

Anodic surface oxidation mechanisms of PAN-based and pitch-based carbon fibres

A. FUKUNAGA*

Nippon Oil Company, Ltd., 8, Chidori-cho, Naka-ku, Yokohama, 231 Japan

S. UEDA, M. NAGUMO

Laboratory for Materials Science and Technology, Waseda University, 8-26, Nishiwaseda 2-chome, Shinjuku-ku, Tokyo, 160 Japan

E-mail: fukunaga.akhiko@necc.nisseki.co.jp

In order to clarify the differences in the anodic surface oxidation mechanisms of PAN-based and pitch-based carbon fibres, the fibres were oxidized in an electrolyte and characterized using the coulometric method, X-ray photoelectron spectroscopy, laser Raman spectroscopy, and X-ray diffraction. The interfacial bonding strength to an epoxy resin was evaluated based on the interlaminar shear strength (ILSS). The results showed a good correlation between the differential double layer capacities, which were measured with the coulometric method, and the ILSS values of PAN-based high tensile strength carbon fibres (PAN-HTCFs), PAN-based high modulus carbon fibres (PAN-HMCFs), and pitch-based high modulus carbon fibres (pitch-HMCFs). Their morphologies for the anodic oxidation were as follows: PAN-HTCFs are anodized homogeneously; pitch-HMCFs are selectively oxidized and promote crevice etching; and PAN-HMCFs resist crevice etching due to the many defects in the hexagonal network. © 1999 Kluwer Academic Publishers

1. Introduction

It is a well known fact that most carbon fibres are oxidized to obtain sufficient adhesion to epoxy resin matrices [1–5]. However, excessive surface treatment reduces the longitudinal strength of the composites [6]. In particular, high modulus carbon fibres do not possess good wettability, so they have to be adequately treated in order to provide good mechanical properties. In our previous study [7], it was proved that the coulometric method [8, 9], an electrochemical method, was very useful for investigating the anodic oxidation mechanisms of carbon fibres. In this study, the differences in the anodic oxidation morphologies of PAN-based and pitch-based carbon fibres were clarified mainly by means of the coulometric method.

2. Experimental

2.1. Sample preparation

PAN-based high tensile strength carbon fibre (PAN-HTCF), PAN-based high modulus carbon fibre (PAN-HMCF), and pitch-based high modulus carbon fibre (pitch-HMCF) [10] whose mechanical properties are shown in Table I were prepared for anodic surface oxidation. The pitch-HMCF has nearly same tensile modulus as the PAN-HMCF. The surfaces of the three kind samples were anodized in 0.1-N NH_4HCO_3 solution by their specific electric charges [electric charge (C) per unit area (m^2)].

2.2. Materials characterization

The surface treated samples and untreated samples were unidirectionally impregnated with epoxy resin consisting of tetraglycidyl diamine diphenylmethane (MY720 Chiba-Geigy), methyl nadic anhydride, and 2, 4, 6-trisdimethylaminomethyl-phenol at 46, 52, and 2 parts by weight, respectively. The samples were cured at 120 °C for 3/4 hours and post-cured at 180 °C for 2 hours. The debonding strength between the fibres and the epoxy resin was evaluated from the interlaminar shear strength (ILSS) using the short beam method.

In order to determine the electrical components on the surface, the differential double layer capacity (C_d) and polarization resistance (R_p), the carbon fibres were immersed in a Clark-Lubs buffer solution (pH 7.2) and measured rapidly and nondestructively using a coulometric apparatus (Hokuto Denko HK201) [7].

The surfaces of the samples were analyzed using X-ray photoelectron spectroscopy (XPS). The spectrometer, which had a monochromatized AlK_α X-ray anode (10 kV, 30 mA), was used in a vacuum of 1×10^{-7} Pa. Laser Raman spectroscopy (Nihon Bunko Kogyo NR-1100) was also employed in order to estimate the surface crystalline sizes corresponding to L_a from the intensity ratio of the Raman spectrum at D-line (1360 cm^{-1}) to that at G-line (1580 cm^{-1}), R [11]. The structural parameters for these fibres were also characterized by powder X-ray diffraction (XRD) using CuK_α α -radiation.

* Present address: Nippon Oil Engineering and Construction Co., Ltd., 1-8, Sakuragicho, 1-chome, Naka-ku, Yokohama, 231 Japan.

TABLE I Mechanical properties of carbon fibres

	Tensile strength (GPa)	Tensile modulus (GPa)
PAN-HTCF	3.61	245
PAN-HMCF	2.93	392
pitch-HMCF	3.44	401

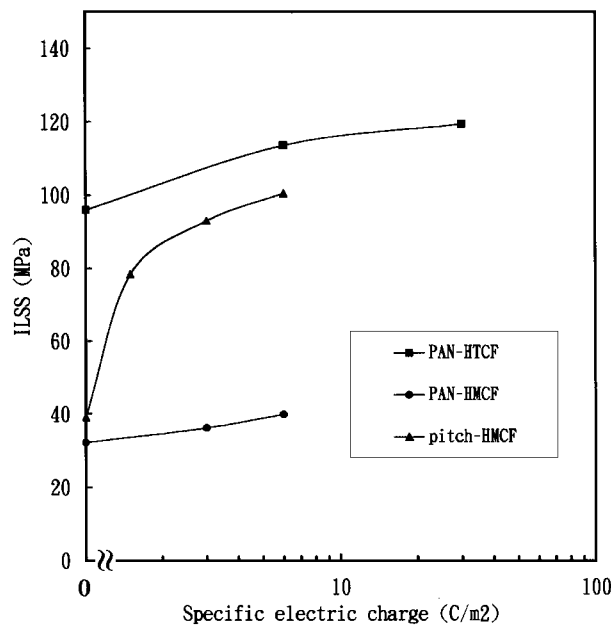


Figure 1 ILSS vs. specific electric charge of surface treatment.

3. Results and discussion

3.1. Anodic oxidation effect

Fig. 1 shows the relationships between the ILSS value as the anodic oxidation effect and the specific electric charge of the surface treatment. The PAN-HTCF with low tensile modulus exhibits a high ILSS value (950 MPa) without being anodized, and the ILSS values further increase slowly with the increase in the specific electric charges. On the other hand, the untreated PAN-HMCF and the untreated pitch-HMCF with high modulus present low ILSS values (32.0 and 38.5 MPa, respectively). However, the ILSS values of the pitch-HMCF increases with a small amount of specific electric charges, while the PAN-HMCF shows different behavior from the pitch-HMCF and could not achieve adequate ILSS values through the specific electric charges 3 and 6 Cm^{-2} . Since the PAN-HMCF and pitch-HMCF are 6 and 9 μm in diameter, respectively, the interfacial area of the ILSS specimen for PAN-HMCF is larger than that for pitch-HMCF. Thus, PAN-HMCF might have an advantage for adhesion to an epoxy resin when compared with pitch-HMCF. However, the results suggest that the adhesion of PAN-HMCF is much lower than that of pitch-HMCF with the same specific electric charge.

3.2. Characterization

In our previous research on thin metal films [9] and pitch-HMCFs [7] using the coulostatic method, it was revealed that the measurement values C_d and R_p could

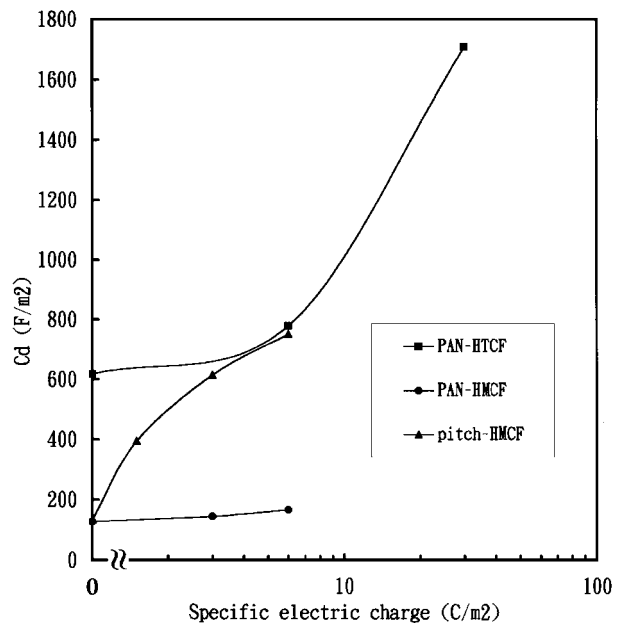


Figure 2 C_d vs. specific electric charge of surface treatment.

sensitively represent slight surface changes caused by oxidation; the values of C_d were related to the apparent surface area and the values of R_p depended on the appearance of the chemically unstable prismatic surface. Therefore, C_d and R_p on the surfaces of those samples were measured by the coulostatic method.

The relationships between the C_d and the specific electric charge are shown in Fig. 2. The C_d tendencies for all fibres, PAN-HTCF, PAN-HMCF, and pitch-HMCF, are very similar to the ILSS tendencies in Fig. 1. The C_d of the anodized PAN-HTCF with 60 Cm^{-2} is much higher than the others.

To confirm the similarity, the ILSS values were plotted against the C_d values for all samples in Fig. 3. As a result, it was found that there was a strong linear relationship for the PAN and pitch-based fibres when the C_d was lower than 750 Fm^{-2} . When C_d became higher

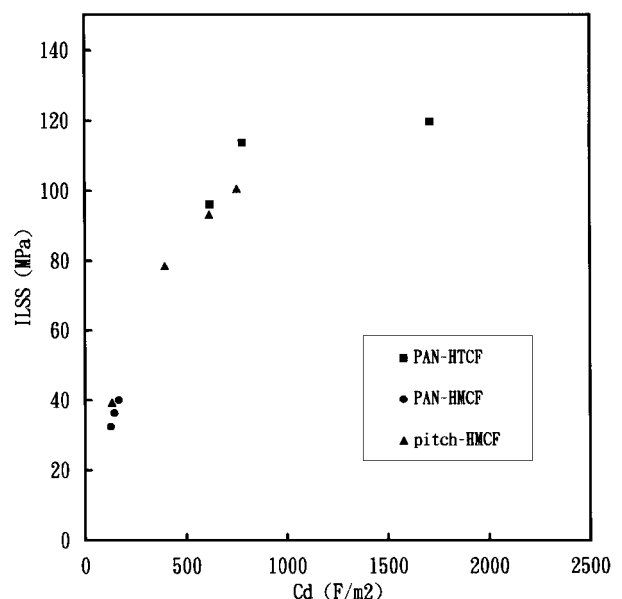


Figure 3 ILSS vs. C_d .

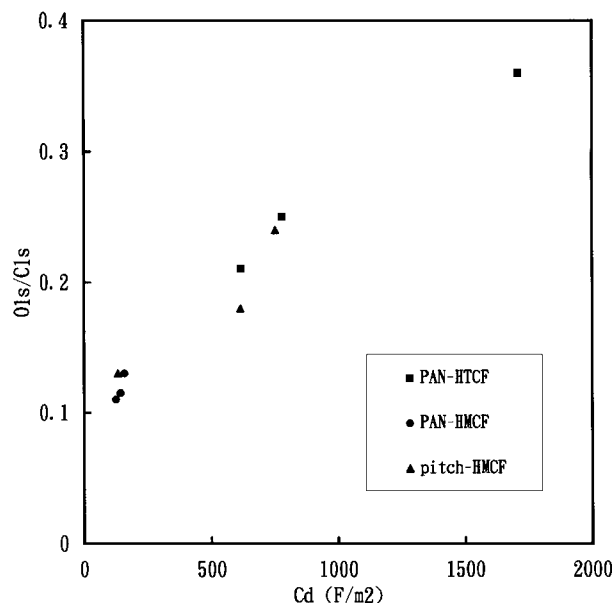


Figure 4 O1s/C1s vs. C_d .

than 750 Fm^{-2} , the slope decreased. The inflection point seems to be around $C_d = 750 \text{ Fm}^{-2}$. In order to investigate the cause of this good relationship, the surface oxygen concentration of the fibres was analyzed by XPS. Fig. 4 shows the relationship between O1s/C1s and C_d . The results suggest that a good correlation was obtained because the oxidation on the carbon fibre surface induces an increase in the apparent surface area.

The relationship between the other electrical component on the surface, R_p , and the specific electric charge is shown in Fig. 5. Unlike the untreated pitch-HMCF, the untreated PAN-HTCF and PAN-HMCF exhibit low R_p values and the changes of their R_p by surface oxidation are much smaller than for pitch-HMCF. Therefore, it is assumed that micro cells have been originally formed on the untreated PAN-based carbon fibres. On the other hand, the untreated pitch-HMCF exhibits a

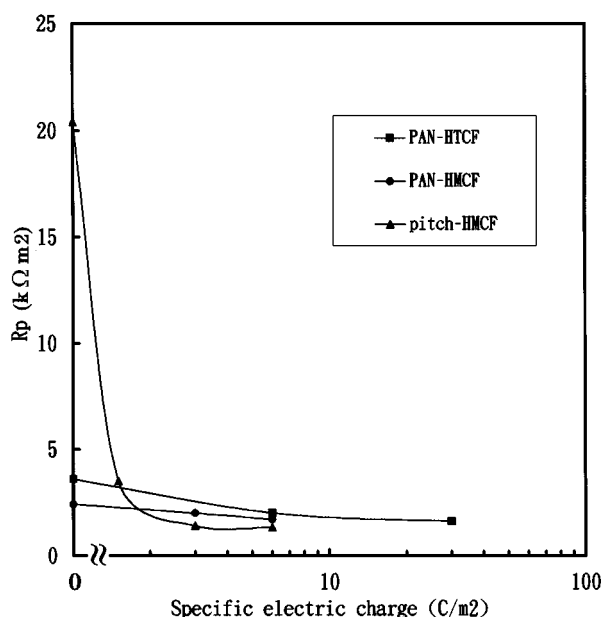


Figure 5 R_p vs. specific electric charge of surface treatment.

TABLE II Structural parameters for carbon fibres

	d(002) (nm)	Le(002) (nm)	La(110) (nm)	Surface La by Raman ^a (nm)
PAN-HTCF	0.357	1.6	—	—
PAN-HMCF	0.344	5.5	4.8	10.2
pitch-HMCF	0.343	8.1	4.9	5.2

^aThe surface La was estimated from the Tuinstra relationship ($La = 4.4R$).

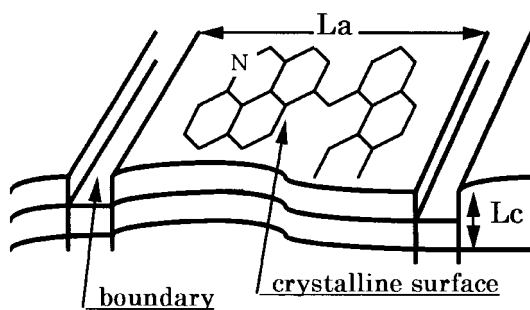
large R_p value, and this value immediately decreases with the increase in the specific electric charge. The different behavior of R_p might come from the difference in the original surface structure.

3.3. Structural difference

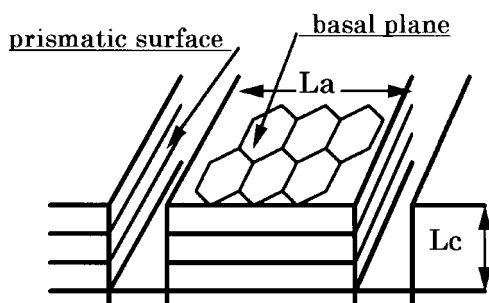
The microstructural parameters of the three kinds of fibres are shown in Table II. From the d(002) space values and crystalline sizes, it was confirmed that the PAN-HTCF with the lowest tensile modulus had the lowest graphitization degree and the smallest crystalline size among the three kinds of fibres and that the PAN-HMCF had nearly the same graphitization degree as the pitch-HMCF. However, the crystalline sizes for PAN-HMCF were quite different from those of pitch-HMCF; the surface crystalline size, La , obtained by laser Raman spectroscopy for PAN-HMCF was twice as large as the average crystalline size, $La(110)$, obtained by powder XRD, although the surface La for pitch-HMCF was almost the same as the average $La(110)$. Thus, PAN-HMCF seems to have a heterogeneous structure, and its surface should be covered with larger crystallites than its interior. On the other hand, from the values of $Lc(002)$ it turned out that the graphite layer of PAN-HMCF is thinner than that of pitch-HMCF.

3.4. Difference of anodic oxidation mechanisms for PAN-based and pitch-based carbon fibres

Because PAN-HTCFs are composed of small crystallites, they have many chemically active sites which can be homogeneously anodized so that they obtain the adhesion to the resin gradually with the increase in the specific electric charges. For PAN-HMCFs and pitch-HMCFs with nearly the same modulus, we would like to propose the different anodic oxidation models shown in Fig. 6a and b. The surface of PAN-HMCF is covered by larger La (graphite layer size) and thinner Lc (graphite layer thickness) than that of pitch-HMCF. However, the low R_p value for untreated PAN-HMCF implies that the graphitic layer is not a perfectly chemically stable basal plane due to the original precursor. The hexagonal network might include heterogeneous atoms or vacancies and be curved so that the potential difference between the crystalline surface and the boundary might be small. Thus, crevice etching seems to be difficult to occur on PAN-HMCF with the large crystalline size as shown in Fig. 6a. Therefore, it is not possible to easily make strong bonding sites, like prismatic surfaces, to the epoxy resin.



(a) PAN-HMCF



(b) pitch-HMCF

Figure 6 Schematic models of the anodic oxidation mechanism: (a) PAN-HMCF; (b) pitch-HMCF.

On the other hand, since the untreated surface of pitch-HMCF is covered with a stable basal plane, there is a large potential difference between the basal plane and the crystal boundary. Therefore, the selective oxidation and appearance of the prismatic surface in the crystal boundary easily occur for pitch-HMCF as shown in Fig. 6b. Therefore, a high ILSS value can be obtained with a small amount of specific charge.

4. Conclusion

The relationships between the ILSS value and specific electric charge for PAN-HTCF, PAN-HMCF, and pitch-HMCF are quite different from each other; an untreated PAN-HTCF with a high ILSS value further increases with the increase in specific electric charges for the

anodic oxidation, an untreated pitch-HMCF with a low ILSS value increases rapidly in particular at the early stage, and an untreated PAN-HMCF with also a low ILSS value increases slightly. In spite of the differences among these three kinds of carbon fibres, there is a strong linear correlation between C_d by the coulometric method and the ILSS values when C_d was lower than 750 Fm^{-2} . PAN-HTCFs are anodized homogeneously, while pitch-HMCFs are selectively oxidized and promote crevice etching, which can become strong bonding sites to epoxy resin. On the other hand, PAN-HMCFs resist the crevice etching due to the defects in the hexagonal network.

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