Polymer Science · Polymere

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Structure analysis of graphite fiber surfaces

I. Mass spectrometry and low temperature adsorption of N₂ and Ar*)

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With 9 figures

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I. Introduction

Production of “Thornel” fibers involves taking a rayon precursor through a series of progressively higher temperature pyrolysis, carbonization and graphitization steps (1). The last of these steps is a rapid “hot stretch” in a nitrogen atmosphere at temperatures approaching 3000 °C, which treatment causes a high degree of preferred orientation of graphite layers parallel to the fiber axis. The oriented graphite fibers so produced are very strong, and may exhibit a Young's modulus in excess of 50 million p.s.i. (2). This characteristic, coupled with lightness and high temperature resistance, has led to the use of “Thornel” fibers as a favored reinforcement for polymer matrices in advanced, high performance composite structures.

A problem with these (and other) graphite fibers, however, has been their poor adhesion to the polymer matrix which surrounds them (3). Attempts to improve this adhesion have led to various treatments of the fiber to produce a more bondable surface. While some gains have been made (4–6), most work has been empirical. Real optimization of adhesion, and interfacial shear, awaits thorough characterization of the fiber surface. The objective of this research has been to make such a characterization, and to predict the effects of present (and future) surface treatments on fiber surface properties.

This paper describes a study of the surface of “Thornel 50” fibers made as a function of vacuum heat treatment. The techniques used are low temperature inert gas adsorption by microgravimetry, and mass spectrometry. From the first is derived information about fiber surface area, energy and heterogeneity. The second gives information about materials volatilized from the fiber surface during vacuum heat treatment. A special effort is made to relate these surface analyses to what is known about the bulk structure of “Thornel 50”, and to the bulk and surface properties of other graphitic carbons.

II. Experimental

A. Materials

1. Adsorbent

The adsorbent was, in all experiments, “Thornel-50” graphite fiber obtained from the Union Carbide Corporation Technical Center in Parma, Ohio. This specially prepared, unsized fiber was identified as Lot 10018T-4E and had a tensile strength of 287 × 10³ p.s.i. and a Young's modulus of 51.2 × 10⁶ p.s.i. The density for “Thornel-50” is 1.63 g/cm³ as measured by the liquid immersion method.

2. Adsorbates

The nitrogen and argon adsorbates were research grade gases obtained from Matheson Gas Products, Joliet, Ill. These gases were used without further purification.

B. Apparatus

1. Balance and pumps

The measurement system as shown in fig. 1 consists of a Cahn Model RG, High Vacuum, Electrobalance (Ventron Instruments, Paramount, California) mounted in a vacuum system largely assembled from standard Varian (Varian Associates, Palo Alto, California) parts. The balance chamber is connected to the gas manifold through vibration damping bellows, and the entire assembly is mounted on a heavy metal table permanently bolted to the concrete floor of an air conditioned room.

The system is pumped by a Varian Vac Sorb cryogenic sorption pump and a Varian 50-liter-per-second ion pump. The system attains a base pressure of $10^{-8}$ torr after the balance chamber is baked out at 100 °C and the pumps and gas manifold are baked out at 250 °C.

![Diagram of gas adsorption apparatus](image)

**2. Pressure measurement**

System pressures below $10^{-4}$ torr are measured with a Varian U.H.V. ion gage. This same pressure range is also covered by a G.E. Minitube ion gage (General Electric Company, Schenectady, New York) which can, in addition, function at pressures up to $10^{-2}$ torr if operated at very low (10 μA) emission currents. Pressures between $10^{-5}$ and 1 torr are determined with a Hastings Model VT-6 thermocouple gage (Hastings-Raydist, Inc., Hampton, Virginia) and from 0.6 to 760 torr with a Kern spiral gage (Electronic Space Products, Inc., Los Angeles, California) which is operated as a null device. Null is detected by noting the position of a spot of light reflected from a mirror mounted on the spiral gage to a calibrated scale. The reference side of the spiral gage is pumped by mechanical and mercury diffusion pumps. Pressure on the reference side is measured with a wide bore (27 mm i.d.) manometer read by a precision cathetometer (Ealing Corporation, Cambridge, Massachusetts) with an accuracy of ±0.01 torr. Low pressure measurements are corrected for thermal transpiration effects according to the equation of Liang (7). All manometer pressures are corrected to 0 °C.

3. Gas handling, analysis and control

The adsorbate gases are admitted to the manifold through a Matheson ultra pure transfer regulator (Matheson Scientific Instruments, Joliet, Ill.) to a Granville-Phillips Series 203 variable leak valve (Granville-Phillips Corporation, Boulder, Colorado). The composition of the gas atmosphere over the fiber sample is monitored by a Veeco SPI-10 Monopole Spectrometer (Veeco Instruments, Plainview, N.Y.).

4. Sample container and support

The sample is contained in a 15 mm diameter, blown, pearshaped thin walled quartz pan suspended from a 56 cm long and 0.003 cm diameter platinum wire. The pan and wire assembly is suspended inside a 25 mm inner diameter quartz hangdown tube connected through graded seals to a standard Varian flange. The hangdown tubes are internally coated with SnO$_2$ in the bottom and Pd near the metal flanges to aid in removal of static electrical charges. Coating of the sample pan with SnO$_2$ was shown to have no effect on mass measurements. The sample itself is grounded through the suspension wire.

5. Temperature control

Sample temperature during an experiment is controlled by direct contact of the hangdown tube with a Dewar flask filled with liquid nitrogen. Liquid nitrogen level is maintained constant (±1 mm) with a special fluidic principle sensor.$^1$ .

Vacuum heat treatments of the fibers are effected through use of a high temperature Lindberg Hevi Duty Mini Mite Tube Furnace (Lindberg Hevi Duty, Watertown, Wis.).

6. Data recording

Sample mass changes, outputs from the ion gage pressure sensors, and the mass spectrometer are all recorded simultaneously and serve as a permanent record of the experiments.

7. Precision and accuracy

With the very thin and annealed platinum hangdown wire a sensitivity of +0.05 μg is achieved at pressures up to 300 torr. Noise level increases at higher pressures due to aerodynamic forces and sensitivity is ±10 μg at 760 torr.$^2$ (This noise level is a function of tube diameter and temperature and can be reduced through use of baffles in the tube.)

The mass readings are taken at approximately the same hours as the blank runs in order to compensate for small daily fluctuations in building conditions. Small instrument drifts are compensated for by extending the blank run time to the same interval as the experiment time.

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1) Designed by E. Samuels of this department.

2) A factor limiting precision at high relative pressures is the ability to maintain constant coolant level around the hangdown tube.