Radiation Enhanced Porosity and Roughness of Biomaterials

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ABSTRACT

Glassy Polymeric Carbon (GPC), made from cured phenolic resins, is sufficiently chemically inert and biocompatible that it is suitable for medical applications, such as heart valves and other prosthetic devices. We have used energetic ion bombardment of the partially and fully cured precursor phenolic resins to enhance biological cell/tissue growth on, and to increase tissue adhesion to, prosthetic devices made from GPC. GPC samples were bombarded with energetic ions to 10 MeV. The surface topography and increased surface roughness was observed using optical microscopy and atomic force microscopy (AFM). The increased porosity was measured by introducing lithium from a molten LiCl salt into the GPC and using (p, α) nuclear reaction analysis (NRA) to measure the concentration of Li retention in the modified GPC. The NRA measurements of increased pore availability were correlated with the observations of increased surface roughness.

INTRODUCTION

Glassy Polymeric Carbon (GPC) is made from cured phenolic resins (resol), Fig. 1.a, in an inert environment. After curing at 60°C, Fig. 1.b, the resin is pyrolyzed at low temperature rates to avoid changing shape or disruption due to volatile decomposition products (1). Heat treatment to 550^0 C produces a conducting material due to hydrogen release and conjugation of the aromatic rings forming graphene planes in random arrangement (2). For heat treatment at 650^0 C, the material still presents open porosity due to space between the ribbons. Further heat treatment to 1000°C the GPC pores remain but progressively close, reducing permeability as the graphitic planes aggregate themselves to form the final structure of the GPC, Fig. 1.c, (3). The final GPC structure is as random graphene planes shown in Fig. 2 and the material appears dark, hard and vitreous. Its density (1.45) is significantly lower than that of graphite from which one may deduce a relative pore volume of about 35%.

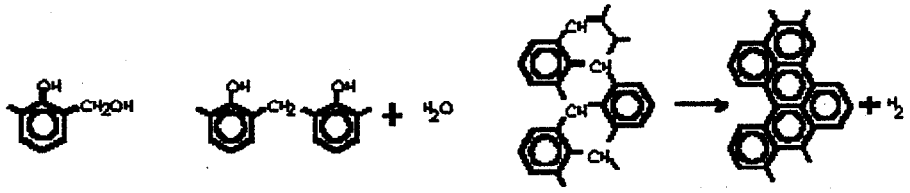

Fig. 1: Structures of a) resol, b) the polymer which forms at 130°C and c) a graphene plane as heat treatment is increased beyond 700°C.

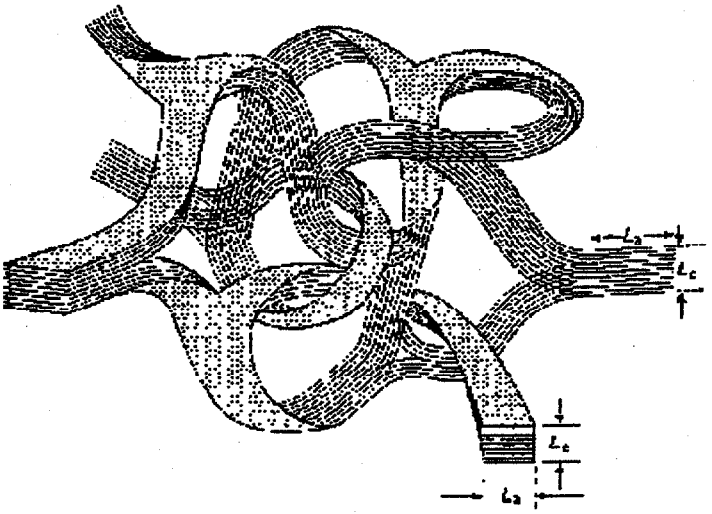

Fig. 2: GPC structure, according to Ref. [1]. L_A and L_C are of the order of 10 nm and the pores are closed such that the material is completely impermeable.

This work has been motivated because GPC is increasingly used in medicine in the manufacture of heart valves due to its inertness and biocompatibility (4, 5). GPC replacement artifacts still present some dysfunction or thromboembolic problems as a result of low adhesion at the interface between its surface and the biological tissue (6, 7). Thromboresistence can be achieved by treatment of the surface of the biomaterial, making it rough. The roughness can increase the adherence of the endothelialized tissue contacting the prosthetic component surface. The texture desired for this medical purpose should be a profile of cavities in the surface whose dimensions are sufficient (about 10-20 μm) to allow formation of tissue that adheres to the material surface. Ion bombardment was used to increase the roughness of GPC samples.

MATERIALS AND METHODS

The samples from phenolic resin were cured following the process described in Ref. (8).

Then, the samples were pyrolysed at 700°C and 1500°C. The heating rates follow (8):
from 20^0C to 100°C, 20°C/h;
from 100^0C to 200°C, 7°C/h;
from 200^0C to 500°C, 2°C/h;
from 500^0C to 700°C, 3°C/h;
from 650^0C to 1500°C, 40°C/h.

Individual samples were bombarded with ions and their range as follows (fluence in units of ions/cm^2) (8):
Oxygen, 8 MeV, 1.0, 2.8 and 10 x 10^{13}, 6.77 μm,
Carbon, 6 MeV, 3.0, 10 and 30 x 10^{13}, 6.75 μm,
Silicon, 5 MeV, 0.5, 3.4 and 10 x 10^{13}, 4.14 μm,
Gold, 10 MeV, 1.0, 10 and 100 x 10^{14}, 2.84 μm.

The roughness of the samples was measured with a Surface Profiler Non-Contact TOPO-3D. Bombarded and unbombarded regions of the samples were compared. The texture was observed with Atom Force Microscopy. The results were correlated with available porosity measured by

lithium absorption in other samples after bombardment with the same ions, energies and fluences. The lithium absorption was carried out at 700°C in a molten 99.6% lithium chloride bath for a duration of one hour. The near surface concentration profile of lithium in these samples was measured by Nuclear Reaction Analysis (RNA). Alpha particles from the Li(p, 2α) (Q=17.256 MeV) reaction were observed from the surface to a depth of about 10 μm below the surface of the GPC, beyond which the energy of the protons is insufficient to react with lithium. A 100 nanoampere 1.03 MeV proton beam and a silicon surface detector, at a back angle of 170° were used to perform the NRA.

RESULTS AND DISCUSSIONS

Fig. 3 shows that the surfaces of all samples become rough after ion bombardment. Samples prepared at 700°C presented greater RMS roughness than for samples prepared at 1500°C. This probably is due to GPC's hardness and purity, both of which increase with heat treatment temperatures. For all ions there is a specific fluence value for which the roughness tends to decrease as the fluence is increased.

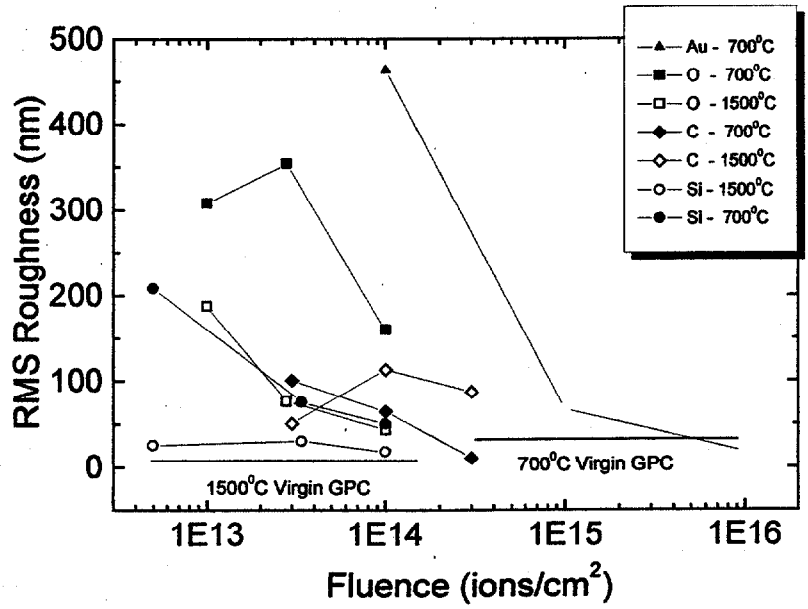

Fig. 3: RMS roughness of GPC as a function of fluence after bombardment with the ion shown. (See text for ion energies).

Fig. 4 shows the AFM surface profile of the 700°C GPC sample without any bombardment to be compared with the texture obtained for the oxygen bombarded sample as is shown in Fig. 5. For these samples AFM showed a specific texture, which presented 40 μm width regions, separated by 10-30 μm gaps. For fluences higher than 2.8×10^{13} oxygen ions/cm^2 the roughness decreased.

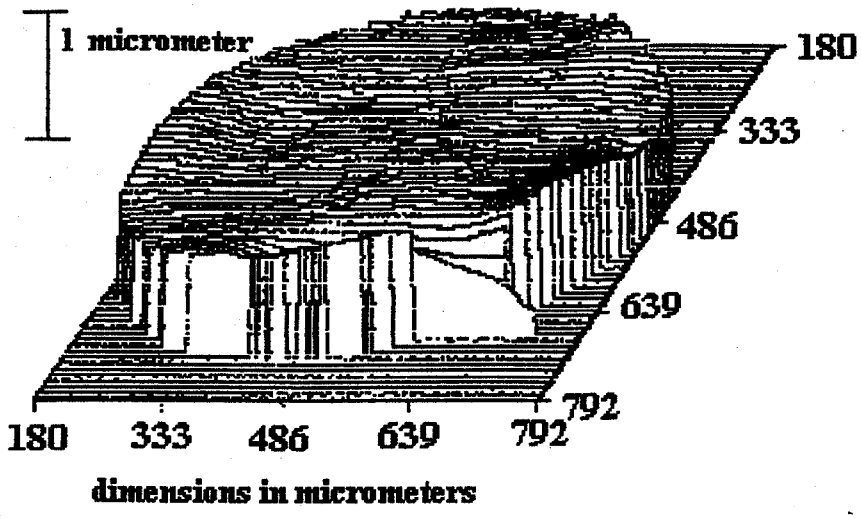

Fig. 4: 700^{0}C GPC before ion bombardment.

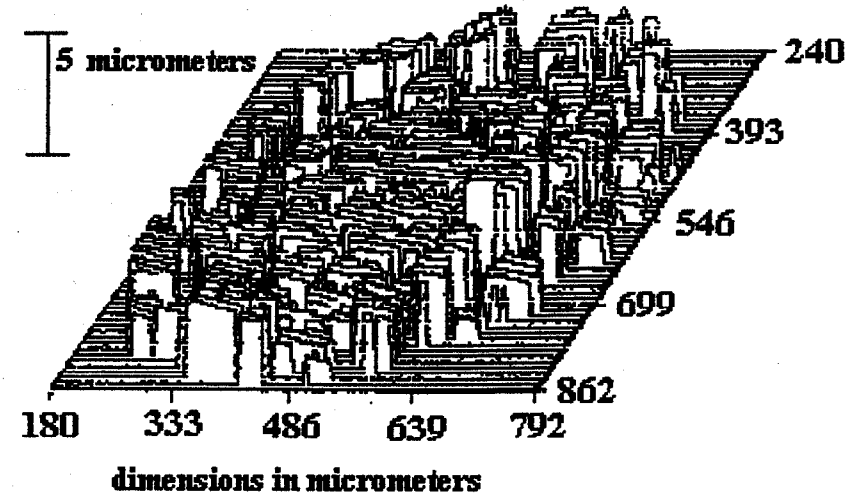

Fig. 5: 700^{0}C GPC after bombardment with 8 MeV oxygen ions at a fluence of 2.8x10^{13} ions/cm^2.

Fig. 6 shows the lithium concentration from the NRA that has diffused into the near surface region of GPC heat treated to temperatures of 700°C and 1500°C in a molten LiCl bath at 700°C. This is a direct measurement of the available porosity. NRA studies showed that lithium diffusion into GPC is enhanced even beyond the range of bombarding ions. The results of Fig. 6 show that ion bombardment improved the lithium absorption relative to the GPC without any bombardment. Similar to roughness results, the absorption was bigger for samples prepared at 700°C. For lithium absorption it was observed a dependence of the enhancement of diffusion on the fluence, saturating or decreasing at high fluences.

Both roughness and available porosity increase with ion bombardment for low fluences, then saturate or decrease at higher fluences. Evidently, ion bombardment beyond a critical fluence causes densification and polishing of the initially rough, porous surface.

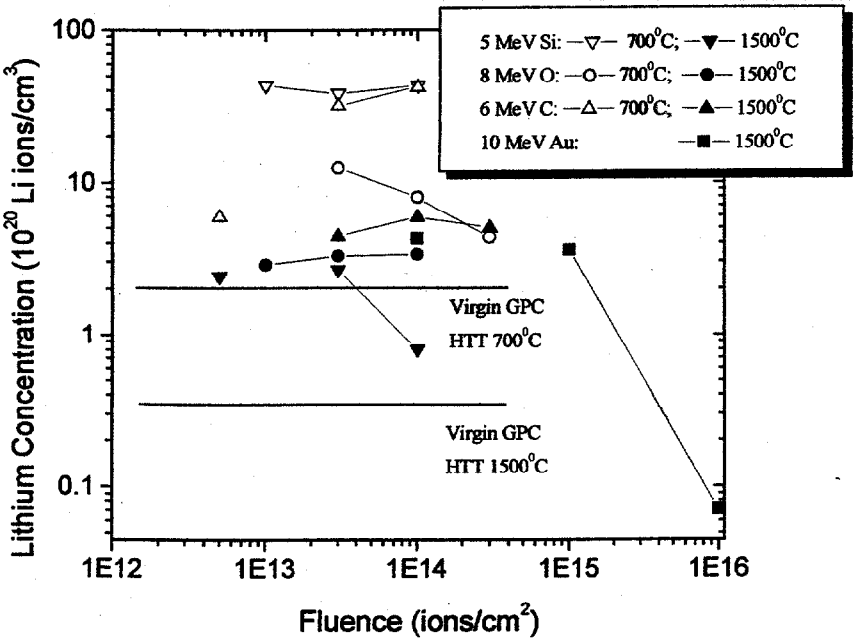

Fig. 6: Lithium concentration into near surface region of GPC heat-treated to temperatures of 700°C and 1500°C in a molten LiCl bath at 700°C.

The value of fluence at which maximum roughness can be achieved has a dependence on the pore density and the size of the ion used for the bombardment. The hypothesis here is that ion bombardment improves the permeability by opening the pores, making them interconnected. If the fluence is higher than the pore density of the material near the surface, ion bombardment makes the pores unavailable (9, 10).

CONCLUSIONS

Our results showed that ion bombardment can be used for the production of GPC artifacts with textured surfaces, which can enhance the biocompatibility of biomaterials. The bombardment improved the absorption of lithium which indicates that a significant transfer of energy to the recoil carbon atoms, as well as the residual positive charge near the primary ion track, leads us to expect that damage along the track might cause neighboring pores to connect. As the diffusion is observed beyond the depth of implantation, the lithium absorption can be correlated with roughness of the surface as well as the available porosity.

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