równo z samego kopolimeru glikolid-laktyd otrzymanego z użyciem $Zr(acac)_4$ jak i z kompozytu tego kopolimeru wzmocnionego włóknami węglowymi. Wprowadzenie włókien węglowych znacznie polepsza właściwości wytrzymałościowe kopolimeru, jednak przyśpiesza proces ich degradacji w środowisku wodnym. Zjawisko to jest spowodowane oddziaływaniem pomiędzy powierzchnią włókien węglowych a osnową polimerową i obecnością granic rozdziału, które stanowią drogi szybkiej dyfuzji cząsteczek wody i produktów rozpadu kopolimeru.

Badane materiały ulegają procesowi biodegradacji w przeciągu kilku tygodni przebywania w środowisku wodnym, co wydaje się być czasem pozwalającym na uzyskanie zrostu kostnego. Jednakże do określenia przydatności opracowanych materiałów w praktyce klinicznej, biorąc pod uwagę obserwowane wcześniej spowolnienie degradacji w tkance kostnej w porównaniu do badań prowadzonych in vitro w środowisku wodnym [18], konieczne wydaje się przeprowadzenie badań in vivo na zwierzętach doświadczalnych.

Podziękowania

Badania prowadzono w ramach projektu badawczego Komitetu Badań Naukowych nr 3 T09B 010 17

Piśmiennictwo

[1] Leenslang J.W., Pennings A.J., R.M. Bos, Rozema F.R., Biomaterials 8, (1987) 70.
[2] Grijpma D.W., Zondervan G.J., Pennings A., J. Polym. Bull. 25 (1991) 327.
[3] Thies C., Formation of degradable drug-loaded microparticles by in-liquide drying processes. In : Donbrow M., editor., CRC Press, Inc. Boca Raton Ann Arbor London 1992. p. 47-71.

Acknowledgements

The work was carried out under Contract No. 3 T0(B010 17 financed by the Polish Committee for Scientific Research.

References

[4] Buntner B., Nowak M., Bero M., Dobrzyński P., Kasperczyk J., J. Bioactive Compatible Polymers 11(2) (1996) 110.
[5] Buntner B., Nowak M., Kasperczyk J., Dobrzyński P., Bero M., J. Contr. Rel. 56 (1998) 159.
[6] Gilding D.K., Reed A.M. Polymer 20 (1979) 1459.
[7] Bezwada R.S., Jamiolkowski D.D., Lee I.Y., Agerwal V., Persivale J., Trenka-Benthin S., Erneta M., Liu S. Biomaterials 16(15) (1995) 1141.
[8] Bero M., Czapla B., Dobrzyński P., Kasperczyk J., Janeczek H., Macromol. Chem. Phys. 200 (1999) 911.
[9]. Schwach G., Coudane J., Engel R., Vert M. J.Polym. Sci. Part A 35 (1997) 3431.
[10] Sax's Dangerous Properties of Industrial Materials. Eight Edition. Levis R.J. editor, Sr. Van Nostrand Reinhold New York 1992
[11] Bero M., Dobrzyński P., Kasperczyk J., Polym.Bull. 42 (1999) 131.
[12] Kasperczyk J. Polymer 37(2) (1996) 201.
[13] Kenley R.A., Lee M.O., Mahoney,II, T.R., Sanders L.M. Macromolecules 20 (1987) 2398.
[14] Christel T.M., Li S.M., Garreau H, Vert M, Biomaterials 13 (1992), 594.
[15] Grizzi I., Garreau H., Vert M, Biomaterials 16 (1995), 305
[16] Błażewicz M., Chomyszyn-Gajewska M., Paluszkiewicz Cz., J. Molec. Struct. 482-483 (1999), 519.
[17] Pamuła E, Błażewicz M., Paluszkiewicz C., Dobrzyński P., Journal of Molecular Structure - in print
[18] Priwałowa LG., Daurowa T.T., Voronkowa O.S., Wysokomoliekularnyje Sojednienia, A, 22(8), 1980, 1891-1894.

STUDY OF THE SURFACE PROPERTIES OF C-C COMPOSITES AS BIOMATERIALS

M. Burešová, K. Balík

Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Introduction

Carbon-carbon composites overcome many of the common problems associated with metal implants. They exhibit a relatively high strength and low modulus of elasticity, which is comparable with that of human bones [1]. Carbon-carbon composites with pores of about 40 mm in diameter can be also favourable for tissue and bone ingrowth. Their application as biomaterials is limited by cost and brittleness of matrix. The brittleness very often leads to the formation of microparticles in the tissue, which may cause inflammations around implants [2]. To prevent the release of carbon particles, the C-C composites were covered with different layers. In our work we studied the physico-chemical character of the C-C composite surface before the application of new layers.

Materials and methods

The samples used in this study were 2-D carbon-carbon composites based on plain-woven cloth (carbon fibres Torayca T800H, Japan) and phenolic resin Umaform LE (SYNPO, Ltd., Pardubice, Czech Republic) as a matrix precursor. The cured samples were cut into 7 mm x 4 mm x 3 mm pieces and carbonised at 50°C/hr up to 1000°C in nitrogen. Three-step impregnation with phenolic resin was used. Subsequently HTT up to 2200°C in argon was applied. Pyrolytic carbon was deposited from propane in a tumbling bed reactor, at ambient pressure, at the reaction temperature 850°C. Final properties of the composites are shown in TABLE 1.

	Open porosity [%]	Apparent density [g/cm^3]	Flexural strength [MPa]	Flexural modulus [GPa]
C-C composite	9	1,4	240	80

TABLE 1. Final properties of the composites.

The surface of composites was scanned by SEM Tesla BS 301.

Open porosity and surface roughness were determined by the image analysis method in the system LUCIA 4.21G

(Laboratory Imaging Ltd., Czech republic), using the metallurgical microscope Nikon Optiphot 100S and the colour CCD camera Hitachi HV-C20 E/K. The original colour-digitised images were taken in polarised light. The green component of image was extracted to create grey picture highly contrasted and tresholded. Contours of the sample open surface were detected using binary operations of the system.

Surface roughness was measured by Talysurf model 3 (Rank Taylor Hobson Ltd., England) in PRAGA Hostivar Inc.

X-ray photoelectron spectroscopic analysis (XPS) was undertaken using ESCA 310 Spectrometer to obtain information on the chemical structure of the composite surface.

Results and discussion

SEM micrographs demonstrate a typical "cauliflower" character of the pyrolytic carbon surface and coarse pores, so-called "pin holes" regularly distributed in fabric bonding point infiltrated by pyrolytic carbon, see FIG. 1.

By image analysis the full surface and smooth surface were automatically measured and compared; typical pore characteristic - the average pore-entrance width was counted out.

The average entrance width of coarse pores [IUPAC, r > 7,5 mm] was measured on the surface sample, with the average value r = 38,35 mm.

The difference between full and smooth surface - see TABLE 2, demonstrates the roughness of the composite surface. The coarse pores were measured on the sample surface separately.

Full surface	16 998,18 µm
Smooth surface	13 651,33 µm
Difference	3 346,85 µm
Pores – surface	203,44 µm
- **number of pores**	54
- **average diameter**	3,76 µm
Coarse pores	r > 7,5 µm
- **number of pores**	23
- **average diameter**	38,35µm

TABLE 2. Surface parameters from Image analysis.

Roughness of the samples was too high to be measured on Talysurf across the whole surface sample. FIG.3 demonstrates difference in profile along and across the fibre bundle.

Roughness of the surface seems to be too high to ensure good adhesion of the new layers on the surface. However, it is evident from FIG. 3 that additional appropriate polishing of the composite can lead to destruction of the upper fibre bundle at the fabric bonding points.

Roughness profile from the mean line Ra was measured across the fibre bundle, with the average roughness profile Ra = 2,25 ± 0,3 mm.

The results of X-ray photoelectron spectroscopic analysis are shown in TABLE 3.

Contrary to the analysis of carbon fibre surface, where relative content of hydroxyl groups prevails [3], the data in

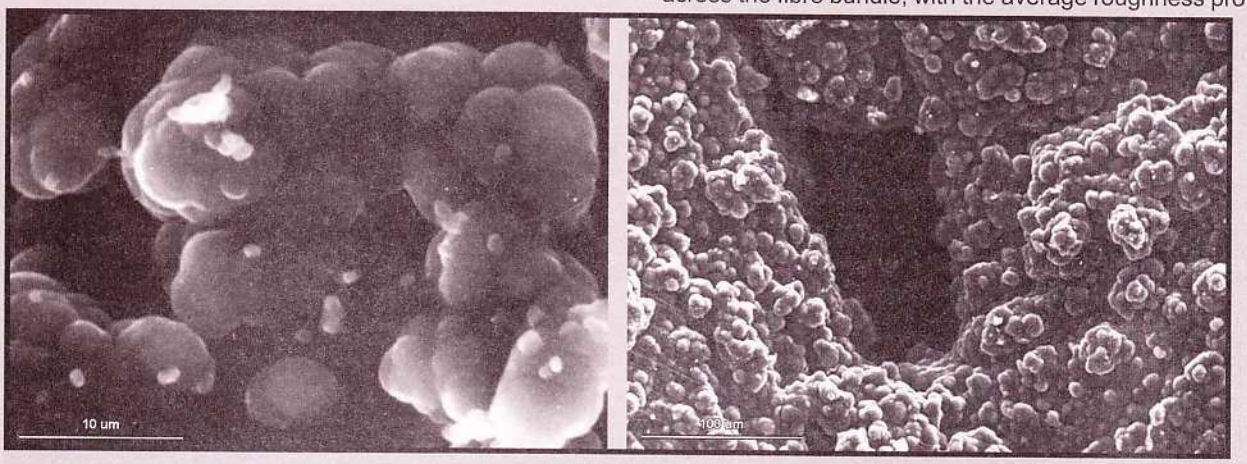

FIG. 1. SEM micrographs of pyrolytic carbon on the sample surface.

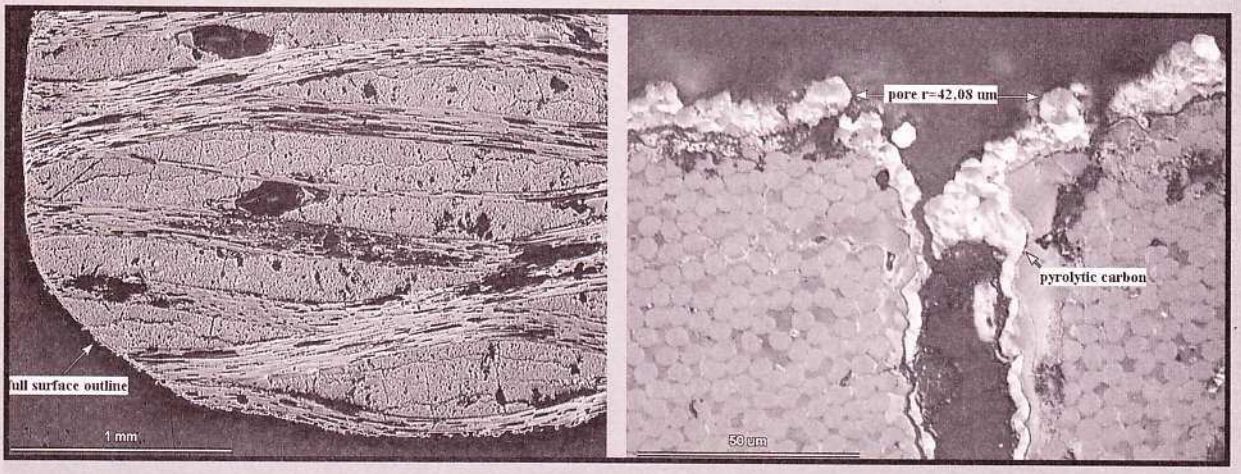

FIG. 2. Optical micrographs for image analysis.

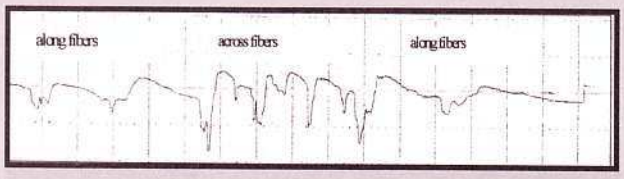

FIG. 3. Plotted profile graph of the sample, magnification 500x/40x.

Table 3 demonstrate a very high content of imine groups on the surface of our samples. This is probably results from the presence of nitrogen in the gas mixture in the tumbling bed reactor.

Element	Binding Energy (eV)	Co-ordination	Population (%)
Nitrogen	399.3	C=NH	76
	400.3	C-NH_2	24
Oxygen	531.3	C=O	47
	532.4	C-OH	10
	533.5	COOH	36
	535.9	H_20	7

TABLE 3. X-ray photoelectron spectroscopic analysis.

Conclusion

The surface of C-C composites infiltrated and covered with pyrolytic carbon shows a typical "cauliflower" character with large "pin holes" - 150x50 μm and open pores (cracks) with maximum diameter ± 40 μm. Concerning the chemical character, the imine groups prevail on the sample surface.

Acknowledgements

This study was supported by the Grant Agency of the Czech Republic under the project No. 106/99/0491.

References

[1] Sochor, M., Balík, K., Cabrnoch, B., Vilímek, M., Křena, J.: Composite plates for osteosynthesis of long bones comparison of experimental and FEM results. Locomotor System, vol. 6, No. 2, (1999), 106 -113.
[2] Pešáková, V., Balík, K., Klézl, M., Adam, M.: Biomechanical and biological properties of the implant material carbon-carbon composite covered with pyrolytic carbon. Journal of Material Science: Materials in Medicine, (in press).
[3] Kučera, M., Glogar, P., Balík, K., Tomanová, A.: Heat treatment of carbon fibres and its influence on mechanical properties of C-C composites. Acta Montana, Ser. B. No. 3 (91), (1994), 91-101.

Warunki prenumeraty

Wydawnictwo Polskie Stowarzyszenie Biomateriałów w Krakowie przyjmuje zamówienia na prenumeratę, która może obejmować dowolny okres, w którym wydawane są kolejne zeszyty. Zamawiający otrzyma zaprenumerowane zeszyty począwszy od daty dokonania wpłaty. Zamówienia wstecz będą realizowane w miarę posiadanych zapasów.

Realizacja zamówienia

Warunkiem realizacji zamówienia jest otrzymanie z banku potwierdzenia dokonania wpłaty przez prenumeratora.

Konto

Polskie Stowarzyszenie Biomateriałów
30-059 Kraków, al.Mickiewicza 30/A-3
Bank Śląski S.A. O/Kraków,
nr rachunku 10501445-1200856001

Należy podać swój adres, tytuł czasopisma, okres prenumeraty i liczbę zamawianych egzemplarzy.

Opłata

roczna - 48,- zł

Subscription terms

Subscription orders should be addressed to the Polish Society for Biomaterials in Kraków.

The ordered issues will be delivered consecutively starting from the date of payment, acknowledged by the bank.

Earlier issues will be supplied if available.

Subscription rates:

12 months - 48,0 zl
6 months - 24,0 zl

Payment should be made to:

Polish Society for Biomaterials,
Al. Mickiewicza 30/A-3,
30-059 Kraków, Poland
Bank Śląski S.A. O/Kraków,
account no. 10501445-1200856001

It is requested to quote the subscriber's name, title of the journal, desired subscription period and number of the ordered copies.