ENGINEERING PROPERTIES OF PYROLYTIC GRAPHITE SURFACES

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Introduction

Carbon fibre reinforced carbon (CFRC) composite materials are the most mature examples of fibre reinforced composites in which the chemical nature of the fibre and matrix is identical. Many of their uniquely combined properties (namely specific strength and thermal resistance in a vacuum or in an inert atmosphere, thermal and electric conductivity) make them indispensable in specialized applications. Their excellent biocompatibility and porosity, coupled with modulus which can be tailored to be similar to that of bone, make them an attractive material for bone plates and implants in orthopaedic and dental surgery. Existing studies have shown the good biocompatibility of CFRC composites of the investigated type, i.e., those with carbon matrix derived from a commercially available thermosetting resin and with ordinary Toray carbon fibres.

As shown in our preliminary experiments, the proneness of carbon-carbon composites to re-lease carbon particles is an unsolved problem. It is caused by the brittle nature of the carbon matrix and it must be considered disadvantageous for medical applications of CFRC composites. Just after preparation, but mainly due to mechanical (especially cycling) loading, carbon particles can appear at or near the surface. These carbon particles can emerge and dissipate during use of the implant and may irritate biological components of the graft as well as the surrounding tissue. A possible solution may consist in covering the surface of the implant with a stronger suitable compatible layer, e.g., of pyrolytic carbon. A pyrolytic carbon (graphite) layer can be prepared by pyrolisis of hydrocarbon gas at a relatively high temperature. From an engineering point of view, the layer and its surface can be characterised by roughness, coefficient of friction, wear resistance, etc. Some of these properties are of great importance for cell growth on this surface. For example, roughness influences cell adhesion and proliferation [1].

The purpose of this paper is to define some of the surface properties by routine engineering methods. Apart from roughness, we measured the coefficient of friction and wear resistance. Finally we studied (rather qualitatively) the release of carbon particles from CFRC with and without a layer of pyrolytic graphite.

Experimental

The preparation of CFRC is described in detail in the accompanying paper by Stary at al. The final heat treatment (graphitisation) was 2200°C. The surface of some CFRC samples was ground by metallographic paper of 4000 grade (CFRC/4000). The manufactured composite specimens were infiltrated and covered by a pyrolytic carbon layer (PyG) generated by butane decomposition using nitrogen as a carrier gas at TESLA Vršovice, Ltd., Prague, CR The working pressure was 4 Pa, temperature 1900°C. After exposition time (about 5 hours), a film 0.4 -0.7 μm in thickness was prepared (CFRC/4000/PyG). The surface roughness was modified by grinding again with met-allographic paper of 4000 grade and was in some cases continued by polishing with diamond paste (3/2 and, 1/0 (CFRC/4000/PyG/4000/3.2/1.0). Finally, we had a set of samples with different roughness and different surface chemical state (CFRC or PyG). The surface roughness measure-ment was performed on a TALYSURF 6 profilometer (Taylor-Hobson Ltd. U.K.), friction coeffi-cient and wear were measured with a HEF tribometer (France) at SVUM, Ltd., Běchovice, CR.

Results and discussion

Preliminary results are shown in TABLE 1 and in FIGS.1,2. The coefficient of friction depends strongly on the load (FIG.1). The coefficient values are nearly the same on samples coated with PyG, but there are different on

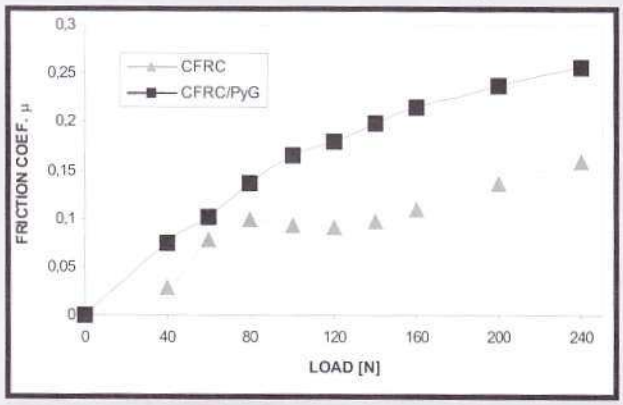

FIG.1.

uncoated samples, where the coefficient of friction does not grow between load values of 100-150 N. We supposed that the lower values for this sample result from the higher hardness of CFRC alone. Moreover, the non-monotonic growth of the friction coeffi-cient may be caused by the presence of two phases of material (matrix and fibres) in the sample, because their mutual relative participation at the surface varies during the test.

In FIG.2, Ra and Rq denote the arithmetic and quadratic

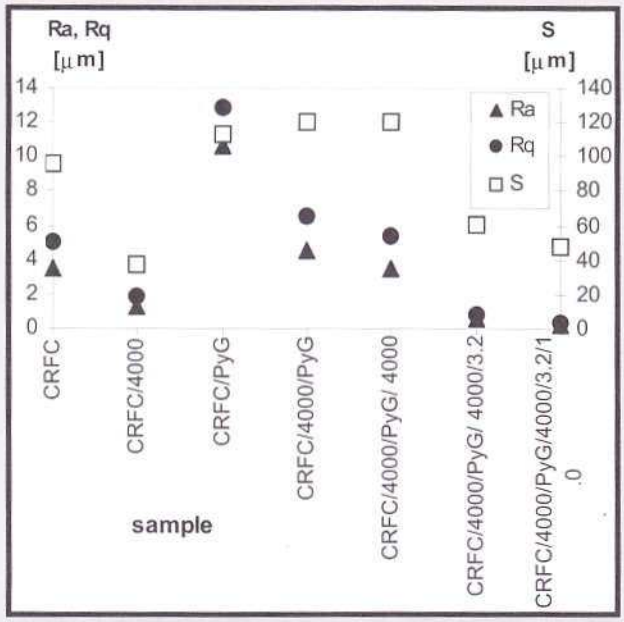

Fig.2.

ΔG [g]	(unground) CFRC/PyG	CFRC/4000/ (thin) PyG	CFRC/4000/ PyG/4000
Load [N]			
50	0.0118	0.0004	0.0066
100	0.0134	0.0018	0.0036

TABLE 1.

mean of the departures of the rough-ness profile from the mean line, S the mean spacing of adjacent local peaks, measured over the as-sessment length. The ground base of the CFRC samples gives a half-size value of Ra compared with the unground samples. The value of Ra thoroughly decreases with degree of polishing.

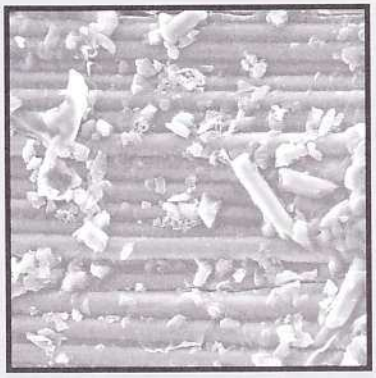

FIG.3.

TABLE 1 shows the results of the wearing test. A relatively high value of wearing for unground CFRC/PyG corresponds with a high value for Ra (FIG.2). Grinding of CFRC substrate under a PyG layer markedly decreases the wear. The surface layer of sample CFRC/4000/ PyG/4000, was probably ground through, so the weight loss is decreased at higher loads, together with the effect of surface roughness, namely the shape of the asperity. The lower friction coefficient value of the CFRC samples (FIG.1) corresponds with the lower Ra value (FIG.2). Simultaneously the hardness of the PyG layer may be lower than CFRC alone.

FIG.3 shows the releasing particles matrix and the fraction of fibers after the bending fatigue test for the CFRC sample. Incidence is higher on the pressure side of the sample (which is loaded by pressure). Coating CFRC with PyG greatly decreases the number of particles that appear.

Conclusion

- Grinding and polishing of the surface effectively decreases the value of Ra.
- Friction coefficient μ is higher for samples coated with PyG.
- A grinding base under a PyG layer caused low weight loss during wearing, and after grind-ing the loss is increased.

Acknowledgements

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References

[1] Bačáková L., Starý V., Glogar P.: Inżynieria biomaterialow V.I, N°2 (1998) 3.

ADSORPTION OF FIBRINOGEN AND ALBUMIN IN A CELLULOSE MEMBRANE FOR HEMODIALYSIS

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The hemocompatibility of a dialysis membrane, which depends on its chemical nature (cellulose or synthetic), is improved when the dialyzer is reused after performing a treatment of regeneration. This regeneration process consists in a cleaning step (often with bleach) followed by a disinfection step (often with formaldehyde). Surface conditioning of the membrane by blood proteins during the successive cycles of dialysis and regeneration process, may thus play a role on the hemocompatibility of the dialyzer. The aim of this work was to characterize the surface properties (chemical composition, hydrophobicity, organization and macromolecular interactions) of a model cellulose dialysis membrane (Cuprophan) before and after adsorption of fibrinogen (Fg) and human serum albumin (HSA).

The surface chemical composition of Cuprophan was determined by X-ray photoelectron spectroscopy (XPS). As expected, it was found to be typical of cellulose materials. However, silicon, nitrogen as well as hydrocarbon-like compounds have also been detected in variable quantity depending on the sample. The morphology of Cuprophan surface, characterized in air or under liquid by atomic force microscopy (AFM) used in contact mode, is dominated by a succession of parallel fibrils (groovy aspect), oriented according to the direction of the membrane extrusion process. Some globular structures (diameter of 100 to 200 nm) were found to be distributed randomly over the surface. These structures are attributed to silica particles, which are sprinkled on the membrane surface at the end of the production process in order to prevent stickiness during storage. If the samples are rinsed and imaged in a physiological buffer (Phosphate Buffered Saline), the groovy aspect is highly pronounced and characterized by the repetition of a structure with a periodicity of 100 to 200 nm. In pure water (water from a milli-Q plus system), this groovy aspect becomes attenuated and the periodicity disappeares. These results indicate that the swelling behavior of Cuprophan is influenced by the ionic strength of the aqueous phase.

The study of albumin and fibrinogen adsorption on Cuprophan (XPS, water contact angle) shows a weaker adsorption capacity of former protein compared to the later. For the concentration range of these proteins in the plasma, the N/C ratio (indicator of protein) determined by XPS, suggests that adsorbed proteins do not form a thick and continuous layer at the surface of Cuprophan. The AFM topographic images do not reveal a significant effect of the adsorption of fibrinogen on the initial morphology of Cuprophan, whatever the imaging conditions are. However, AFM force-distance curves show that the frequency of adhesion phenomena, which could occur when the AFM probe is retracting from the surface, increases in a weak ionic strength medium (milli-Q water) and after fibrinogen adsorption. Moreover, a statistical analysis of height variations on the AFM topographic images show that fibrinogen adsorption decreases the pronounced surface relief of Cuprophan observed in PBS.