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Silicon oxycarbide glasses for blood-contact applications ☆

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Abstract

Silicon oxycarbide (SiO_xC_y) glass compositions are shown to exhibit a variable propensity to contact activate coagulation of whole human blood plasma that depends on $X:Y$ surface stoichiometry. SiO_xC_y exhibit activation properties similar to pyrolytic carbon (PC) over a broad range of $X:Y$ ratios. Surface composition of SiO_xC_y glass powders prepared by pyrolysis of thermosetting polysilsequioxanes roughly correlated with total carbon concentration of precursor resins and could be significantly modified by etching in alkaline solutions. Results suggest that SiO_xC_y may offer unique properties as a substitute for PC in medical-device applications demanding excellent tribological properties, such as artificial heart valves.

Keywords: Blood coagulation; Silicon oxycarbide glass; Pyrolytic carbon

1. Introduction

Hard biocompatible materials exhibiting excellent tribological (friction and wear) properties are of considerable value in a wide variety of medical-device applications ranging from dentistry to orthopedics to reconstructive surgery. Pyrolytic carbon (PC), either in monolithic form or applied as a coating, has been a material of choice for such applications for more than 50 years [1], offering a bioadhesive surface [2,3] with good hemocompatibility [4,5]. In particular, PC has been widely applied in heart-valve applications and is successfully used in a number of commercial products [5]. However, PC physical properties can be a limitation for applications demanding long-term mechanical stability under applied stress. Herein we report development of silicon oxycarbide (SiO_xC_y) glass compositions that may find biomedical applications as an alternative to PC.

Silicon oxycarbide (SiO_xC_y) glasses are novel amorphous materials in which carbon is substituted for oxygen within the Si–O matrix, greatly strengthening the molecular structure of the resulting glass network. Silicon is thus simultaneously bonded to carbon and oxygen in a configuration that can be controlled by the synthesis procedure [6,7]. Carbon content can be as high as 70 mol%, depending on precursor materials used or the processing approach adopted [8]. SiO_xC_y glasses have tailorable physical properties that strongly depend on the microstructure (presence of phase separation and bonding state of carbon) and composition (carbon content). SiO_xC_y glasses exhibit remarkable mechanical properties including: elastic modulus, bending strength, hardness; chemical durability superior to conventional silicate glasses in aggressive environments; and

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resistance to oxidation at high temperature, devitrification, and creep. These unique properties strongly correlate with the increase in the average coordination number in the glass network [9–14]. SiO_xC_y can be fabricated by pyrolysis of suitable organosilane precursors at a temperature >800 °C [6–14], by chemical vapor deposition (CVD) [15], or by reactive sputtering. The use of organosilane precursors permits fabrication of variously shaped (monolithic) ceramic objects (bulk or porous components [1,16,17], fibers [18], microtubes [19], coatings [20]—provided that the substrate can withstand processing at moderate-to-high temperatures). Plasma and sputter deposition methods permit formation of SiO_xC_y glass layers on a variety of substrata, especially including polymers with a relatively low-process-temperature window.

Herein we report structure–property relationships connecting SiO_xC_y composition with the propensity to activate coagulation in whole human blood plasma. Results show that activation of the intrinsic pathway of the plasma coagulation cascade by contact with SiO_xC_y powders scales with oxygen content X. SiO_xC_y formulations with narrow range of X:Y ratios were developed that exhibited activation properties as low as hydrophobic silane-treated glass and it was found that a relatively broad range of X:Y ratios exhibited activation properties similar to PC. Results thus suggest that SiO_xC_y has utility in blood-contacting medical-device applications.

2. Materials and methods

2.1. SiO_xC_y compositions

Materials tested were all in powder form prepared by pyrolysis of precursor resins. Table 1 compiles sources and identities of thermosetting silicone resins (polysilsesquioxanes) used for preparation of test materials, along with sample identification applied herein. Total bulk-resin C content (from literature data [8] or estimated using the rule of mixtures on the basis of the data reported in the cited literature) and the density of the SiO_xC_y glass samples (after pyrolysis at 1200 °C in inert atmosphere) are also collected in Table 1. SiO_xC_y with X:Y ratios intermediate of those prepared from as-received resins were prepared from mixtures of SILRES 601 and SILRES 610. Weighed proportions were thoroughly mixed and melted together at 90–110 °C, which is well above the glass transition temperature for both resins. The resulting mass was crushed using a mortar. These samples were labeled 25-SILRES and 50-SILRES, respectively. Several grams of the various powder samples were (partially) cross-linked by condensation of Si–OH groups by heating at 70 °C for 24 h in air and were then pyrolyzed by heating at 1200 °C (10 °C/min heating rate; 2 h dwelling time; alumina crucibles) in inert atmosphere (N_2 99.99%, flow rate of 50 cm^3/min). The resulting black, glass powders were ground using a ball mill and sieved to produce powders with a controlled size of 425–600 μm. Surface composition of each of the specimens listed in Table 1 was altered by chemical etching in an alkaline solution containing Na_2CO_3 and NaOH (pH 12.3, prepared according to Ref. [14]) at 80 °C for 2 h.

2.2. Analytical

Test materials were analyzed using X-ray diffraction (Philips mod. PW1710, CuKα, operating at 40 kV and 30 mA, step of 0.05° every 4 s, Philips Analytical, Almelo, The Netherlands) and scanning electron microscopy (SEM) (mod. XL-20, Philips Analytical, Natick, MA). Surface composition was measured using X-ray photoelectron spectroscopy (XPS, also known as electron spectroscopy chemical analysis, ESCA) using a Model Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) with monochromatic AlKα radiation

Table 1
Polysilsequioxane prepolymers used in preparation of SiO_xC_y glasses

Sample designation	Organofunctional group	Total carbon		SiO_xC_y glass density (g/cm^3)
		(wt.%)	(at.%)	
SILRES 610	Methyl	12.8	20.2	2.255 ± 0.001
SOC-A35	Methyl	13.7	21.6	2.228 ± 0.002
25 wt.% SILRES 601–75 wt.% SILRES 610[a]	Methyl–phenyl	20.6[b]	29.6[b]	2.101 ± 0.002
50 wt.% SILRES 601–50 wt.% SILRES 610[c]	Methyl–phenyl	28.4[b]	38.9[b]	1.974 ± 0.002
SR 355	Methyl–phenyl	32.7	45.3	1.889 ± 0.002
H44	Methyl–phenyl	39.1	52.6	1.894 ± 0.002
SILRES 601	Phenyl	44.0	57.6	1.799 ± 0.001
Reference glass	–	n.d.	n.d.	2.496 ± 0.001
Glass OTS-coated	–	n.d.	n.d.	2.496 ± 0.001

[a] Sample labeled 25-SILRES.
[b] Estimate; n.d. = not determined.
[c] Sample labeled 50-SILRES.