Modification of carbon fiber surfaces by direct fluorination

Yong-bo Chong and Hidehiko Ohara

Research Institute for Applied Science, 49, Tanaka Ohi-cho, Sakyo-ku, Kyoto 606 (Japan)

Abstract

The wettability of carbon fiber was improved without decrease of tensile strength by slight fluorination The adhesive property of such fluorinated fibers with epoxy resin was also evaluated, and it was found that the higher the wettability of the carbon fiber, the greater the adhesion of fiber

Introduction

Reinforcement in composites is only achieved by efficient stress transfer between fiber and matrix. Such stress transfer can be realized by mechanical interlocking, physical adhesion and chemical bonding.

A better adhesion of carbon fibers to the polymer matrix is firstly achieved by improving the surface of the carbon fibers to allow a good wettability and physical interlocking of the fibers with the matrix, and secondly by forming surface groups on the surface of carbon fiber and surface active resins [1]. Various methods employed to improve the surface of carbon fibers include polymer grafting to the surface [2, 3], etching of the fibers by air oxidation [1], anodic oxidation and nitric acid treatment [5–7]. In the case of oxidation treatment, the decrease in tensile strength of carbon fiber due to etch pits on the surface is a problem [8].

Recently fluorine gas has been used as a surface treatment for many kinds of organic and inorganic plastic materials, because of its very high reactivity. We investigated the hydrophilicity of slightly fluorinated carbon fiber as a new method of surface treatment, and found that through this treatment, wettability of the surface of carbon fibers increased drastically compared with oxidation treatment without decrease in tensile strength. This new method is a dry process, and requires a relatively simple device compared with such methods as anodic oxidation.

In this report, we will describe the effect of fluorine pressure and treatment time on the wettability, which is investigated by the contact angle using the Whilhelmy method [9], and the adhesion of this fluorinated carbon fiber with epoxy resin by τ^*

Experimental

Materials

Experiments were performed with pitch-based carbon fibers without sizing agents; the epoxy used was the diglycidylether of bisphenol A (EP-828, Shell). The curing agent was hexahydrophthalic anhydride (HHPA), and the catalyst benzyldimethylamine (BDMA).

Treatment of carbon fiber with fluorine gas

Fluorine gas was supplied by Daikin Kogyo Co. at 99.7% purity. The impurity was almost only nitrogen and the amount of hydrogen fluoride was under 0.01 mol%. Trace amounts of hydrogen fluoride in the fluorine gas were removed by sodium fluoride pellets heated at 100 °C. A schematic of the device for fluorination is shown in Fig. 1. The reaction tube and vessel were made of nickel, with pipe and valves of stainless steel. The carbon fiber (~ 0.2 g) within the Ni vessel was inserted into the reactor, and the system was evacuated to $\sim 10^{-2}$ mmHg. Fluorine gas was introduced to the system from a buffer tank for the fluorine reservoir. After reaction, fluorine gas was removed quickly through the exhaust line from the reactor

Measurement of contact angle

For investigation of the wettability of carbon fibers, we measured the contact angle to water using the Whilhelmy method

The principle of the method is explained in Fig. 2 The adhesive force, F_A, was measured at the moment when the fiber touched the liquid. By use of the equation in Fig. 2, the wetting angle can be evaluated from the experimental data of F_A and F_R. On using only a single monofilament, F_A (and F_R) were too small to detect, so we used 15 monofilaments for measurement.
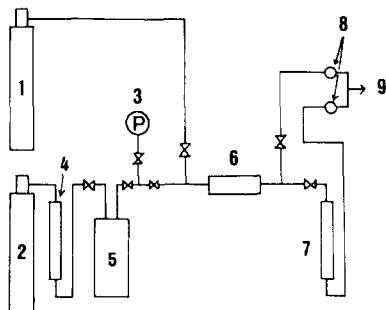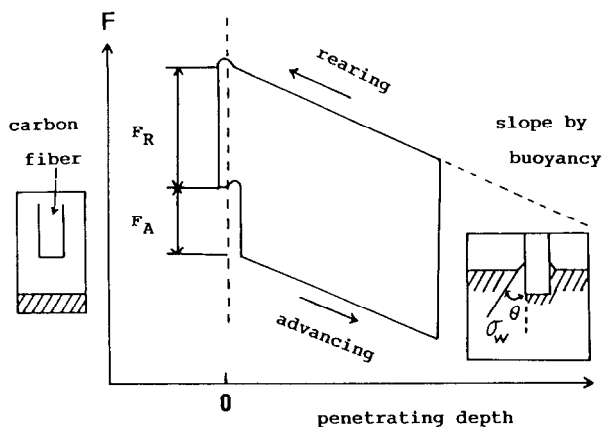

Fig 1 Schematic diagram of fluorination reactor 1 N_2 gas cylinder, 2 F_2 gas cylinder, 3 pressure gauge, 4 HF absorber 5 buffer tank, 6 reactor, 7 F_2 absorber, 8 glass cock 9 to rotary pump

F_A , F_R = adhesive force

Fig. 2. Principle of contact angle measurement by Whilhelmy method, where:

$$\cos \theta = \frac{F}{U} \cdot \sigma_w$$

σ_w: surface tension of liquid (dyne/cm), θ: contact angle (deg), U: circumference of fiber (cm).

ESCA measurement

The changes in the surface of carbon fiber after fluorination were analyzed by ESCA measurement. Spectra were obtained on an ESCA 750 electrometer (Shimadzu Seisakusho Ltd.) with an Mg K$\alpha_{1,2}$ X-ray source (1253.6 eV). We obtained the C 1s, F 1s and O 1s spectra, and calculated the surface chemical compositions of carbon fibers from their peak areas.

Adhesion to epoxy resin

For the investigation of the adhesive property of fluorinated carbon fibers, we measured the interlayer shear strength τ^*.

In Fig. 3, the carbon fiber monofilament is buried in the dumbell shape of epoxy resin, and cured first for 2 h at 85 °C, then 12 h at 150 °C. After curing, the carbon fiber was stretched from both ends until the fiber snapped. The higher the adhesion of the carbon fiber to epoxy resin, the larger the number of parts the carbon fiber is snapped into and the smaller the critical fiber length, l_c. We obtained the value of τ^* using the Kelly–Tyson equation.

Results and discussion

Effect of fluorine pressure on the wettability

The effect of fluorine pressure on the contact angle is shown in Fig. 4. The contact angle of the original fiber to water was 95°. At room
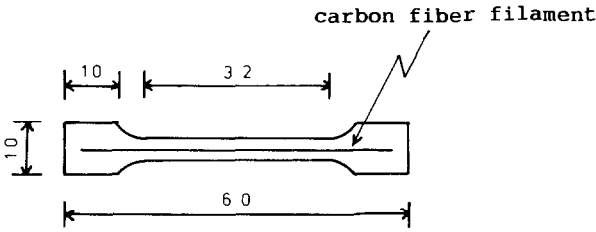
carbon fiber filament

Fig 3 Principle of interlayer shear strength (τ^*) measurement with epoxy resin according to the Kelly–Tyson equation

$$\tau^* = \sigma_f \ d/2 \ l_c$$

where σ_f = tensile strength of carbon fiber monofilaments (25 mm) d = diameter of carbon fiber, l_c = critical fiber length

temperature, 3 min treatment gave an angle of only 77^c. The hydrophilic-ity of carbon fiber was particularly improved by slight fluorination, i.e. up to 50 mmHg fluorine pressure. At higher fluorine pressures, the contact angles tended to increase. It is known that at 600 $^\circ$C, graphite reacts with fluorine to form graphite fluoride $((CF)_n)$ [10–13], which has C–F covalent bonding and hydrophobic character. In the room temperature reaction, it seemed to form some C–F covalent bonding, so the higher the fluorine pressure, the more C–F covalent bonding is formed and the more hydro-phobic the character [14]

Effect of fluorination time on wettability
      The effect of fluorination treatment time on contact angle is shown in Fig. 5. The contact angle was drastically lowered by only a few minutes'
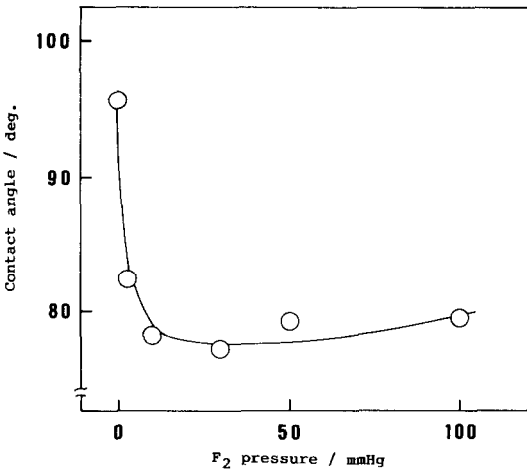

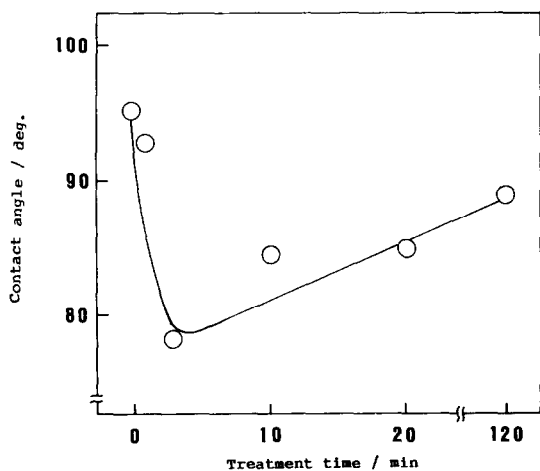Fig 4 Effect of F_2 pressure on contact angle, reaction temperature 25 $^\circ$C, reaction time 3 min

Fig 5 Effect of treatment time on contact angle; reaction temperature 25 °C, reaction pressure 10 mmHg

treatment. The contact angle also tended to increase with longer treatment times, as in the case of greater fluorine pressure. As the treatment enhanced the wettability of carbon fibers sufficiently, the decrease in tensile strength was negligible. The hydrophilicity induced by this method lasts for a least six months.

ESCA measurement of fluorinated carbon fibers

The F 1s ESCA spectra of the surface of the fluorinated carbon fiber is shown in Fig. 6. The binding energy of the F 1s peak is ~688 eV. In the case of a covalent C–F bond such as graphite fluoride, the binding energy
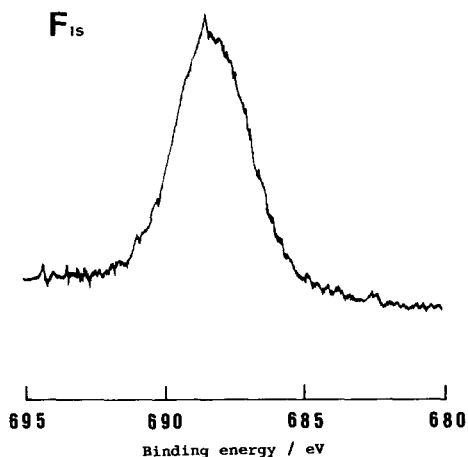

Fig 6 ESCA spectra of F 1s

TABLE 1

Atomic ratios of carbon fiber surface

	Original	Oxidation[a]	Fluorination[b]
C(%)	93 9	70 6	77 3
O(%)	6 1	29 4	12 2
F(%)	0	0	10 5
contact angle (deg)	96	89	78

[a]Oxidation fiber anodic oxidation with 1 N NaOH solution 10 C/g CF
[b]Fluorination fiber fluorination pressure 10 mmHg, reaction time 3 min, reaction temperature 25 °C

of the F 1s peak is ~ 689 eV, and in the case of an ionic fluoride such as LiF, the peak is near 684 eV. That is, the F 1s peak of slightly fluorinated carbon fibers has a value between that of a covalent and that of an ionic bond.

The chemical composition of the carbon fiber surface examined by ESCA is shown in Table 1. The amount of oxygen, O(%), increased on fluorination [5]. The C–H bonding of the surface of the fiber is weakened by the attached fluorine, which has an extremely high electronegativity Due to this effect, oxygen species should be introduced onto the surface of the fiber.

Surface oxidation seems to contribute to the hydrophilicity of slightly fluorinated carbon fibers. However, compared with oxidized fibers, the amount of surface oxygen of the fluorinated carbon fibers is less and the hydrophilicity of fluorinated fibers is better than that of oxidized fibers.
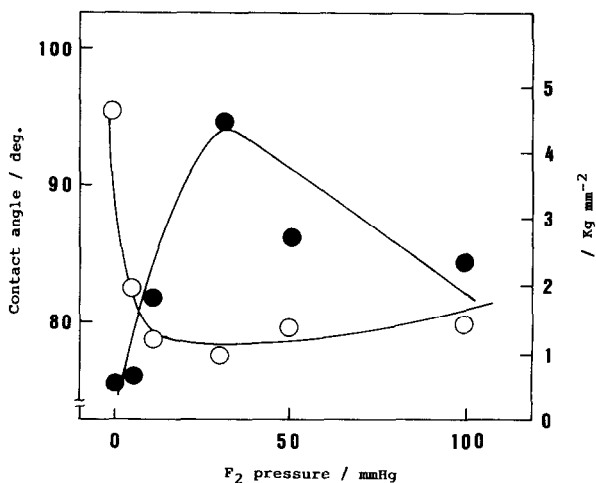

Fig 7. Effect of F_2 pressure on contact angle to water and adhesion to epoxy resin, reaction temperature 25 °C, reaction time 3 min

The effect of fluorine pressure on the adhesion to epoxy resin

The effect of fluorine pressure on the contact angle with water and on the adhesion of fluorinated carbon fibers to epoxy resin is shown in Fig. 7. The lower the contact angle to water with wettability, the higher the adhesion τ^* with epoxy resin. On the surface of fluorinated carbon fibers, there exists more oxygen-containing species to bond with epoxy resin than on the original fiber. Thus in the case of fluorinated fibers, both good wettability and an increase in surface oxygen-containing groups contribute to the good adhesive properties of fluorinated carbon fibers.

Acknowledgements

References

1 D Ehrburger, J J Herqne and J B Donnee, *Proc 4th Conf Industrial Carbon and Graphite*, London, 1974, p 201
2 R. V Subramanian, V Sundram and A. K Patel, *Proc 33rd Annual Technical Conf SPI*, Washington, DC, Section 20-F, 1978
3 G. Riess, M. Bourdeux, M Brie and G Jonquet, *Proc. 2nd Carbon Fiber Conf*, London, 1974, p 52
4 B H Eckstein, *Proc 13th Biennial Conf Carbon*, Irvine, CA, 1977, 433
5 J W Herrick, *23rd Annual Technical Conf SPI Reinforced Plastics/Composite Division*, Washington, DC, Section 16-A, 1968
6 D McKee and V. Mimeault, *Report 70-C-247*, General Electric Co, 1970
7 E Fitzer, K. H Geigl and L M Manocha, *Proc 5th Int Conf Industrial Carbon and Graphite*, London, 1978, p 405
8 L M Manocha, *J Mater Sci*, *17* (1982) 3039
9 E. Fitzer, K H Geigl, W Huttner and R Weiss, *Carbon*, *18* (1980) 389
10 O Ruff and O Bretschneider, *Z Anorg Allgem Chem*, *217* (1934) 1
11 W Rudorff and G Rudorff, *Z Anorg Chem*, *253* (1947) 283
12 N Watanabe, Y Chong and S Koyama, *Nippon Kagaku Kaishi*, (1978) 228
13 N Watanabe and A Shibuya, *Kogyo Kagaku Zasshi*, *71* (1968) 963
14 N Watanabe, H. Takenaka and S Kimura, *Nippon Kagaku Kaishi*, (1975) 1655.
15 P Cadman, J D Scott and J M Thomas, *Carbon*, *15* (1977) 75