

OXIDATIVE MODIFICATION OF CARBON FIBER SURFACES

A.S.Tikhomirov, N.E.Sorokina, O.N.Shornikova and V.V.Avdeev

Chemistry Department, Lomonosov Moscow State University, Moscow, 119991

Introduction

Carbon fibers (CF) are known to be an important reinforcement component of many composites [1]. The properties of the composites depend both on components properties and the binding strength between them [2]. To increase adhesion between carbon fiber and matrices oxidative modification can be used. In this kind of process the number of changes takes place. They are specific surface growth, appearance of roughness, oxygen containing groups formation, polarity increase and so on. All of them lead to better binding between components in the composite. Therefore there are many techniques to obtain materials with specific characteristics. Our work deals with chemical modification of carbonized PAN-based CF by direct chemical reaction with fuming nitric acid, anodic oxidation in concentrate HNO_3 and in its solutions.

Experimental

Intermediate modulus carbonized PAN-based carbon fibers produced by Zoltec was used. For cleaning of the fiber surface acetone flushing was applied. The flushing time was of 24 hours. Then CF were predried at 100°C in air (2 hours).

Anodic oxidation of CF in HNO_3 solutions was carried out in a three-electrode Teflon cell with an Ag/AgCl reference electrode (Fig. 1). A disk-shaped titanium indicator electrode of 20 mm in diameter, with the carbon fiber powder uniformly spread over its surface by applying a controlled load of 200 kPa, served as an anode, and another platinum electrode served as a cathode.

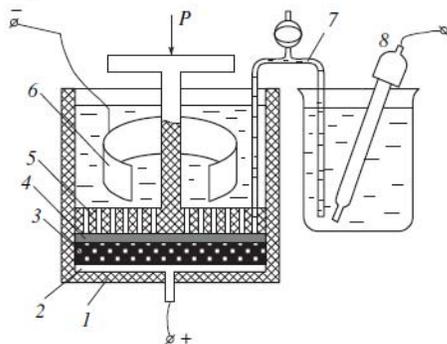


Fig.1 Scheme of the electrochemical cell for anodic oxidation of carbon fiber: (1) Teflon case, (2) Ti current terminal, (3) carbon fiber anode, (4) propylene cloth diaphragm, (5) perforated Teflon piston, (6) Pt cathode, (7) electrolytic seal (Luggin capillary), (8) reference electrode.

Oxidation was performed in a galvanostatic mode at currents in the range of 100 mA ($j = 32 \text{ mA/cm}^2$) for 1.4–8.3 h at room temperature using a PI-50 potentiostat. The potential was monitored by a KSPP-4 potentiometer. The oxidation products were hydrolyzed in distilled water (100 ml of H_2O per gram of carbon fiber) with a constant stirring and then washed on a filter. The modified CF was dried at 60°C in air (24 hours). One part of it was thermally treated at 400°C in air (1 hours). The CF samples were studied by SEM, AFM, TG-methods, strength tensile examine, specific surface area, Raman-spectroscopy and others.

Results and Discussion

Table 1 shows modification conditions and characteristics of the modified carbon fiber samples.

Table 1. Characteristics of carbon fibers according to modification method

Sample	Acid conc.	τ (h)	Q^c	T^a	S_{BET} (m^2/g)	-dm ^b (%)	Strength (GPa)
Orig.	-	0	0	No	<1	No	3.1
98	98%	1.4	0	No	<1	No	2.9
98	98%	8.3	0	No	1.1	No	2.4
500-60	60%	1.4	500	No	1.3	No	2.7
500-98	98%	1.4	500	No	1.4	No	2.6
1500-60	60%	8.3	1500	No	1.7	No	2.2
1500-98	98%	8.3	1500	No	1.7	No	2.1
98	98%	8.3	0	Yes	6.4	8.0	1.9
500-60	60%	1.4	500	Yes	8.5	10.3	1.6
500-98	98%	1.4	500	Yes	10.2	11.8	1.4
1500-60	60%	8.3	1500	Yes	10.8	12.2	1.3
1500-98	98%	8.3	1500	Yes	14.2	16.6	1.0

^aThermal treatment: 400°C in air (1h)

^bMass decrease resulted by thermal treatment.

^cSpecific quantity of electricity (coulomb/g)

The specific surface area was used as an efficiency value of modification method. As showed in Table 1, original (after surface cleaning) carbon fiber had low S_{BET} (less that 1 g/m^2). The fuming nitric acid treatment allowed to increase specific surface area of the samples, however, better results were obtained in case of multiply concentrate acid and anodic oxidation. It was found fibers modified in nitric acid (both we used anodic oxidation or not) after thermal treatment acquired more defective surface ($S_{\text{BET}} = 6.4\text{--}14.2 \text{ g/m}^2$ in the table 1).

Similar to process of oxidation graphite in strong Brensted acids schemes for carbon fiber oxidation can be supposed. Carbon fibers gain a few delocalize positive charges under reaction with an oxidant (nitric acid and current in our case). In nitric acid solution weak electrostatic binds of carbon matrices with $\text{NO}_3^-\cdot\text{aq}$ can be formed. Sorbed $\text{NO}_3^-\cdot\text{aq}$ is removed due to hydrolysis, positive charge is localized and oxygen-contained groups are formed. Anodic oxidation favour to Cp^+ macrocation formation, because larger amount of

oxygen-contained groups is formed. Under thermal treatment $-COH$, $-COOH$, $-CH_2OH$ and other groups are easily oxidized to CO or CO_2 . This process leads to appearance of a large amount of defects and specific surface area increasing [3].

Fig.2 shows SEM images of samples of original and modified carbon fibers. As it is shown in Fig. 2a, original carbon fibers had smooth surface. The action by fuming nitric acid gave friable surface with not enlarge defects amount (fig.2b). The carbon fiber with more defective surface can be obtained by anodic oxidation in nitric acid solutions. The sample has not only injury of surface but also laminations scales of fiber (fig.2c). Thermal treatment results in very damaged carbon fiber (fig.2d).

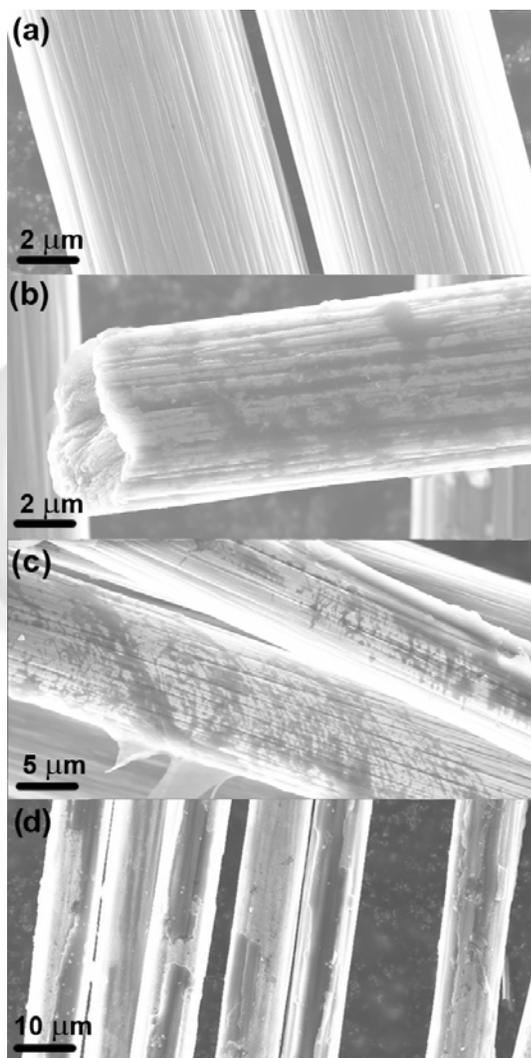


Fig.2. SEM images of the surface of the original and modified carbon fibers: (a) original CF, (b) CF modified in by 98% HNO_3 for 8.3h (CF-98), (c) CF modified by anodic oxidation in solution of 60% HNO_3 (CF-1500-60), (d) CF modified by oxidation in solution of 60% HNO_3 with thermal treatment (CF-1500-60 after thermal treatment).

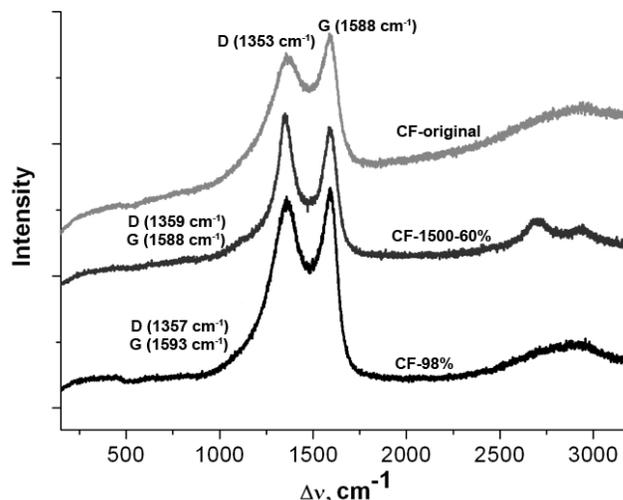


Fig.3 Raman-spectra of original and modified carbon fiber samples.

Raman spectroscopy was applied to estimate faultiness of CF samples [4]. All of them (including original CF) had a large amount of defects (intensive D-band on curves, fig.3). The G and the D bands in the CF-98 spectrum are almost equivalent in intensity. For CF-1500-60 the D band intensity is more than the G band intensity. It is one more evidence of the greater faultiness of fiber modified by anodic oxidation in HNO_3 solution.

Conclusions

In present work modification carbon fiber methods of nitric acid oxidation were studied. We found that exposure to even 98% HNO_3 does not permit a sufficiently modified fiber. The significant increase in specific surface area was achieved by anodic oxidation in solutions of nitric acid with subsequent thermal treatment. It should be noted that apart from increasing the surface modification significantly reduces the strength. Thus, to create the most durable composites it is necessary to find the optimum ratio of modified surface-strength fibers.

Acknowledgment. Authors are indebted to A.A. Eliseev for the Raman-scattering-investigations and Dr. E.Kudrenko for SEM investigation.

References

- [1] Morgan P. Carbon fibers and their composites. L.: Taylor and Francis. 2005. 1166 p.
- [2] Fitzer E, Geigl KH, Huttner W, Weiss R. Chemical interactions between the carbon fibre surface and epoxy resins. Carbon 1980; 18: 389-93.
- [3] Sorokina NE, Maksimova NV, Avdeev VV. Anodic Oxidation of Graphite in 10 to 98% HNO_3 . Inorganic Materials 2001; 37(4):360-65.
- [4] Montes-Mora'n MA, Young RJ. Raman spectroscopy study of HM carbon fibres: effect of plasma treatment on the interfacial properties of single fibre/epoxy composites. Carbon 2002; 40: 845-55.