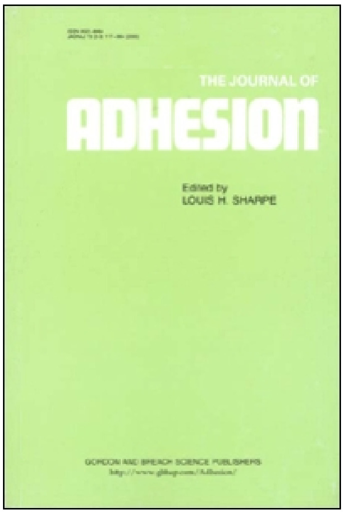

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Wettability and Adhesion Characteristics of Plasma-Treated Carbon Fibers

K. Tsutsumi[a]; K. Ban[a]; K. Shibata[a]; S. Okazaki[b]; M. Kogoma[b]
[a] Toyohashi University of Technology, Toyohashi, Japan [b] Sophia University, Tokyo, Japan

To cite this Article Tsutsumi, K. , Ban, K. , Shibata, K. , Okazaki, S. and Kogoma, M.(1996) 'Wettability and Adhesion Characteristics of Plasma-Treated Carbon Fibers', The Journal of Adhesion, 57: 1, 45 — 53

To link to this Article: DOI: 10.1080/00218469608013642

URL: http://dx.doi.org/10.1080/00218469608013642

J. Adhesion, 1996, Vol. 57, pp. 45–53
Reprints available directly from the publisher
Photocopying permitted by license only

Wettability and Adhesion Characteristics of Plasma-Treated Carbon Fibers*

K. TSUTSUMI†, K. BAN and K. SHIBATA

Toyohashi University of Technology, Tempaku-cho, Toyohashi 441, Japan

S. OKAZAKI and M. KOGOMA

Sophia University, Tokyo 102, Japan

(Received November 30, 1994; in final form February 27, 1995)

The surface free energy (γ_S) of modified carbon fibers was determined by tensiometry and effects of CF_4-O_2 plasma treatment were evaluated. The treatment with the gas mixture in which oxygen was above 40% accelerated preferentially the oxidation of fiber surfaces and the nondispersive component of the surface free energy, γ_S^p, increased to about three times that of the untreated fiber. On the other hand, the treatment with the gas containing CF_4 above 80% induced fluorination and surface species such as $-CF$, $-CF_2$, or $-CF_3$ were formed. The γ_S^p values decreased to almost zero and the dispersive component became about 18 mJ/m^2. The calculated work of adhesion between various fibers and the epoxy resin was well correlated with the interfacial shear strength of the composites formed with these materials.

KEY WORDS: plasma-treated carbon fiber; wettability; work of adhesion; surface free energy; tensiometry; interfacial shear strength

INTRODUCTION

Carbon fibers have been widely used as a reinforcing agent in composite materials. A durable bond is required at the interface between the reinforcing agent and the matrix in order to achieve the mechanical performance of the composite materials. The adhesion strength of the interfacial zone has been known to depend on the thermodynamic work of adhesion, which is closely related to the surface free energy of the fiber and the matrix.[1–10] The quantitative determination of the surface free energy of fibers has been done by measurements of the contact angles of liquids by use of tensiometric methods.[8,10–14]

The purpose of the present study was to evaluate the influences of plasma-fluorination and -oxidation on both the dispersive, γ_S^d, and nondispersive, γ_S^p, components of the surface free energy of PAN-based fibers. The surface characteristics of the fibers were also studied by XPS. The work of adhesion at the interface between the fiber and the epoxy resin matrix was calculated and compared with the interfacial shear strength measured by the fragmentation method.[7,8,10]

---

* One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

† Corresponding Author.

EXPERIMENTAL

1 Materials

The original PAN-based carbon fiber was kindly supplied by Asahi Chemical Industry Co. It had been carbonized at 1553 K and was unsized. The plasma treatment was carried out by the procedures similar to those reported elsewhere.[15] Two aluminum plate electrodes (4 cm in diameter) were placed in a Pyrex® bell jar (about 4 L capacity) and carbon fibers 20 cm in length were placed on the lower aluminum electrode which was grounded. Radio-frequency power of 50 W at 13.56 MHz was applied to the electrodes and a mixture of CF_4-O_2 gas, the total pressure of which was 667 Pa, was allowed to flow in the bell jar. The plasma treatment time was 5 min. The various plasma-treated samples obtained are designated as shown in Table I. They were cleaned in n-hexane in an ultrasonic cleaner and dried at 383 K before tensiometry measurements.

2 Determination of Surface Free Energy

The surface free energy and its components were determined from the contact angle values of reference liquids measured on fibers by tensiometry. The method used was similar to that reported previously.[10, 13] The fiber was suspended vertically from the arm of an electro-microbalance. The other end of the fiber was immersed in the two-phase liquid; either in the lower liquid, at the interface, or in the upper liquid, depending on the level of the liquid surface. The difference (Δp) of the force when the fiber is in the lower liquid, F (formamide), and when it is in the upper liquid, H (n-alkane), can be expressed as

$$\Delta p = C\gamma_{FH}\cos\theta_{SF/H} \tag{1}$$

where C is the fiber perimeter, γ_{FH} the $F - H$ interfacial free energy, and $\theta_{SF/H}$ the contact angle of the liquid F on the fiber in the liquid H. The value of C was determined by wetting the fiber filament in n-perfluorooctane, which can be assumed to wet and spread completely on the fiber because of its low surface free energy (14 mJ/m^2).[13]

TABLE I
Samples used and their preparation method

Sample	CF_4/O_2
F100	100/0
F80	80/20
F60	60/40
F50	50/50
F40	40/60
F20	20/80
F0	0/100

Young's equation for the $S-H-F$ system is

$$\gamma_{SH} = \gamma_{FH}\cos\theta_{SF/H} + \gamma_{SF} \tag{2}$$

where γ_{SH} and γ_{SF} represent the interfacial free energy of $S-H$ and $S-F$ interfaces, respectively. By employing Fowkes' expression, we obtain the following relationship:[10,13,16]

$$\begin{aligned}&\gamma_F - \gamma_H + \gamma_{FH}\cos\theta_{SF/H}\\&= 2(\gamma_S^d)^{1/2}[(\gamma_F^d)^{1/2} - \gamma_H^{1/2}] + I_{SF}^p\end{aligned} \tag{3}$$

where γ_F and γ_H are the surface free energy of F and H, respectively, γ_F^d the dispersive component of γ_F and I_{SF}^p the nondispersive interaction between S and F. The last term can be empirically expressed as[2,13,17]

$$I_{\mathrm{SF}}^p = 2(\gamma_{\mathrm{S}}^p\gamma_{\mathrm{F}}^p)^{1/2} \tag{4}$$

where γ_F^p is the nondispersive component of γ_F. By use of a series of n-alkanes, eqs. (3) and (4) give values of γ_S^d and γ_S^p. In the present study, n-hexane, n-heptane, n-octane, n-decane, n-dodecane and n-hexadecane were used.

The force difference, Δp, was measured by lowering the liquid level (emersion process) at a rate of 0.1 to 0.2 mm/min in which the solid-liquid interface was found to be equilibrated.[13,18] The buoyancy was found to be negligible. Between five and ten monofilaments were measured for each fiber-liquid combination and an average of the values of $\cos\theta$ was determined.

An electrobalance of the Cahn 2000 type was used to record the force change and all experiments were carried out in a thermostated chamber at 298 ± 0.5 K.

The liquids were of guaranteed grade and used without further purification. The values of surface free energy and its components of liquids were taken from the literature.[10]

3 XPS Analysis

XPS measurements were carried out on a Perkin Elmer ESCA 5400 spectrophotometer using the MgK_α line, 1253.6 eV. Fibers of size below 1 mm in length were fixed on "double-stick" adhesive tape and analyzed. The quantitative analysis of the surface elements was carried out by taking into account the cross section[19] and the sensitivity factor.

4 Determination of Interfacial Shear Strength

The fiber-epoxy resin adhesion was analysed by the fragmentation method.[7,8,10] The monofilament embedded in the resin test piece was broken into small fragments by a tensile force. On the basis of the average length (critical fiber length) of the fragments and the tensile strength at this length, the interfacial shear strength was calculated. The epoxy resin used was Epicote EP 828® and was cured with m-phenylenediamine at 393 K.

RESULTS AND DISCUSSION

The contact angle, $\theta_{SF/H}$, of formamide on the fiber in a series of n-alkanes was determined by the procedure mentioned above and the values $[\gamma_F - \gamma_H + \gamma_{FH}\cos\theta_{SF/H}]$ are plotted against $[(\gamma_F^d)^{1/2} - \gamma_H^{1/2}]$ in Figure 1. A linear relationship is obtained for each fiber, and values of γ_S^d and γ_S^p are calculated from the slope and intercept, respectively. These values are shown in Table II and Figure 2. The original fiber had γ_S^d of 35.8 and γ_S^p of 8.5 mJ/m^2, but when the CF_4 content was high in the plasma gas, both values decreased and γ_S^p became almost nil when 100% CF_4 gas was used. The value of 18 mJ/m^2 for γ_S^d and almost zero for γ_S^p corresponds to those of polytetrafluoroethylene.[20] This means that the surface characteristics of sample F100 is similar to those of polytetrafluoroethylene, which is evidenced by XPS analysis.

When the oxygen content increased in the plasma gas, the γ_S^p values increased while γ_S^d remained almost constant. Such a tendency was also observed in the case of surface oxidation of carbon fibers either in the gas or liquid phase.[10] It is of interest that the tendency to become polar by oxidation was preferred over that of becoming nonpolar by fluorination in the region of oxygen concentration above 40%. Since the contact

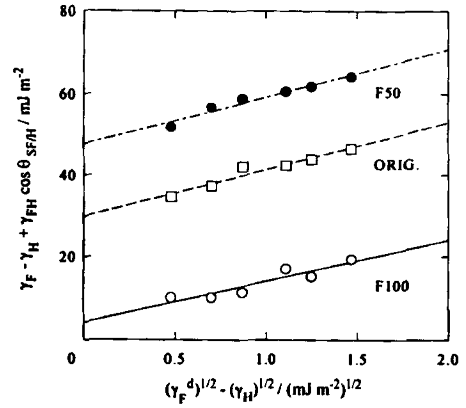

FIGURE 1 A plot according to Eq. (3) for the fiber-formamide-*n*-alkane system.

TABLE II
Surface free energy and its components of carbon fibers

Fiber	Surface Free Energy/mJ/m^2			Polarity[a]
	γ_S^d	γ_S^p	γ_S	
F100	17.7	0.2	17.9	0.01
F80	21.7	0.4	22.1	0.02
F60	36.8	21.8	58.6	0.37
F50	36.9	22.3	59.2	0.38
F40	33.6	24.3	57.9	0.42
Orig.	35.8	8.5	44.3	0.19

[a] defined by the ratio of γ_S^p to the total surface free energy.

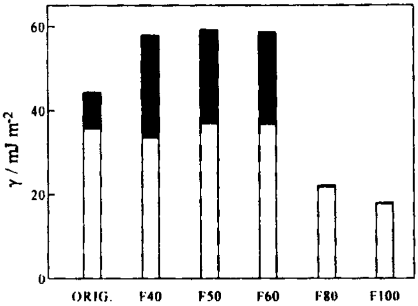

FIGURE 2 Change in surface free energy of carbon fibers treated under different plasma conditions. Open and shaded bars indicate γ_S^d and γ_S^p, respectively.

angle $\theta_{SF/H}$ became zero in samples F20 and F0, equation (2) could not be applied in these cases. Therefore, the quantitative determination of γ_S^d and γ_S^p was unsuccessful by the present method. Since γ_S^d values of F40, F50 and F60 remained unchanged compared with that of the original sample, those of F20 and F0 can also be assumed to be similar and of about 35 mJ/m^2. Therefore, in view of the observation that the contact angle $\theta_{SF/H}$ was zero in samples F20 and F0, the value of γ_S^p of these samples should be higher than 25 mJ/m^2. The polarity, which was defined by the ratio of γ_S^p to the total γ_S, depends largely on the composition of the plasma gas. Therefore, the plasma treatment under the proper conditions can control the wettability of carbon fibers to the desired extent.

The surface species of solids analyzed by XPS are known to be related to their adhesion properties.[21, 22] Figure 3 shows wide-scan XPS spectra of the original and treated fibers. On the original fiber, the O_{ls} peak was observed in addition to that of C_{ls}, which might be due to the formation of oxygen-containing surface groups during the preparation of PAN fiber.[10] When the fiber was treated by a plasma gas of equimolar mixture of oxygen and CF_4, the relative intensity of O_{ls} increased and no fluorine signal was observed. This indicates that oxidation occurred in preference to fluorination in this experimental condition. An increase in the value of γ_S^p shown in Figure 2 could be explained by the increased amount of oxygen-containing functional groups. On sample F60, an increase in O_{ls} signal intensity and the appearance of the F_{ls} signal at about 600 eV occurred simultaneously. The intensity of the F_{ls} signal became significant when the CF_4 mole ratio exceeded 0.8, which coincided with the variation in values of γ_S^d as well as of γ_S^p. On the fiber treated with 100% CF_4 gas plasma, the intense F_{lS} signal was accompanied by a fluorine Auger peak, $F(A)$, at about 600 eV, while the signal due to oxygen almost disappeared.

Figure 4 shows narrow-scan spectra of the C_{ls} region. In the spectra of fibers F60 and F0, a slight shoulder is observed at about 289 eV, which is due to the presence of oxygen species bonded to surface carbons.[10] On the F80 and F100 samples, satellite signals between 290 and 295 eV are observed. These signals could be assigned to fluorine-containing C_{ls} representing surface species such as $-CF$, $-CF_2$, or $-CF_3$[23] and the energy shift was due to the high electronegativity of the F atom.

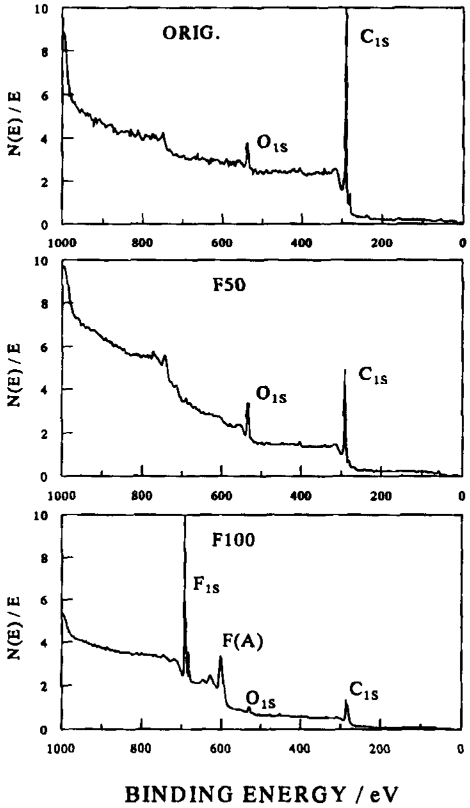

FIGURE 3 Wide-scan XPS spectra of carbon fibers.

In Table III, atomic concentrations of surface elements calculated by graphical integration of corresponding peaks are shown. The results show that fluorination proceeds remarkably with a plasma gas containing more than 80% CF_4, which is consistent with the values of surface free energy. Under such conditions, the fluorination occurred either directly on the surface carbon or was accompanied by the removal of surface oxygen. With a plasma gas containing less CF_4, both fluorination and oxidation occurred or, rather, the latter was predominant. Among samples modified by either oxidation or hydrogen reduction, a linear relation was found between the [O]/[C] ratio and the polarity.[10] Although the [O]/[C] ratio of the F80 sample is similar to that of the original, the surface polarity shown in Table II is significantly less in the former. This indicates that the polar character of the fiber surface is dependent on the [F]/[C] ratio as well as on the [O]/[C] ratio. With an increase in [F]/[C] ratio and a decrease in [O]/[C] ratio, the surface becomes less polar. The reverse concentrations of F atoms observed in F100 and F80 samples may be ascribed to a slight difference in the experimental conditions used for the preparation of the two samples.

Values of the interfacial shear strength (τ) of the carbon fiber-epoxy resin composite measured by the fragmentation method are shown in Table IV. A relationship between the interfacial shear strength and the reversible work of adhesion at the fiber-epoxy

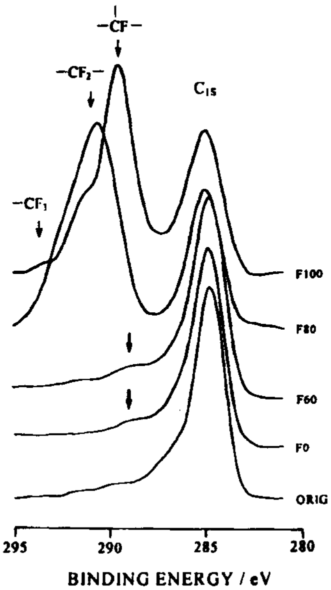

FIGURE 4 Narrow-scan XPS spectra of carbon fibers. Arrows correspond to oxygen species bonded to surface carbons.

TABLE III
Surface atomic concentration of carbon fibers

Fiber	Atomic Concentration/%			[O]/[C]	[F]/[C]
	[C]	[O]	[F]		
F100	60.6	3.3	36.1	0.05	0.60
F80	56.4	6.6	37.0	0.11	0.66
F60	80.3	15.5	4.2	0.19	0.05
F50	85.1	13.6	1.3	0.16	0.02
F40	86.7	13.2	0.1	0.15	0
F0	68.5	31.5	0	0.46	0
Orig.	89.7	10.3	0	0.12	0

resin interface (W_{SE}) is illustrated in Figure 5. The reversible work of adhesion was calculated by eq. (5).

$$W_{SE} = 2(\gamma_S^d \gamma_E^d)^{1/2} + 2(\gamma_S^p \gamma_E^p)^{1/2} \qquad (5)$$

The surface free energy of the epoxy resin, γ_E, and its components, were determined from contact angles of various liquids including n-alkanes, ethylene glycol, formamide and water, and the values obtained were as follows: $\gamma_E^d = 36.7\,\mathrm{mJ/m^2}$, $\gamma_E^p = 7.4\,\mathrm{mJ/m^2}$. The points without label of the sample name in the figure were taken from the data on carbon fibers, modified either by oxidation or by hydrogen reduction, which have been reported in a previous paper.[10] The work of adhesion relates well with the interfacial shear strength, which suggests that the adhesion is highly dependent on the values of

TABLE IV

Reversible work of adhesion (W_{SE}) and interfacial shear strength (τ) of fiber-epoxy resin

Fibers	W_{SE}/mJ/m^2	τ/MPa
F100	53.4	13.7
F80	59.9	19.6
F60	98.9	56.9
F50	99.3	66.6
F40	97.1	55.0
Orig.	88.4	28.0

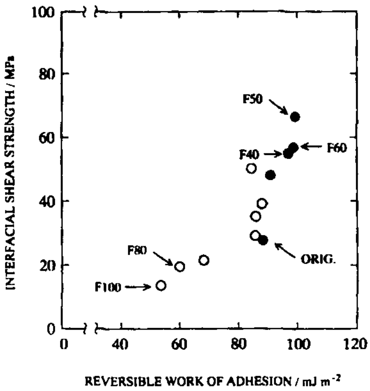

FIGURE 5 Relationship between interfacial shear strength and reversible work of adhesion for carbon fiber-epoxy resin system. See text for details.

surface free energies, as well as on their components, of both phases of the composite material.

From values of γ, γ^d and γ^p of the epoxy resin and the fiber, the imaginary contact angle (θ_{SE}) of the former on the latter can be calculated by use of Young's equation (6) as well as of the extended Fowkes' expression (7) of the S-E system, under the supposition that the former would be a liquid.

$$\gamma_S = \gamma_E \cos\theta_{SE} + \gamma_{SE} \tag{6}$$

$$\gamma_{SE} = \gamma_S + \gamma_E - W_{SE} \tag{7}$$

The closed symbols in Figure 5 represent data for the fibers, on which the epoxy resin could be expected to have zero contact angle. It is evident that a necessary condition to obtain good adhesion at a composite interface is a complete wetting of the fiber by the resin.

Recently, acid-base interactions have been shown to play an important role in an adhesion system.[24] If both the fiber and the resin are amphoteric, in the sense of acid-base character, an additional interaction may exist at the interface. The oxygen-containing functional groups on solid carbon and carbon fiber surfaces can be considered to be of acidic character, though different in their acidic strength.[25-27] Therefore, it seems likely that carbon fibers used here may also be acidic, which leads to the notion that the adhesion with the epoxy resin could be reasonably interpreted by the dispersive and nondispersive interactions. The acid-base interactions of acidic sites of fibers with basic sites of the resin should be involved in the nondispersive interaction.

CONCLUSION

The surface free energy, and its components, of carbon fibers modified by the $CF_4 - O_2$ treatment was determined by tensiometry by use of the two-phase liquid system, n-alkane-formamide. Carbon fiber surfaces were also characterized by XPS. The dispersive component of the surface free energy remained almost constant except for the fibers treated with a CH_4-rich gas mixture. When the fiber was treated with 100% CF_4, its surface became as that of polytetrafluoroethylene. This was also evidenced by XPS analysis. The treatment with the gas mixture in which oxygen was above 40% accelerated surface oxidation of fibers and γ_S^p values increased. The reversible work of adhesion between various carbon fibers and the epoxy resin was well correlated with the interfacial shear strength of the composite with these two materials.

References

1. H. Schonhorn and H. L. Frisch, *J. Polym. Sci.* **11,** 1005 (1973).
2. J. Schultz and A. N. Gent, *J. Chim. Phys.* **70,** 708 (1973).
3. D. H. Kaelble, *J. Appl. Polym. Sci.* **18,** 1869 (1974).
4. K. L. Mittal, *Polym. Eng. Sci.* **17,** 467 (1977).
5. T. Smith, *J. Adhesion* **11,** 243 (1980).
6. D. R. Absolom and A. W. Neumann, *J. Adhesion* **22,** 329 (1987).
7. J. Schultz, L. Lavielle and C. Martin *J. Adhesion* **23,** 45 (1987).
8. J. Schultz, L. Lavielle and C. Martin, *J. Chim. Phys.* **84,** 231 (1987).
9. A. J. Vukov and D. G. Gray, *Langmuir* **4,** 743 (1988).
10. K. Tsutsumi, S. Ishida and K. Shibata, *Colloid Polym. Sci.* **268,** 31 (1990).
11. J. Schultz, M. Cazeneuve, M. E. R. Shanahan and J. B. Donnet, *J. Adhesion* **12,** 221 (1981).
12. J. B. Donnet, M. Brendle, T. L. Dhami and O. P. Bahl, *Carbon* **24,** 757 (1986).
13. K. Tsutsumi and Y. Abe, *Colloid Polym. Sci.* **267,** 637 (1989).
14. M. Tagawa, A. Yasukawa, K. Gotoh, M. Tagawa, N. Ohmae and M. Umeno, *J. Adhes. Sci. Technol.* **6,** 763 (1992).
15. M. Kogoma, H. Kasai, K. Takahashi, T. Moriwaki and S. Okazaki, *J. Phys. D: Appl. Phys.* **20,** 147 (1987).
16. J. Schultz, K. Tsutsumi and J. B. Donnet, *J. Colloid Interface Sci.* **59,** 272 (1977).
17. J. Schultz, K. Tsutsumi and J. B. Donnet, *J. Colloid Interface Sci.* **59,** 277 (1977).
18. Y. K. Kamath, C. J. Dansizer and H. D. Weigmann, *J. Appl. Polym. Sci.* **29,** 1011 (1984).
19. J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* **8,** 129 (1976).
20. D. H. Kaelble, *Physical Chemistry of Adhesion* (Wiley-Interscience, New York, 1970), pp. 153–170.
21. H. F. Webster and J. P. Wightman, in *Acid-Base Interactions: Relevance to Adhesion Science and Technology*, K. L. Mittal and E. R. Anderson Jr., Eds. (Zeist, Utrecht, 1991), pp. 329–342.
22. L. J. Gerenser, *J. Adhes. Sci. Technol.* **8,** 1019 (1993).
23. D. T. Clark, in *Polymer Surfaces*, D. T. Clark and W. J. Feast, Eds. (John Wiley & Sons, New York, 1978), pp. 309–351.
24. F. M. Fowkes, in *Acid-Base Interactions: Relevance to Adhesion Science and Technology*, K. L. Mittal and E. R. Anderson Jr., Eds. (Zeist, Utrecht, 1991), pp. 93–115.
25. H. P. Boehm, *Adv. Catal.* **16,** 179 (1966).
26. J. B. Donnet and R. C. Bansal, in *Carbon Fibers* (Marcel Dekker Inc, New York, 1984), pp. 139–144.
27. R. C. Bansal and J. B. Donnet, in *Carbon Black: Science and Technology*, J. B. Donnet, R. C. Bansal and M. J. Wang, Eds. (Marcel Dekker Inc., New York, 1993), pp. 193–201.