LTI CARBON SURFACES

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Background

LTI carbon is one of the very few synthetic materials generally recognized as suitable for long term blood contact applications (1). Although a large number of hypotheses have been formulated with respect to the blood tolerability of materials, a general theory or mechanism is not yet available. It is known that in certain situations the local hemodynamics can play a predominant role (2) and in most cases the solid-blood interfacial properties can play a predominant role (2,3). It is assumed that understanding the plasma protein adsorption process onto solids used for blood-contact applications will lead a better understanding of solid-blood interactions (1-3).

A number of preliminary studies of plasma protein adsorption onto LTI carbon surfaces are available (4-7). Radioiodinated -(I^{125})-proteins have been utilized by Kim, et al. (4) to measure adsorption of individual proteins and protein mixtures on LTI carbon. His results indicate the carbon very rapidly adsorbs albumin. This is consistent with Kim's model of blood interactions via a platelet-adhesion mechanism (8). Microcalorimetric and electrophoretic mobility studies of proteins onto LTI carbon have been done by Nyilas, et al. (5). The extension of the adsorbed layers have been measured directly using ellipsometry by Fenstermaker et al. at NBS (6,7).

Characterization of surface properties of LTI carbons has been rather limited. Baier, utilizing contact angles and infrared spectroscopy (9, 10),and Schoen, utilizing scanning electron microscopy (11), have studied such surfaces before and after blood exposure. Epstein et al. have utilized electrochemical methods to study the LTI carbon-aqueous solution interface (12, 13).

Extensive measurements have been made on the bulk, composition and structure of LTI carbons and experiments with modified surfaces have been reported (15). Direct measurement of the composition of LTI carbon surfaces by modern surface analytical tools however are not available. Here we report Auger and X-ray photoelectron spectroscopy studies of such surfaces. It is expected that such data, coupled with electrochemical and protein adsorption data, may aid in understanding why LTI carbon is relatively blood compatible.

Materials and Methods

Unalloyed LTI carbon samples were prepared in the conventional manner (14). For the photoelectron studies, three lots of samples (A, B, C) from the same coating run were prepared. Specimens from a different coating run (Lot D) were used for Auger studies.

Lot A was placed in clean glass vials immediately after coating and examined without any subsequent handling or treatment. Lot B was ultrasonically cleaned in isopropyl alcohol, air dried, and stored in glass vials prior to study. Lots C and D were ground and polished in several steps and contacted metal oxides, silicon carbide, diamond, water, detergent, isopropyl alcohol, and ethyl alcohol. The final cleaning was done in ethyl alcohol. The samples of Lot C were packaged in a soft blue foam and are representative of the surface which is normally delivered to medical device manufacturers for further processing. Lots A and B have very rough porous surfaces. Lot C and D are highly polished yet still shows some porosity and microscratches at 100X magnification.

X-ray photoelectron spectorscopy was done on a Hewlett-Packard 595B ESCA utilizing monochromatic $AlK\alpha_{1,2}$ radiation. The samples were mounted in air, inserted into the spectrometer and analyzed in a 10^{-9} torr vacuum at ambient temperature utilizing 800 watts of x-ray power (at the x-ray anode, not at the sample). The instrument resolution was normally 0.8 eV measured as the full width at half maximum of the C-1s line from graphite. All spectra are charge referenced to the C-1s line at 284.0 eV. Wide scans (0 to 600 eV) were performed for surface elemental analyses as well as detailed 20 eV scans of the C-1s (275 to 295 eV) and O-1s (520 to 540 eV) regions. The spectra were not resolution "enhanced" or curve resolved.

Auger electron spectroscopy was done on a Physical Electronics Industries Auger microprobe Model 541. Surface analyses were carried out at 10^{-9} torr. Depth profiling was performed using the in-situ ion beam sputtering gun at 10^{-5} torr. Scan speeds used were on the order of 2-5 eV per second. The primary beam voltage was generally maintained at 3KV while the modulating voltage was 3V at low energies (<600 eV) and 6V for higher energies.

Please note that the ESCA and Auger studies were not obtained on identical lots. Auger studies were performed at the General Atomic Co. in Oct. 1976, the ESCA studies were done at the University of Utah in February, 1977.

Results and Conclusions

Lot A had a highly porous surface with carbon particulate matter on the surface. The surface composition as determined by ESCA is given in Table 1. Note the low oxygen content, which appears to be part of a carbon-oxygen bond. No other elements are evident on the surface.

Lot B had finer carbon particulates on the surface but otherwise is identical to A, including the ESCA results (Table 1).

The as received Lot C shows a much higher oxygen concentration and substantial quantities of silicon (Table 1). Other elements present in the surface include traces of sulphur, phosphorous, chlorine and possibly aluminum.

Lot C prewashed in methanol shows no evidence of silicon. The carbon/oxygen ratio is ca. 10:1. Traces of chlorine were present on the surface. The fact that the silicon lines were readily removed by a brief ultrasonic methanol wash suggests a surface contaminant as the source of silicon, perhaps a silicone release agent. The only likely source of such a contaminant is the blue foam in which the samples were packaged. ESCA examination of the foam revealed relatively high concentrations of silicon on the surface as well as nitrogen and chlorine suggesting a polyurethane foam with a silicone anti-stick or release agent and traces of possible NaCl from handling. Thus we tentatively identify the silicon on the as received Lot C as silicone material transferred from the foam packing material. Studies of methanol-cleaned Lot C material (Silicon-free) contacted with the foam confirmed that the silicon (silicone) on the foam readily transfers to the carbon.

Auger analysis of Lot D confirm the ESCA results obtained on C. Oxygen was found on the surface at a level on the order of 10 atomic percent. A trace amount (< 1 percent) of sorbed nitrogen was also generally detected. Depth profiling showed that both the oxygen and nitrogen are found only on the surface. At a depth of approximately 30-50 Å into the carbon, the oxygen signal had dropped by a factor of 10; nitrogen was no longer detected. Since Lot D was not packaged for shipment, these specimens did not contact the polyurethane foam.

Table I

Surface Elemental Ratios for Various LTI Carbon Samples

C:O:N:Si Ratio (Normalized to 100 Carbon Atoms)

LTI Lot Code	Ratio
A	100:1.8:0:0
A	100:1.2:0:0
B	100:1.4:0:0
C	100:8.5:0:1.9
C	100:11.0:1.0:1.5
C"Methanol Cleaned"	100:8.2:0:0
Foam Packing Material	100:39.3:2.8:12.3
D	100:10: <1:0
D (50Å)	100:1:0:0

These initial results from direct measurements of the composition of LTI surfaces confirm previous conclusions (15). The history of a biomaterial surface is important. Variability in test surfaces can be unintentionally produced by very subtle means. The fact that the impurities found on the LTI carbon surfaces could be readily removed shows that the material is inert but leaves open the question in the case of less inert materials. Furthermore, the role of tightly bound surface impurities in activating the clotting mechanisms should be investigated. Similar studies on alloyed LTI carbons will be performed in the future.

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