Carbon Fibers: I. Physical Characterization of Pitch and PAN Fibers

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Introduction

Surface properties of carbon fibers are of technological importance to rocket nozzle manufacturing and performance. These properties could influence the adhesion of an impregnant to the fiber surface during the early stages of billet manufacturing, or they may have a direct impact on nozzle recession rates during actual rocket firing. Most of the surface area studies on carbon fibers have been determined from the adsorption measurement of N2 or Kr at 77 K and the use of the Brunauer Emmett and Teller (BET) equation. Depending on the outgasing temperature or heat treatment, e.g., graphitization, the surface area of the final fiber may change. The objectives of the present work were: (1) to explore the effect of some of these parameters on selected carbon fibers, and, meanwhile (2) to construct a new facility at the AFRPL capable of generating a new data base for the surface properties of carbon fibers and carbon-carbon composites.

Experimental

A Micromeritics Digisorb 2500 apparatus was used to measurer the N2 and Kr BET surface areas of the fibers and to perform the pore size distribution analysis. Briefly, a known weight of the fiber (12-15 g) was evacuated overnight at 150°C prior to the adsorption measurements. The equilibrium times for the first 2 and the last 4 data points were 55 and 30 minutes, respectively. Shorter equilibration intervals (10-12 minutes) did not affect the results. The adsorption measurements at 77K were continued up to a relative pressure of 0.2, and the BET equation was used to compute the surface area: [1]

$$\frac{P}{V(P^o-P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}(P/P^o) \qquad (1)$$

where V is the total volume (at STP) adsorbed at an equilibrium pressure P, P^o is the saturation pressure of adsorbate, C is a constant, and Vm is the monolayer volume. Assuming the areas occupied by one gas molecule as 0.162 nm2 for N2 and 0.195 nm2 for Kr, the value of Vm was used to compute the surface area of the fibers. In order to perform the pore size distribution analysis, the adsorption and desorption isotherms in nitrogen at 77K were obtained at P/P^o = 0.050 - 0.985. For each fiber, both isotherms coincided; thus indicating that the fibers have little porosity. The fiber pores were assumed to be cylindrical, and the Kelvin equation [1] was adopted to compute pore volume and internal surface areas of the mesopores, i.e., pores having diameters of 2-60 nm. Several attempts were also made to determine the volume of pores having diameters $>$ 60 nm, from mercury intrusion measurements, using an Aminco 60,000 porosimeter. The fibers used in this study, supplied by the Union Carbide Co., were unsized T-300 (Poly Acrylo Nitrile; PAN) and VSB-32 (pitch). These are referred to here as the as-received (A. R.) fibers. A portion of these fibers were graphitized at 2700°C in argon for 15 minutes. Table I displays the physical properties and chemical analysis of the fibers before and after graphitization. Graphitization increases the density ρ (g/cc), reduces the ash content and practically eliminates the nitrogen. By knowing the average diameter, d (nm), of the fiber and ρ, the Geometric Surface Area (GSA) was calculated as:

$$GSA \quad (m^2/g) = 4000/d\rho \qquad (2)$$

Results and Discussion

Values of N2 and Kr BET surface areas as well as the GSA are summarized in Table I. The results indicate that: (1) all the fibers have a small BET area of about 0.5 m2/g, (2) these fibers may be considered, in general, as non-porous materials, (3) graphitization of the as-received fibers does not affect the BET area, (4) the ratios of BET/GSA are 1.5 for the PAN fiber and 3.35 for the pitch fiber, and (5) the Digisorb 2500 apparatus is reliable for measuring small values of surface areas. The results obtained for pore size analysis show that: (1) the total mesopore volume for all fibers is very small; 0.0014-0-0022 cc/g, (2) graphitization does not significantly affect the pore structure; it neither opened any of the closed pores nor collapsed the existing ones, (3) smaller pores contribute more to the internal surface areas than larger ones, and (4) larger pores contribute more to the total pore volume. It is also noted that the total surface area inside the pores is essentially the same for both fibers and amounts to 0.5 m2/g. This is equivalent to the BET value given above. The results obtained from mercury porosimetry are shown in Figure 1. As the pressure, applied to force mercury above the sample, was increased, the apparent volume of mercury intruded kept increasing up to 800 psia. Thereafter, there was no penetration up to 60,000 psia. The increase in volume penetrated up to 800 psia would suggest the presence of macropores having a corresponding equivalent pore diameter

Table I: Properties of Carbon Fibers: chemical analysis, surface areas, and pore size analysis

Property	T-300 A.R. [a]	VSB-32 A.R. [a]	T-300 - Graphitized	VSB-32 - Graphitized
Type of fiber	PAN	Pitch	PAN	Pitch
# of filaments	3K	2K	3K	2K
Diameter (nm)	6150	10670	5810	10990
Density (g/cc) [b]	1.743	2.037	1.880	2.128
Mercury density (g/cc) [c]	1.767	2.022	1.881	2.182
Moisture %	0.05	0.04	0.10	0.15
C %	95.17	99.58	99.56	99.78
H %	0.09	0.08	0.03	0.07
N %	4.77	0.007	.001	.001
S %	.0062	0.64	0.017	0.0036
Ash %	.10	0.05	.08	0.02
O %	.1	0.21	.1	0.17
Kr BET (m^2/g)	0.559(4) [d]	0.655(6) [d]	0.589(4) [d]	0.576(4) [d]
Standard deviation	0.010	0.083	0.048	0.027
N_2 BET (m^2/g)	0.556(4)	0.566(4)	0.514(5)	0.539(5)
Standard deviation	0.005	0.017	0.009	0.015
Average BET (m^2/g)	0.558	0.611	0.552	0.558
GSA (m^2/g)	0.37	0.18	0.37	0.17
BET/GSA (ratio)	1.51	3.39	1.49	3.28
Total Pore Surface area; 20-600A°(m^2/g)	0.44	0.64	0.49	0.50
Pore Surface area; 20-50A°(m^2/g)	0.18	0.25	0.14	0.16
Pore Surface area; 150-300A°(m^2/g)	0.07	0.13	0.07	0.12
Pore Surface area; 300-600A°(m^2/g)	0.05	0.06	.06	0.05
Total Pore Volume; 20-600A°C(cc/g)	0.001390	0.002245	0.001427	0.001796
Pore Volume; 20-50A°(cc/g)	0.000119	0.000191	0.000186	0.000133
Pore Volume; 50-150A°(cc/g)	0.000335	0.000479	0.000320	0.000396
Pore Volume; 150-300A°(cc/g)	0.000331	0.000532	0.000348	0.000636
Pore Volume; 300-600A°(cc/g)	0.000605	0.001043	0.000573	0.000631

a. As Received b. From density gradient techniques c. at 60,000 psia
d. parenthesis indicate number of runs

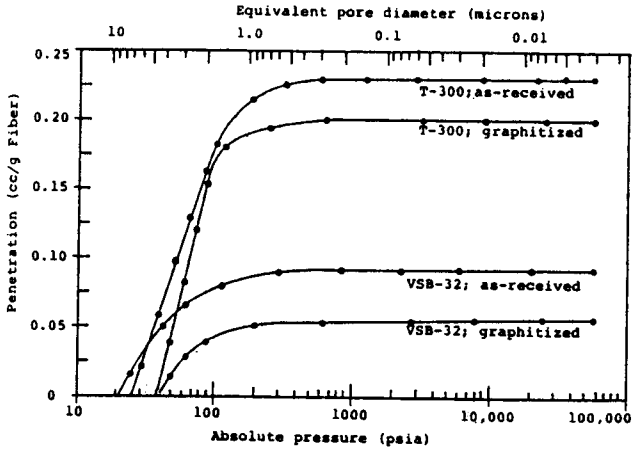

Figure 1. Mercury porosimetery data for pitch and PAN fibers.

greater than 5000 nm (0.5-3 microns). This does not seem to be the case because when each fiber was examined using scanning electron microscopy, the surface was smooth and there was no indication of the presence of such large pores. Therefore, the penetration can only be attributed to the mercury being forced to fill the voids between the fiber filaments. Nevertheless, the final values of penetration at 60,000 psia can be used to calculate the true density of the fibers; provided that the volume of micropores can be neglected. These values are presented in Table I along with those determined from density gradient techniques using chlorobenzene as a solvent. Agreement between both values is acceptable which confirms that the micropore volume of these fibers is very small.

Conclusions

For both pitch and PAN fibers examined here, whether as supplied by the manufacturer or after graphitization to 2700°C, the BET surface area was essentially the same; 0.5 m2/g. The volumes of micro-and meso-pores are negligible. Thus, when these fibers are subjected to the severe rocket nozzle firing conditions, the chemical reaction taking place between the propellant exhaust gas species and fiber is not controlled by the diffusion of the reacting species to some point underneath the fiber surface. This suggests that for the chemical recession of fibers in a rocket nozzle, the reaction is controlled by either the chemical reactivity of the fiber or by diffusion of reactants from the main exhaust stream to the outer surface, or a combination of both. In all cases, the chemical recession takes place only at the external surface of the fiber.

References

(1) S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area, and Porosity, Academic Press, 1982, p. 45