SUPERCRITICAL FLUIDS NANOTECHNOLOGIES AND THEIR APPLICATIONS

Ernest Said-Galiev[1*], Alexander Nikolaev[1], Alexander Krasnov[1],Mukhamed Keshtov[1], Alexander Vasilkov[1], Marat Gallyamov[1], Alexander Naumkin[1], Alexei Khokhlov[1], Natalia Bakuleva[2], Eleonora Shtykova[3],

[1]Nesmeyanov Institute of Organoelement Compounds, RussianAcademy of Sciences, ul. Vavilova 28, Moscow 119991,Russia

[2]Bakulev Research Center for Cardiovascular Surgery, RussianAcademy of Sciences, Rublevskoe sh. 135, Moscow 121552,Russia

[3]Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Moscow 119333, Russia

E-mail: ernest@ineos.ac.ru

The report discusses the peculiarities of supercritical (SC) technologies and provides examples of their effective practical use: in the field of friction (very long wearlife metal-composites), biomedical tribology (nanoporous ultra high molecular weight Polyethylene for implants)(UHMWPE), for creation of bacteriostatic and bactericidal drugs (Ag- and Cu-chitosan composites) and effective catalysts Pt / C of fuel cells cathode, the bimetallic catalysts Au-Pt/γ-Al_2O_3 for complete oxidation of CO into CO_2 and development of polymer materials with ultralow ($\varepsilon = 1.58$) dielectric constant.It is shown that the specific properties of fluids hold promise to create new materials with unique properties.

INTRODUCTION

Supercritical technology uses the physical properties of the fluid: density close to the liquids, viscosity close to gases, a high coefficient of self diffusion and diffusion in other environments, inertness of CO_2 in absence of catalysts, environmental cleanliness , lack of surface tension and absolute wettability of any surfaces, high extracting and dispersing ability, plasticizing capacity of supercritical carbon dioxide (SC CO_2) and the processes of reduced temperature.

SC CO_2 is used as a solvent, diluent, catalyst, monomer, and transport medium. Materials used for modifying: a gaseous, liquid or SC CO_2 in pure form or as a transport medium and a solvent for the introduction of various functional additives (FA): organometallic complexes (ML, M-metal, L- ligand), bioactive substances, dyes, monomers (impregnation process) into polymeric or inorganic matrices.

Features of supercritical impregnation:

1. the modification of polymeric , carbon-black- and metal- carboxylic matrices using ML always gives rise to nanosize particles ;
2. diffusion of ML into polymer matrices, followed by reduction of the metal is available to form modified layer with a depth from some micrometers to several millimeters, and the content of metal nanoparticles reaches ~ 10 % ;
3 in the case of the good solubility of the metal precursor following deposition on the support gives a high concentration of functional additive , besides the metal nanoparticles have a high adsorption capacity and good retained on the carrier particles;

4. it is possible to achieve a concentration of metal nanoparticles to 1-4 wt. % in the case of poorly soluble FA often due to a favorable distribution coefficient. The quantity is enough to create heterogeneous catalysts;
5. a cluster size can be controlled by temperature monitoring;
6. if it is necessary to obtain a large concentration of PA in the surface layer the features of anomalous impregnation can be used so as the extreme dependence [C] = f (τ)in the first 10-15 minutes of the experiment (where C is the concentration of PA and τ - time of impregnation) conducting a rapid reactor decompression and re- impregnation within the specified time.

The report discusses the features of supercritical technologies and examples of their effective practical use: in the field of friction (very long wearlife metal-composites), biomedical tribology creation of bacteriostatic and bactericidal drugs, effective catalysts Pt / C of fuel cells cathode, bimetallic catalysts for complete oxidation of CO into CO_2 and development of polymer materials with ultralow dielectric constant.

MATERIALS AND METHODS

Organometallic complexes of silver cyclopentadienyl hexafluoroacetylacetonate COD Ag [hfacac], hexafluoroacetylacetonate hydrate copper Cu $(hfacac)_2$ x H_2O , cyclopoctadiene dimethyl platinum COD Pt $(CH_3)_2$ were obtained from the Aldrich. Matrices: polyarylate based on tere - isophthalic acid (1 : 1) and bisphenol A with MW = 60 kDa and a fluorinated polyphenylenes synthesized in the laboratory [1]. Soot marks "Vulcan" with S_{sp} = 150 m^2/ g and chitosan with MW = 160 kDa and deacetylation degree ~ 98 % were purchased from "Aldrich". Metal-polymer composites are prepared by impregnation or by precipitation of metal precursor in the matricesfrom the SC CO_2solutions followed by reduction with a helpof temperature or hydrogen. Abrasion model samples were performed on the“home-made” friction set. Biological tests were carried out on bacteria S. epidermidis, E-coli and spore form of B-cerius pre-adapted to acidic medium with pH 4-5. Preparation of polymers with ultralow dielectric constant were carried out by -swelling of polyphenylene films in SC CO_2 at 25° C and 0 ° C and following thermal shock at 250-280° C for 30 s. Nanoporous UHMWPE was obtained by treating of the polymer powder with SC CO_2 at 80 ° C and 10 MPa, followed by pressing of the model sample at 190^o C. The methods of investigation: X-ray fluorescent elemental analysis, ESCHA, SAXS, TEM were used.

RESULTS

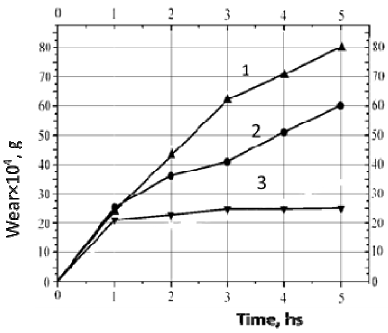


Figure 1. Dependence of linear wear value on abrasion duration for samples:
1 - initial, impregnated with Cu $(hfacac)_2$,
2 – initial after heating for 5 hs at 225^{o}C ,
3 - initial impregnated and reduced at 225^{o}C

Antifriction materials based on synthetic polymers (polyarylates) impregnated with copper chelate complexes, showed a dramatic decrease in the coefficient of friction and temperature in the contact area and this way have good prospects for the creation of so-called "very long wearlife " materials [2].

By impregnation of several types of chitosan derivatives with metal-organic complexes COD Ag [hfacac] and Cu $(hfacac)_2$ were obtained nanometal- chitosan complexes with a strong bactericidal effect not only with respect to microbes but also to spores[3].

Clinic culture E-coli, exposition in aquatic solutions of Cu- and Ag-metal-complexes of chitosan derivatives.

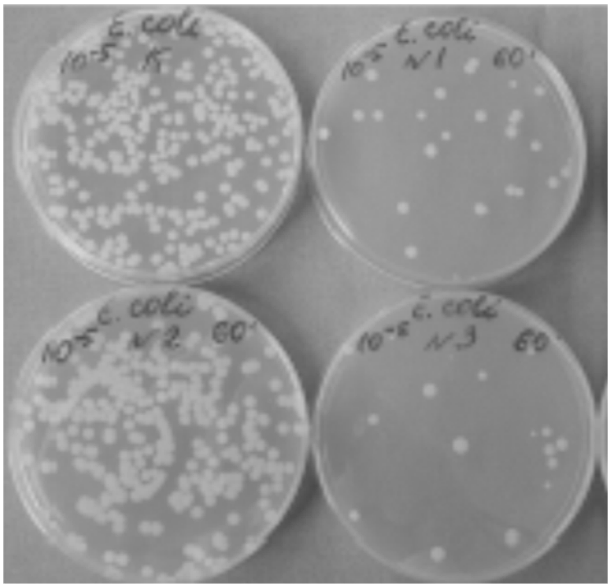


Figure 2a. Cu^{2+}-chitosan specimens, Kis control sample.

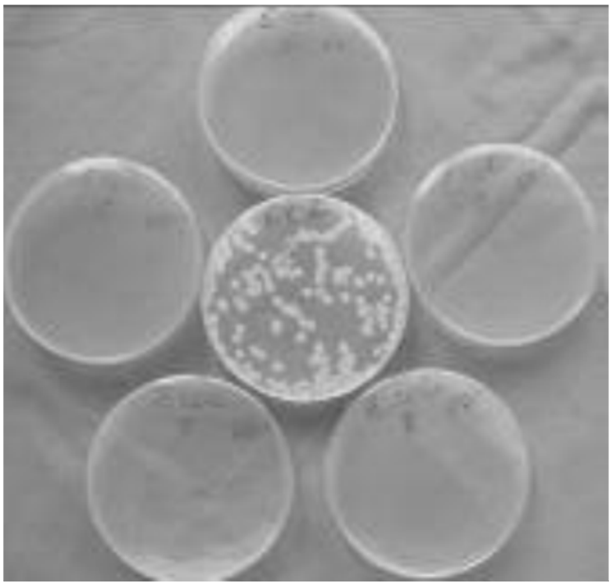


Figure 2b.Ag^{0}- and Cu^{0}- -chitosan specimens, K is control sample. Ag^{0}claster sizes are lower than 10 nm.

It is seen from Figure 2a that bacteria growth becomes slower but is not completely suppressed. It is seen from Figure 2b, that bacteria growth is completely suppressed (bactericidal effect)**.** The same result is obtained with S. epidermidis and B-cereus.

Polymeric Ag^{0}и Cu^{0}-chitosan nanocomplexes, synthesized in $SCCO_2$ and reduced with hydrogen from Cu^{2+} have shown the highest antimicrobial activity with respect to E-coli, S-epidermidis and even to spore form B-cereus as compare with Cu^{2+}chitosan salts, obtained by routine solution methods. Dimensional effect also matters.

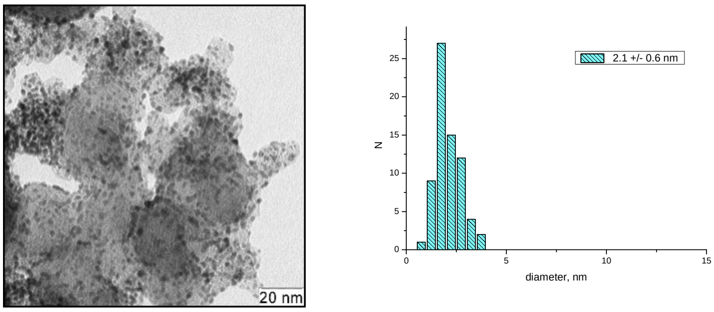


Figure 3. Micrograph Pt/C catalyst and size distributionhistogram

Reproducible laboratory technology of electrocatalysts (EC) synthesis in SC CO_2 medium permitting to synthesize monodisperse nanosize Pt particle regardless of wettability degree of carbon substrate surface was developed [4].

The size of obtained particles and Pt specific surface including electrochemical active one for synthesized EC are identical to specifications of best commercial materials HiSPEC3000 and HiSPEC4000of Johnson-Mattheycompany.

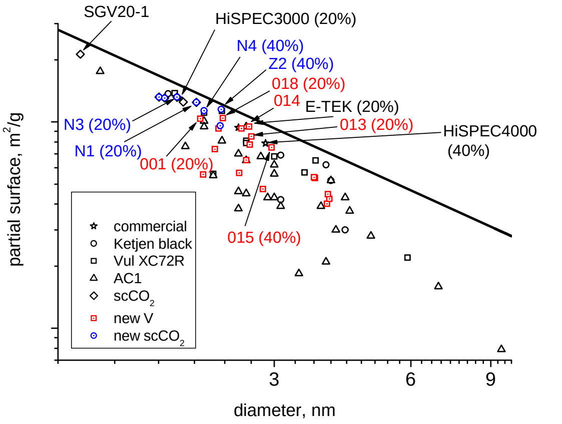


Figure 4. The theoretical dependence of specific area of catalyst surface on Pt particles size.

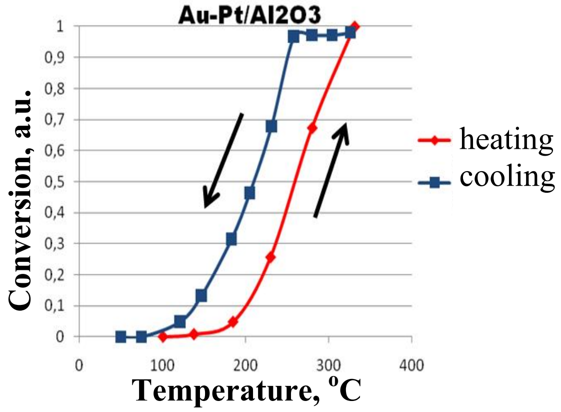


Figure 5. Full oxidation of CO into CO_2 using bimetallic catalyst Au-Pt/γ-Al_2O_3 (Pt, 0.34%, Au, 0.1%, catalytic circulation set, GC analytical method).

It is seen from the plot that our specimens (abbreviation "N" and "Z") are located closer to theoretic straight line than commercial and another ones.

Bimetallic catalysts Au-Pt/γ-Al_2O_3 synthesized by SC CO_2 (first metal Pt) and metal-vapor synthesis (second metal Au) have proven to be effective catalysts of CO to CO_2 complete oxidation [5].

The specimens does not demonstrate any activity up to temperature of 180°C.100% conversion was reached at the temperature of 330°C. At the other way a conversion corresponds to 180°C was 31%. As can be seen a strong activation has occurred and besides the sample did not lose its activity at repeating cycles.

It was shown that an insertion of a second noble metal increases monometallic catalyst effectiveness.

The material based on UHMWPE for artificial joints is developed [6]. It has a high ductility and friction coefficient close to a cartilage in natural joint.

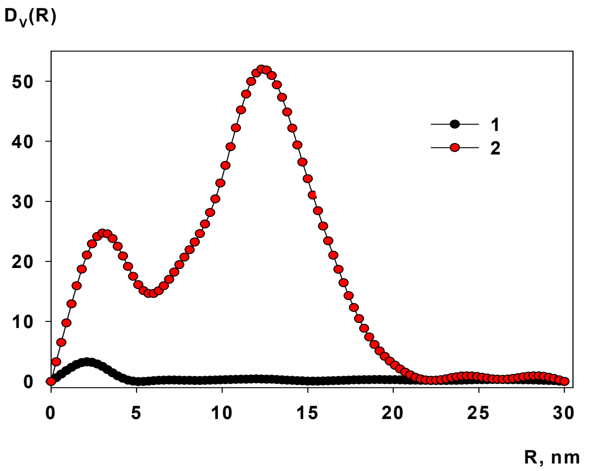


Figure 6. The curve of pores size distribution (SAXS-method)

1-UHMWPE initial (powder), 2- molded thin disc from powder exposed in SC CO_2.

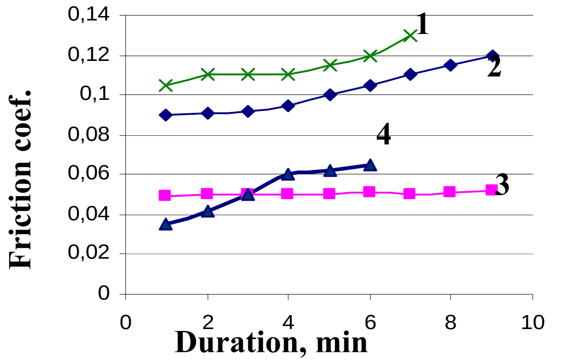


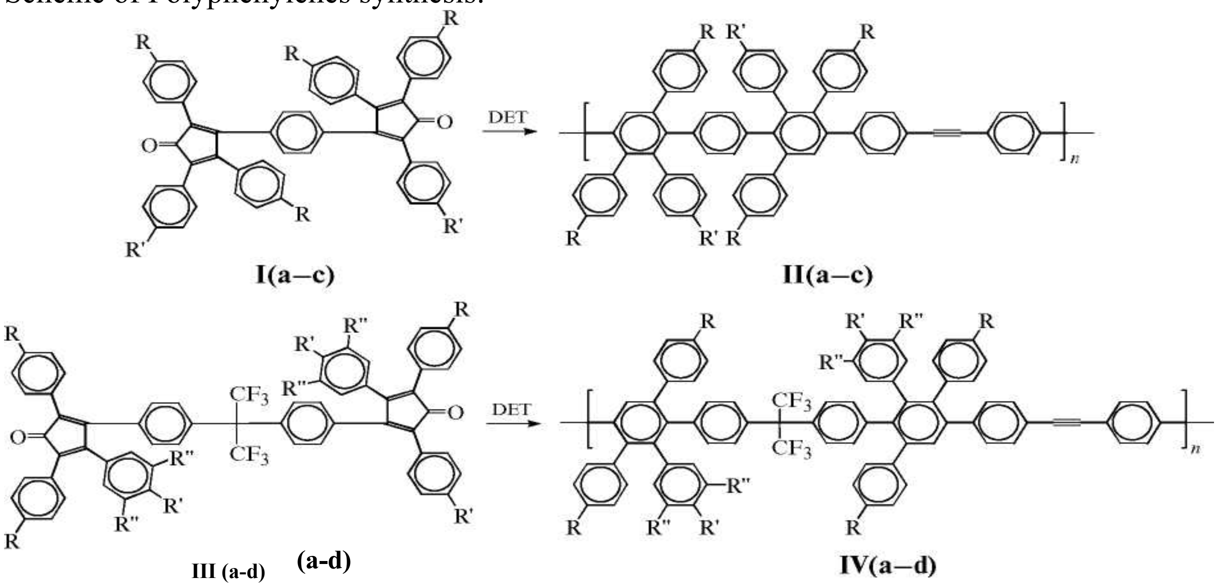
Figure 7. Results of abrasion tests. Pair of friction: 1 – metal (Ti) – cartilage, 2 - composite(AP + UHMWPE) – cartilage; 3 – composite (AP+ nano UHMWPE) – cartilage; 4 – cartilage on cartilage.

Unique results is obtained: the friction coefficient of the composite on cartilage is closed to one of natural joint (cartilage on cartilage).

An exposition of UHMWPE powder in SC CO_2 gives rise to formation of closed pores in it where gas formed at depressurization of a reactor accumulates. After molding of a model specimen for abrasion by sintering mode the gas stays in its body and remains in closed pores for a long time. The material acquires a high ductility. Gas microquantities escape during abrasion and acts as a “chemical lubricant” decreasing strongly the friction coefficient and the temperature in contact zone. The material was proposed as an additive to reinforced acrylic polymers for making of artificial joint.

Plasticizing and pore-forming ability of SC CO_2 were used for development of polymer materials with ultralow (ε = 1.58) dielectric constant [1].

Scheme of Polyphenylenes synthesis:



Ia: R = R' = H, Ib: R = H, R' = F; Ic: R = F, R' = H ;**DET = diethynyltolane**

IIa: R = R' = H, IIb: R = H, R' = F; IIc: R = F, R' = H.

IIIa: R = R' = R'' = H, IIIb: R = R'' = H, R' = F; IIIc: R'' = R' = H, R = F; IIId: R'' = H, R' = R = F'.

IVa: R = R' = R'' = H, IVb: R = R'' = H, R' = F; IVc: R'' = R' = H, R = F; IVd: R'' = H, R' = R = F).

The films of synthesized polymers swelled in CO_2 at the temperature of 25°C and 0°Cfor 2-3 hs and then were subjected to thermal shock at 250-280 °Cfor 30s for formation of porous material.

Table1. The conditions of pores formation, morphology and dielectric constant of nanoporous polyphenylenes.

Polymers	P_{swell} MPa.	T_{swell} (°C)	Theat (°C)	Tg, (°C)	Density (g/cm³)	Morphology	k
VIIB	-	-	-	340	1.28	compact	**2.80**
	5.0	25	250		1.22	micropores	2.58
	5.0	25	290		0.98	nanopores	2.00
	5.0	**0**	**290**		**0.89**	**nanopores**	**1.81**

VIIIa	-	-	-	297	1.24	compact	**2.63**
	5.0	25	240		1.08	micropores	1.97
	5.0	25	280		0.86	nanopores	1.68
	5.0	**0**	**280**		**0.84**	**nanopores**	**1.60**
VIIIб	-	-	-	290	1.24	compact	**2.58**
	5.0	25	240		1.10	micropores	1.91
	5.0	25	280		0.71	nanopores	1.65
	5.0	**0**	**280**		**0.70**	**nanopores**	**1.61**
VIIIв	-	-	-	303	1.24	compact	**2.54**
	5.0	25	240		1.02	micropores	1.88
	5.0	25	280		0.70	nanopores	1.65
	5.0	**0**	**280**		**0.70**	**nanopores**	***1.58***
VIIIг	-	-	-	299	1.23	compact	**2.54**
	5.0	25	240		0.98	micropores	1.81
	5.0	25	280		0.73	nanopores	1.61
	5.0	**0**	**280**		**0.71**	**nanopores**	***1.59***

CONCLUSION

The report discusses the peculiarities of supercritical technologies and provides examples of their effective practical use: in the field of friction (very long wearlife metal-composites), biomedical tribology (nanoporous ultra high molecular weght Polyethelene for implants), for creation of bacteriostatic and bactericidal drugs (Ag- and Cu- chitosan composites) and effective catalysts Pt / C of fuel cells cathode, the bimetallic catalysts Au-Pt/γ-Al_2O_3 for complete oxidation of CO into CO_2 and development of polymer materials with ultralow ($\varepsilon = 1.58$) dielectric constant.

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