obviously found that there is no good correlation between IFDS and -COOH/C ratio. As mentioned above, most of the carboxyl groups are considered to be added to edge carbon atoms in a broken weak surface structure. Namely, the number of carboxyl groups increases as the surface structure becomes weak. When the strength of the weak surface structure becomes lower than the interfacial strength between the edge surface and epoxy resin, debonding occurs within the edge surface layers. Therefore, an increase in the number of carboxyl groups cannot be necessarily related to an increase in IFDS.

Fig. 9 shows IFDS as a function of -OH/C ratio. IFDS increases initially with increasing -OH/C ratio up to about 0.02, and thereafter remains constant at about 9 MPa. This increase in IFDS indicates that hydroxyl groups can form strong bonds with epoxy groups. It is concluded, as in Section 3.1, that hydroxyl groups in the edge surface play the most important role in improving IFDS. Moreover, a plateau in IFDS suggests that only the amount of hydroxyl groups up to an -OH/C ratio of ~ 0.02 is effective in improving the IFDS for the edge surface-epoxy resin combination used in this study. Excessive hydroxyl groups (more than 0.02) may be present without forming any bonds with epoxy groups in the surface. The effective-OH/C ratio for chemical bonding in the interface will be mainly dependent upon the kind of epoxy resin.

3.3. FE-SEM results

FE-SEM photographs of fraction surfaces after the debonding test as a function of the treatment level of the edge surface are shown in Fig. 10. In the case of the unoxidized edge surface, attachment of epoxy resin to the edge surface is not observed (Fig. 10a); neither is the attachment of PG to the cured epoxy resin surface. This indicates that the fracture has occurred in the interface.

In both acid and alkaline electrolytes at 500 C m^{-2} specific electric charge, the attachment of cured epoxy resin to the edge surface is partially recognized after the debonding test (Fig. 10b). On the other hand, the attachment of PG to the cured epoxy resin surface is not recognized (Fig. 10c). The same phenomena are recognized for the alkaline electrolyte at 5000 C m^{-2}. These results show that covalent bonds stronger than the weak parts of the resin are formed in the interface between the edge surface and epoxy resin. Taking into account the results described in Section 3.2, it is concluded that some of the hydroxyl groups on the edge surface form covalent bonds with epoxy groups.

For the acid electrolyte at 5000 C m^{-2}, not only is the attachment of epoxy resin partially observed on the edge surface, but the attachment of PG is also observed on the resin surface (Fig. 10d). Also in this case, covalent bonds are thought to be formed in the interface. However, at 5000 C m^{-2}, the attachment of PG to the resin surface occurs over a wider range on the resin surface. Moreover, in the case of 50 000 C m^{-2}, the attachment of PG to the whole resin surface is observed for both acid and alkaline electrolytes (Fig. 10e). These results indicate that debonding occurs mainly within the edge surface layers of the PG side. Therefore, it is concluded that a reduction in IFDS, as seen in Fig, 6, is due to the destruction of the edge surface structure weakened by the severe anodic oxidation.

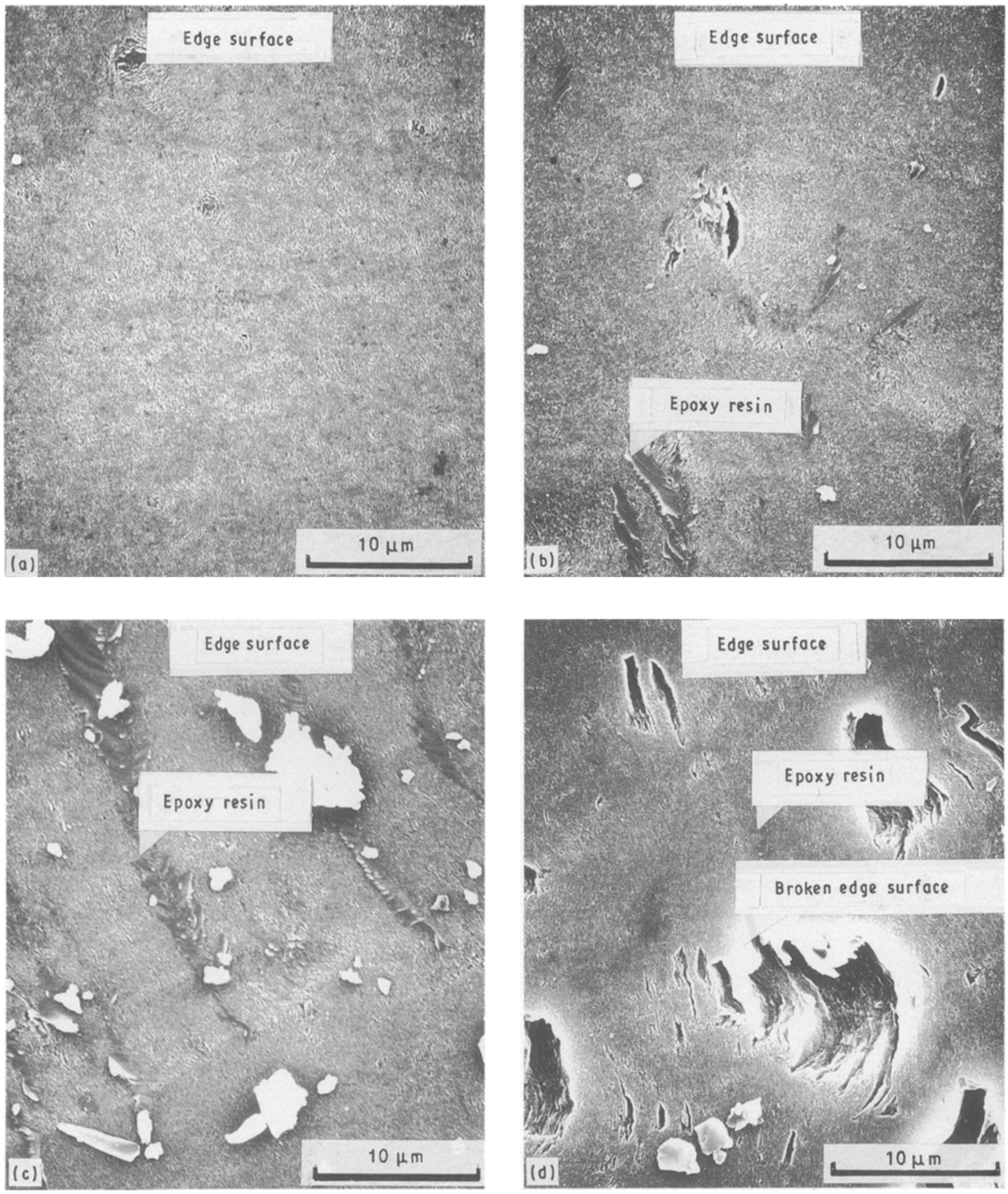

Figure 10 FE–SEM photographs of fracture surface of the edge: (a) 0 C m^{-2}, (b) 500 C m^{-2} for the acid electrolyte, (c) 5000 C m^{-2} for the alkaline electrolyte, (d) 5000 C m^{-2} for the acid electrolyte, (e) 50 000 C m^{-2} for the alkaline electrolyte.

Where IFDS falls to 0 MPa with severe oxidation, the strength of the edge surface structure must be reduced from 62 MPa to almost 0 MPa. Then, a weak structure which diffuses from the edge surface into the alkaline solution is present on its surface and may be a factor which significantly reduces the interfacial strength. In the case of high-strength CFs, the alkaline solution becomes dark even at 50 C m^{-2}. This would suggest that a surface structure which is easily weakened is initially present on the unoxidized CF surface and hinders the improvement of ILSS.

4. Conclusion

IFDS in the edge surface–epoxy resin composite has been discussed in relation to the structure of the edge surface anodically oxidized. The maximum IFDS in the composite is lower than the tensile strength of PG and epoxy resin. In this case, fracture always occurs at the interface between the edge surface and epoxy resin. Hydroxyl groups in the edge surface play an important role in improving the interfacial adhesion through the covalent bonds between hydroxyl and epoxy groups. Excessive hydroxyl groups amounting to an

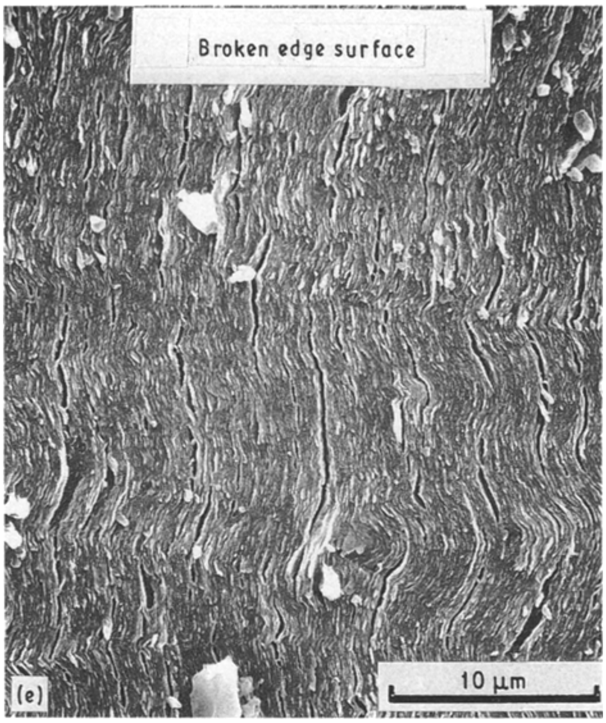

Figure 10 continued.

–OH/C ratio of more than 0.02 for the composite used in this study do not contribute to the improvement of the interfacial adhesion. With severe treatment, many carboxyl groups are added to the edge surface accompanied by the destruction of its structure, and as a result IFDS is reduced. These findings will be applied to the investigation of the adhesion mechanism in CF–epoxy matrix composites.

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