DIAMOND-LIKE CARBON FILMS--FACTORS LEADING TO IMPROVED BIOCOMPATIBILITY*

S. Aisenberg, Ph.D.
Gulf + Western Applied Science Laboratories
(formerly Space Sciences Division of Whittaker Corporation)

The various physical and chemical properties of Ion Beam Deposited diamond-like carbon were studied in order to determine the factors related to improved blood compatibility. The insight gained can contribute to the development of a "unified theory of blood compatibility."

Ion Beam Deposited Carbon (IBDC) is produced by means of an energetic beam of carbon ions derived from a plasma of inert gas and carbon atoms (1,2). This carbon ion beam is extracted into a low pressure deposition chamber and accelerated to the deposition substrate with an energy of 50-100 electron volts.

As a result of the high ion energy the carbon film grows with many properties similar to that of diamond. During the ion beam deposition, simultaneous ion beam etching occurs so that impurity atoms and atoms with weaker bonds are removed giving a film with a composition of atoms having the strongest bonds. Typical of the properties measured (3) are the following:

1. Essentially amorphous in structure with grain size in the range of 5-30 (X-ray diffraction).
2. Smooth surface, closely conforming to substrate as observed with scanning electron microscope.
3. Good adhesion to polymeric and other substrates, typically 700 psi (as high as 5,000 psi on metal substrates).
4. Typical coating thickness 500-1000Å.
5. High critical surface tension, 40 dynes/cm.
6. Low gas permeability.
7. Transparent.
8. Surface charge is low, less than 10^{-11} coul/cm^2 (vibrating capacitor measurements).
9. Density of 2.36 gm/cm^3.
10. Good performance in vena cava and renal embolus tests.
11. Dielectic constant is approximately 16.
12. Insulating, with a high resistivity of 10^{11} ohm-cm.

Bell Telephone Laboratories reported using procedures similar to that of Aisenberg and Chabot (1,2) to also obtain Ion-Beam-Deposited polycrystalline diamond-like films. The characteristics they reported include:

1. Films are insoluble in all common inorganic acids (as well as numerous inorganic and organic solvents) including HF, HNO_3, HCl, H_2SO_4, HCOOH, Acetone, Trichloroethane, Chloroform, Ethyl Acetate and others.
2. Films are optically transparent (either pale yellow or water clear with bright colored interference rings for thicker films).
3. The thin films have a smooth surface.
4. DC and AC resistivities are about 10^{12} ohm/cm.
5. The index of refraction is about 2.
6. All thin free standing films were quite flexible.
7. Film curling was not observed for stripped films indicating the essential absence of strain.
8. X-ray diffraction studies showed that "in many cases definite, but usually very weak lines assignable to diamond were recorded." The average grain size was 50-100Å according to line broadening.

Hard carbon films have been reported for plasma glow discharge deposition (5) but the film properties have not been characterized.

In reviewing the results of biocompatibility tests such as the vena cava and renal embolus tests for our IBD carbon and for other materials that are also blood compatible, it became apparent that a "unified theory of biocompatibility" is needed to guide future development and testing.

The unified theory should be consistent with the results reported for the better biocompatible material such as:

1. Collagen
2. Hydrogels
3. Natural endothelium
4. Various forms of carbon (pyrolytic, ion beam deposited, plasma deposited)
5. Glow discharge polymers
6. Heparinized polymers
7. Fluroesters of ethyl cellulose
8. Various polymers (such as Avcothane which is a compound of polyurethane and silioxyane).

It is proposed (3) that if surfaces are going to form clots in varying degrees, the best surfaces will be those that release the emboli while they are in the early, seed, or juvenile stage. There are two reasons for this. First, the mass release rate of the clots increases approximately as the square of the clot diameter at release so that the sooner the clots are released the smaller the total mass of clots released per nucleation site. For example, if the material and test conditions permit the clot release at a size of 100 microns rather than 1,000 microns, then the total rate of clot mass throw-off is reduced by a factor of 100 and has a better chance of quickly being reabsorbed by the body before prohibitive damage is caused.

Second, small clots are less likely to close off an important artery, but instead will lodge in the smaller arteries and/or capillaries so the necessary blood is more likely to be supplied by collateral circulation with less chance of severe necrosis. The

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damage to tissue downstream is thus less serious in the case of early shedding of seed clots.

Third, the smaller the size of the necrosis (if present), the better chance of being reabsorbed before irreversible damage is produced.

Thus, it appears logical that a figure of merit for a blood compatible surface is the release radius, R_R, of typical blood clots released from the surface. The smaller R_R, the better it is for the subject.

As an extreme example of the above argument, it is better for a subject to continuously release large numbers of small thrombi that can be reabsorbed quickly and safely, than one large thrombus one year later. Note also that the body is able to cope with small thrombi expected to result from long term atherosclerotic deposits frequently present in people.

In addition to the basic fabrication properties of blood compatible materials (fabrication ease, flexibility, flex life, and stability) it is postulated that the following factors will be important for blood compatibility:

1. Smooth surface, free of defects, or inclusions to aid early release of thrombi and to reduce thrombi formation caused by local stagnation due to defects.

2. Fast flow to give greater removal forces and earlier release (small sizes).

3. Fast flow to increase removal of clotting factors at surface.

4. Smooth surfaces also prevent local trapping of clotting factors due to stasis.

5. The use of heparinized polymers and blood will aid the early release of any thrombi that form.

6. Ability to flex without permanent damage such as development of cracks and loss of protective coatings.

7. Non molecular structure of IBD carbon film can avoid the configuration change of protein molecules that can occur with polymer substrates encouraging protein change.

8. Absence of impurities to migrate to surface (such as plasticizers, catalysts, fillers, stabilizers, additives).

9. An impermeable barrier to substrate impurity migration (such as IBD carbon with its tight lattice structure). Even if there are micro cracks in film due to flexing, the micro crack area will be many orders of magnitude smaller than the geometric area and the out migration of substrate impurities will be much smaller than for uncoated substrates.

10. No impurities in coating itself--this is true for the case of IBD carbon because of the use of vacuum and sputtering techniques. This is true for other vacuum-plasma deposited films as well as for pyrolytic carbon formed under high temperature.

11. The coating must also be chemically inert (as well as the substrate).

12. Critical surface tension in correct range.

13. Stability of physical strength in contact with blood.

14. Uniformity of surface properties. Patches of bad materials will make the whole surface act bad from the observers view.

15. Surface charge (slightly negative) and uniformity.

16. Surface is contamination free--otherwise growth and adhesion of thrombi are encouraged.

Some of the problems of more efficient development and use of blood compatible materials are:

a. Lack of reproducibility of tests from same source and same testing groups.

b. Long time involved for tests resulting in slow feedback.

c. Few data points--usually at the end of test.

d. Contradictory data and interpretations are frequently found in literature.

There is a need for in vitro, ex vivo, and in vivo tests that can give data continuously during each test.

There is also a need for a simple test for the reproducibility of the materials surface, both for uniformity within a batch, and for different batches. We have a vibrating capacitor electrode test system that can determine the surface potential to within a few millivolts. For example, this system can easily detect a fingerprint on the surface and has a detection limit of the surface potential corresponding to one hundredth of a fingerprint. Use of such techniques can be of help in comparing IBD carbon films and other blood-compatible surfaces.

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