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Effects of electrolyte on the structure of pyrolytic graphite surfaces in anodic oxidation

MASANORI NAKAHARA, KAZUHARU SHIMIZU*
*Composite Materials Research Laboratories and *Polymers Research Laboratories, Toray Industries Inc., 3-2-1, Sonoyama, Otsu, Shiga 520, Japan*

Anodic oxidation effects on the structure of the basal and edge surfaces of pyrolytic graphite in alkaline electrolytes have been studied. Laser Raman spectroscopy, a gas-phase chemical modification method, coupled with X-ray photoelectron spectroscopy and secondary ion-mass spectroscopy techniques, were used. Anodic oxidation of the surfaces of pyrolytic graphite in alkaline electrolytes does not cause destruction of their surface structure, even at a higher level of treatment, unlike oxidation of acid electrolytes. In alkaline electrolytes, the number of hydroxyl groups added on the edge surface gradually increases with the increase in treatment level, whereas the number of carboxyl groups does not increase. It was found that anodic oxidation in alkaline electrolytes has a wider permitted range of treatment, in which hydroxyl groups can be added without destroying the edge surface structure, than that found in acid electrolytes. On the other hand, the number of hydroxyl groups added by treating with alkaline electrolytes is smaller than that with acid electrolytes. At a higher treatment level with acid electrolytes, oxidation occurs, even to a depth of 40 nm from the edge surface, whereas with alkaline electrolytes, oxidation occurs only at the surface. On the basis of these results, the effects of electrolytes on the adhesion between carbon fibres and epoxy resin matrix are discussed.

1. Introduction

Surface treatment of carbon fibres (CFs) increases the interlaminar shear strength of the resulting CF-reinforced epoxy resin matrix composites, namely the adhesion between CFs and matrix in the cured composites [1–4]. Such surface treatment procedures usually consist of the oxidation of CF surfaces. In particular, an anodic oxidation method is generally applied in industrial processes because of the shorter oxidation time and the superior processing control possibilities [5].

In order to optimize anodic oxidation of CFs, the effect of the kind of electrolyte on the adhesion between CFs and epoxy resin, and on the structure of CF surfaces, has been investigated. For example, Ehrburger and Donnet [6] performed anodic oxidation experiments on CFs in HNO_3 and NaOH, and suggest that the presence of stronger acidic groups (COOH and OH) on CF surfaces results in the strong interfacial bonding of the composites, and that the treatment of CFs in NaOH yields comparatively stronger acidic groups. Kozlowski and Sherwood [7], using X-ray photoelectron spectroscopy (XPS), have shown that the amount and type of surface oxides varies considerably depending upon the pH of the electrolyte, and suggest that different oxidation mechanisms work at different pH values. Harvey *et al.* [8] examined the effects of a variety of factors, including the kind of electrolyte, on the interlaminar shear strength of composites, and concluded that the rise in interlaminar shear strength with surface treatment is not dependent upon the O/C ratios or on the amount of carboxyl functionality present on the CF surface, inferring that mechanical keying of epoxy resin to the CF surface plays an important role in forming the fibre–resin bond. On the other hand, Fitzer and Rensch [9] have carried out the anodic oxidation of CF surfaces in acid and alkaline electrolytes, and report that the improvement in adhesion between CFs and epoxy resin due to the treatments is mainly caused by the chemical interaction at the interface, and that NaOH electrolytes improve the adhesion much better than an acid type electrolyte such as H_2SO_4. As mentioned above, the mechanism of the improvement in interfacial adhesion by anodic oxidation is still a controversial subject. One of the reasons for this is that the extremely complex structure of CF surfaces makes it difficult to understand the adhesion mechanism.

Therefore, studies on anodic oxidation have been performed by using the basal and edge surfaces of pyrolytic graphite (PG) as a model of CF surfaces. This paper describes the effects of anodic oxidation in alkaline electrolytes on the structure of their surfaces, comparing with the results obtained with acid electrolytes in our previous paper [10]. In addition, the interfacial adhesion between CFs and epoxy resin is discussed based on these results.

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2. Experimental procedure

Basal and mirror-polished edge surfaces of PG were prepared in the same manner as described in the preceding paper [10]. Basal surfaces were perpendicular to the c-axes of graphite crystallites, and edge surfaces were parallel to the c-axes. These surfaces were oxidized anodically in a tetraethylammonium hydroxide solution (0.1 N). Anodic oxidation was also carried out by the method described in our previous paper [10]. Specific electric charges [electric charge (C) per unit area (m^2)] applied on the surfaces were 50, 500 and 5000 C m^{-2}. When NaOH (0.1 N) is used as an alkaline electrolyte, sodium remains on the surfaces even after washing in distilled water. The same phenomenon has been reported for CFs by Kozlowski and Sherwood [7]. If sodium exists on the surfaces of PG in the form of NaOH, errors may appear in the quantitative analysis of hydroxyl group (C–OH). Thus in this study, tetraethylammonium hydroxide solution free from sodium was used as an alkaline electrolyte instead of NaOH which is the most commonly used alkaline electrolyte.

Laser Raman spectroscopy was used to characterize the structural changes in the basal and edge surfaces of PG anodically oxidized in the alkaline electrolyte. A gas phase chemical modification method coupled with XPS was used for detecting hydroxyl and carboxyl groups added on the edge surfaces by anodic oxidation in the alkaline electrolyte. These experiments were also carried out as described in the previous paper [10]. Moreover, secondary ion mass spectroscopy (SIMS) was used for characterization of oxygen and sulphur concentration in the direction of depth from the edge surface, that is, in the region from the edge surface to 40.0 nm depth. The SIMS measurement was taken using A-DIDA 3000 (Atomika Ltd, Germany). A primary Cs^+ ion beam of 12 keV energy and 20 nA current was used.

3. Results and discussion

The Raman spectra of the basal and the edge surfaces of PG treated with an acid electrolyte have already been reported [10]. The Raman spectra of the oxidized basal and edge surface in the alkaline electrolyte, together with those of the unoxidized basal and edge surface, are shown in Fig. 1. In the case of the alkaline electrolyte, any changes in the spectra are not recognized up to 5000 C m^{-2}. Two Raman bands are observed at 1580 and 1355 cm^{-1}. According to Tuinstra and Koenig [11], the intensity ratio, R, of the 1355 cm^{-1} band against the 1580 cm^{-1} band of PG can be related to the number of defects, such as the edges and lattice vacancies of the graphite basal plane, in the surface of PG. Fig. 2 shows the change in R as a function of the specific electric charge for the basal and the edge surfaces of PG treated with the alkaline electrolyte, comparing with the results obtained with

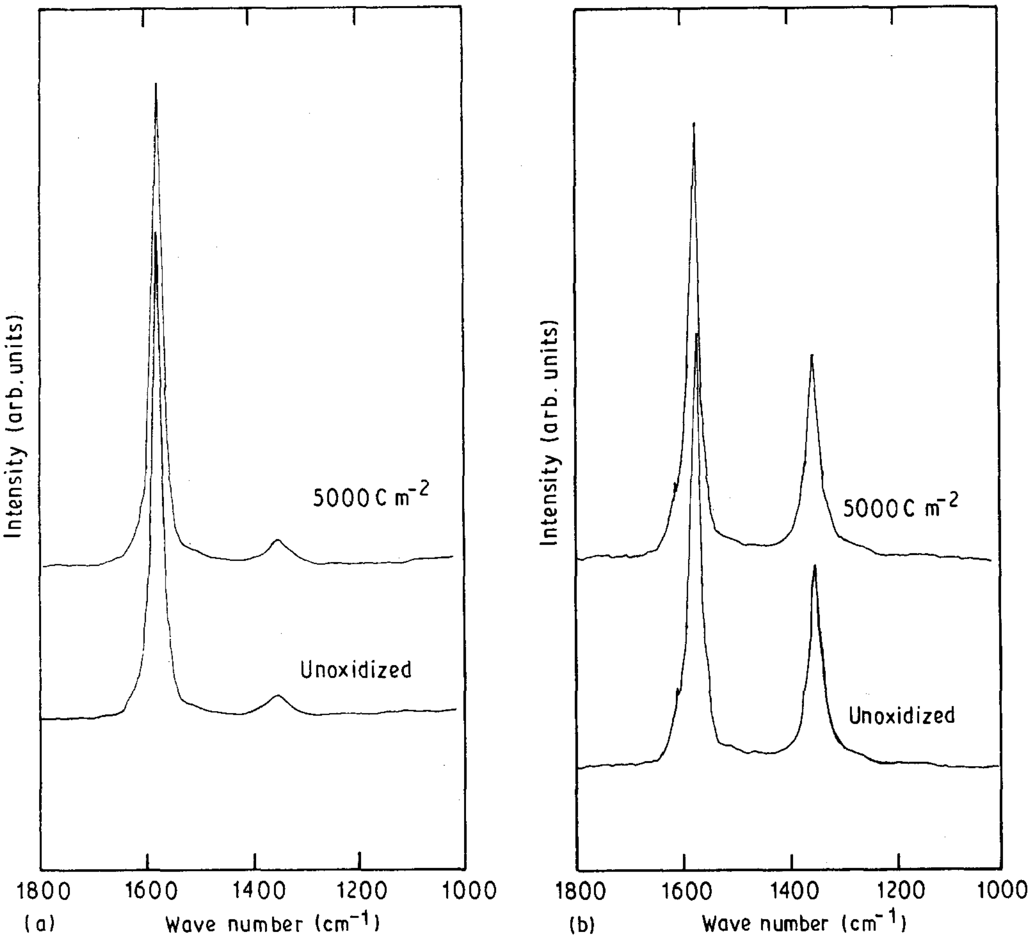

Figure 1 Raman spectra of the unoxidized and oxidized surfaces of PG treated with alkaline electrolyte. (a) Basal surface; (b) edge surface of PG.

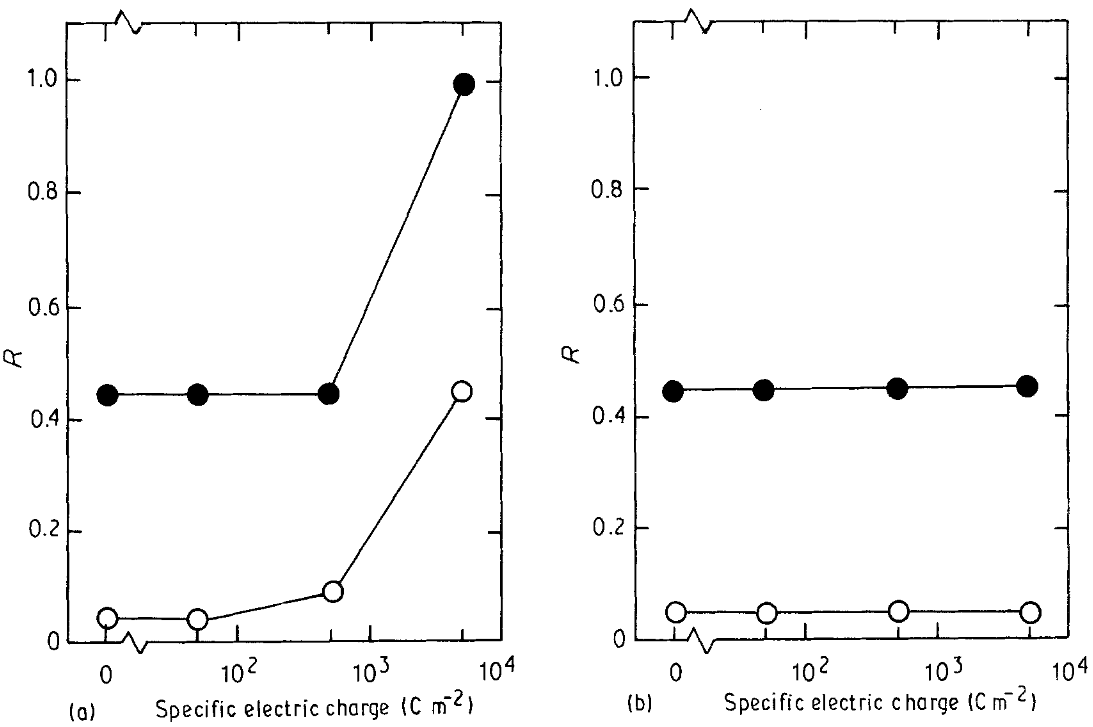

Figure 2 Change in R as a function of specific electric charge for (○), basal and (●), edge surfaces of PG. (a) Acid; (b) alkaline electrolytes.

the acid electrolyte. Any changes in R for the alkaline electrolyte are not recognized in the range of 0–5000 C m^{-2}, whereas the increase in R for the acid electrolyte is recognized in the range of 500–5000 C m^{-2}. These results suggest that, with the alkaline electrolyte, the surface structure is not destroyed up to 5000 C m^{-2}, unlike the case for the acid electrolyte. The effect of an alkaline electrolyte on the surface structure is therefore different from that of an acid electrolyte.

A quantitative analysis [12] determining the amount of hydroxyl and carboxyl groups present on the edge surface of PG has been carried out. Since the edge surface is considered to play a much more important role in improving the shear strength of the CF/epoxy matrix than the basal surface, judging from the results obtained in our previous paper [10], the quantitative analysis is performed only with the edge surface of PG. Fig. 3 shows the change in –COOH/C ratio, –OH/C ratio, and the sum of these ratios as a function of the specific electric charge for the alkaline electrolyte, comparing these with data for the acid electrolyte. In the case of the acid electrolyte, where the specific electric charge increases from 500 to 5000 C m^{-2}, a rapid increase in the –COOH/C ratio is recognized. On the other hand, in the case of the alkaline electrolyte, no increase in –COOH/C ratio is found up to 5000 C m^{-2}. The increase in –COOH/C ratio of the edge surface is considered to be related to the destruction of the surface structure [10].

In fact, the structure of the edge surface in the alkaline electrolyte is found to be free from destruction up to 5000 C m^{-2}, as mentioned above. The degree of surface destruction seems to be related to the increase in the number of carboxyl groups. The –OH/C ratio, on the other hand, increases gradually with the increase in the specific electric charge. Therefore with the alkaline electrolyte, we see that hydroxyl groups can be added on the edge surface without destroying its structure, up to at least 5000 C m^{-2}. This treatment level is higher than that for the acid electrolyte. The total amount of functional groups (–COOH and –OH) added on the edge surface in the alkaline electrolyte is shown in Fig. 3c, compared with the data obtained for the acid electrolyte. The functional groups can form covalent bonds with epoxy groups [10]; as a result the formation of the covalent bonds improves the adhesion between the edge surface and the epoxy resin. We find that the total number of functional groups added in the alkaline electrolyte is much smaller than that in the acid one, in the range of 500–5000 C m^{-2}. From the above-mentioned results, it becomes clear that the type of electrolyte used in anodic oxidation has a considerable effect on the amount and type of functional groups added on the edge surface.

Fig. 4 illustrates the depth profiles of oxygen with the anodically treated edges of PG. In the case of anodic treatment in the acid electrolyte, oxygen concentration increases with an increase in treatment level in the region of 0–40 nm. However, with the alkaline electrolyte the marked rise in oxygen concentration (which is found in the acid electrolyte) is not observed, even at the high treatment level of 5000 C m^{-2}. It can be seen that in the acid electrolyte, the increase in oxygen concentration occurs not only at the edge surface but also up to a depth of 40 nm, whereas in the alkaline electrolyte, oxygen atoms are restricted only to the surface.

The rise in the interlaminar shear strength of the resulting CFs and epoxy resin matrix composites by anodic oxidation may occur because the functional groups described above at the edge surface can form covalent bonds with epoxy groups [10]. The amount of functional groups added in the alkaline electrolyte at 5000 C m^{-2} is smaller than that added in the acid

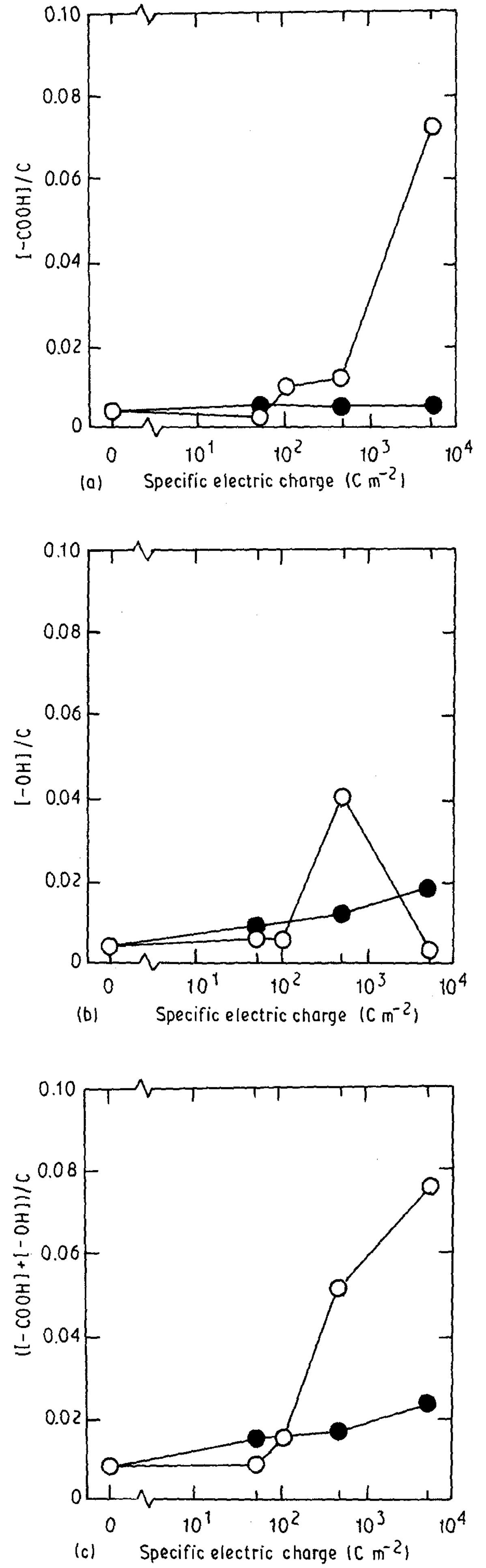

Figure 3 Relation between specific electric charge and amount of functional groups for (○), acid and (●), alkaline electrolytes. (a) [-COOH]/C; (b) [-OH]/C; (c) {[-COOH] + [-OH]}/C.

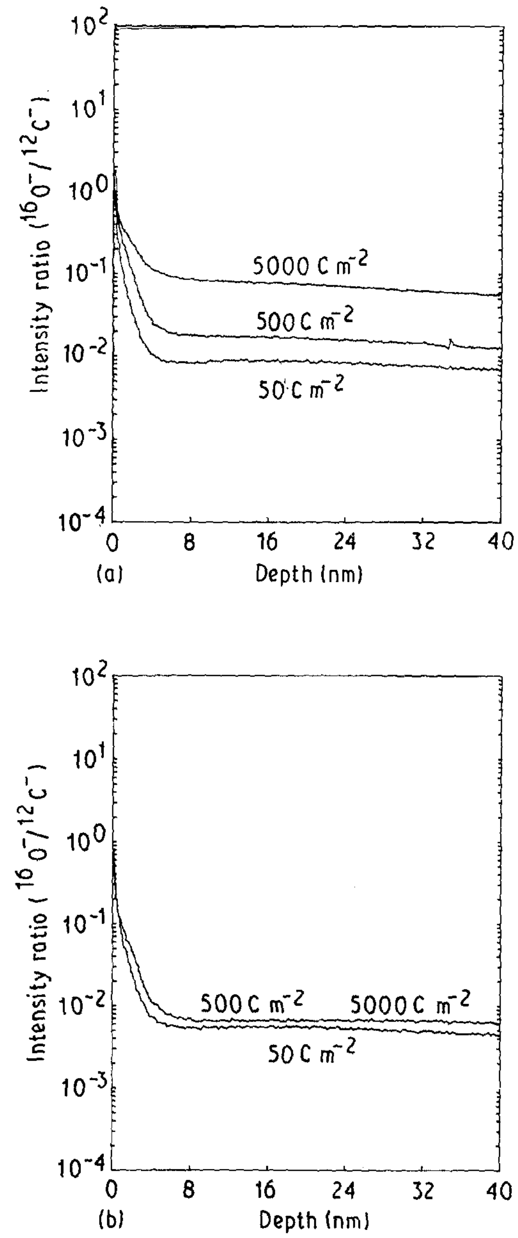

Figure 4 Depth profiles of oxygen in anodically treated edge surfaces of PG. (a) Acid; (b) alkaline electrolytes.

electrolyte at 500 C m^{-2}. Judging from the amount of functional groups only, the acid-type electrolyte is expected to be more efficient in increasing the interlaminar shear strength of the composites than the alkaline electrolyte. Fitzer and Rensch [9], however, have reported that an alkaline electrolyte improves the adhesion between CFs and epoxy resin matrix much better than an acid one. This suggests that there are other factors to be considered in addition to covalent bonds with functional groups in improving the interlaminar shear strength of the composites.

Kozlowski and Sherwood [7] report that acidic solutions give rise to substantial surface oxidation, in contrast to alkaline solutions. In addition to the substantial surface oxidation, the above results obtained by SIMS suggest that acidic solutions give rise to the internal oxidation of well graphitized materials such as high-modulus PAN-based CFs. Fitzer *et al.* [5] have assumed that acidic solutions cause an intercalation of some sulphuric acid into the highly oriented layers of high-modulus CFs. Actually, in the case

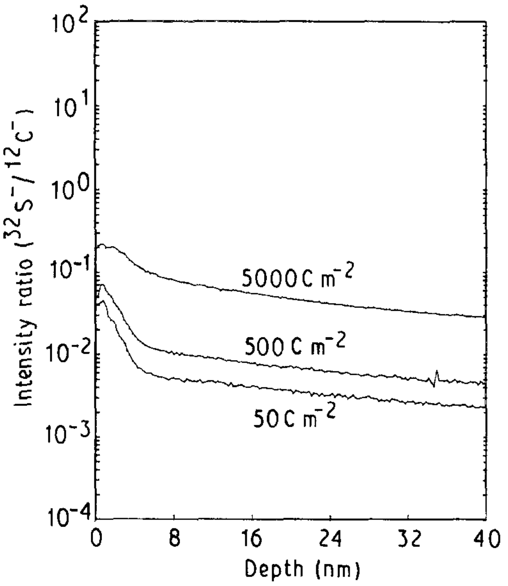

Figure 5 Depth profiles of sulphur in the anodically treated edge surfaces of PG in acid electrolyte.

of anodic treatment of the acid electrolyte, the increase in sulphur concentration is observed from the edge surface to the depth of 40.0 nm as the level of treatment increases (Fig. 5). The increase in oxygen concentration in the region of 0–40 nm and the destruction of the edge structure detected by Raman spectra are considered to be caused by an intercalation of sulphuric acid into the oriented graphite layers. In the case of anodic treatment in the alkaline electrolyte, the traces of intercalation are not found over the range of 0–5000 C m^{-2}. Thus the destruction of the surface structure in anodic oxidation may be caused by an intercalation of electrolyte into the oriented carbon layers. The destruction of the edge structure in CF surfaces anodically treated in acid-type solutions thus reduces the interlaminar shear strength of the resulting CFs and epoxy resin matrix composites.

Moreover, Kozlowski and Sherwood [7] have reported that clouding in an alkaline solution occurs during anodic oxidation of CFs. On the other hand, the anodic oxidation of PG in the alkaline solution used in this study gives no clouding of the alkaline solution. PG has a much narrower 1580 cm^{-1} band and a much smaller 1355 cm^{-1} band, compared with the 1580 and 1355 cm^{-1} bands of high-strength PAN-based CFs [13]. From these characteristics of Raman bands, it can be seen that PG has a much more graphitized structure than CFs such as T1000 and AS4. A highly graphitized structure such as PG seems not to be readily attacked by anodic oxidation in the alkaline electrolyte. The clouding of the solution is considered to be closely related to the presence of less graphitized and weakly bonded structure in the CF surface layer. Probably, during anodic oxidation in an alkaline electrolyte, the less graphitized structure is removed from the CF surfaces into the alkaline electrolyte, causing clouding of the electrolyte. When an alkaline electrolyte removes the weak structure from the CF surfaces during the treatment and adds the functional groups mentioned above on the new strong surface structure, the interlaminar shear strength of the composites may increase rapidly. On the other hand, in the case of the acid electrolyte, a part of the functional groups is possibly added on the edge surface damaged by anodic oxidation and the edge sites of the weak structure initially present in the CF surface layer. In this case, it seems that the rise in interlaminar shear strength cannot be related only to the number of functional groups.

4. Conclusions

The anodic oxidation in the alkaline solution has the following influences on the structure of PG surfaces.

1. Oxygen functional groups, mainly hydroxyl groups, capable of forming covalent bonds with epoxy groups are added on the edge surface of PG.
2. The destruction of graphite surface structure does not take place, even at the high treatment level of 5000 C m^{-2}, unlike the case for acid solutions.
3. Oxidation is limited only to the edge surface up to the 5000 C m^{-2} treatment level.

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