

CREATION OF METAL-POLYMER NANOCOMPOSITES IN SUPERCRITICAL CO₂ AND THEIR STRUCTURE INVESTIGATION

Schaumburg K.^a, Jespersen H.^a, Khokhlov A.^b, Said-Galiev E.*^b, Grishin D.^c, Nikitin L.^b,
Vinokur R.^b, Galliamov M.^c, Kurykin M.^b, Volkov V.^d, Aliev A.^e, Lebedeva O.^c, Tameev A.^f

^a Centre for Interdisciplinary Studies of Molecular Interactions, Department of Chemistry,
University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

^b A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
Vavilova Str., 28, Moscow, 119991 Russia. ^c Physics Department of Lomonosov State

University, Vorob'evy gory, 119992 Moscow, Russia

^d Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia

^e Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia

^f Institute of Electrochemistry, Russian Academy of Sciences, Moscow, Russia

E-mail: ernest@ineos.ac.ru, Fax: 7(095)1355085

This report deals with introduction of Pt, Co, Ni, Fe, Cu, Ag, Pd-organic complexes from their solutions in sc CO₂ into polyarylate (PAR), PTFE, PC and PS matrices. Metal-polymer nanocomposites have been produced by metal reduction and were characterized by gravimetric, FTIR, UV-VIS, SAXS, SEM, TEM and EPMA methods. Metal-polymer composites which were obtained in our work can be interesting for applications as catalysts, conductive, optical and other advanced materials.

INTRODUCTION

Metal-polymer complexes find their application as catalysts, conductive layers, light-emitting materials, energy transducers, polymer electrolytes, materials for nonlinear optics and electrode coatings for electrocatalysis and photoelectrode reactions, as metal-supramolecular initiators and more [1]. The size of metal particles is very important because in many respects it determines the physical properties of appropriate metal-polymer composite [2]. For many applications nano-sized structures are most interesting. A modern method to create nanocomposites is a diffusion of metalloorganic complexes from their solutions in supercritical fluid [3]. Our previous article was dedicated to the impregnation of polyarylate (PAR) films with copper and iron hexafluorodimines [4]. Here we report a new results on diffusion of Pt, Co, Ni, Fe, Cu, Ag, Pd-organic complexes from their solutions in sc CO₂ into PAR, PTFE, PC and PS matrices for creation of new functional materials. Metal-polymer nanocomposites have been obtained and their structure and morphology were investigated. Some functional properties of the materials were also tested.

I - MATERIALS AND METHODS

Materials

Aminoimines and their Cu-, Fe-, Co-, Ni-chelate complexes were synthesized according to [3]. Ferrocene, COD Pt (CH₃)₂, Pd (acac)₂, [Ag (COD) hfacac]₂ were purchased from "Aldrich" and used without additional purification. Polymer films: PET (thickness 50±1 μm), PC (130±5 μm)

were received from “NKT”(Denmark); PMMA and PS in the form of granules were purchased from “Aldrich”. The films with a thickness of $30 \pm 2 \mu\text{m}$ were performed by casting from their chloroform solution on to cellophane substrate. Polyarylate (a polyester of bis-phenol A and tereisophthalic acids) film with a thickness of $39 \pm 2 \mu\text{m}$ was received from “Plastpolymer”. PTFE film ($10 \pm 1 \mu\text{m}$) was received from “Triada-Plastik” (Russia).

Experimental set-up

A syringe pressure generator, valves and cappillars from ”High Pressure Equipment Company” were used to deliver pressure to a custom-made stainless-steel cell (Fig. 1) with a reaction volume 10 cm^3 .

Impregnation

A crystalline metalloorganic complex and magnetic stir bar were loaded in to the cuvette. The film sample with the square of 1 cm^2 was placed on a wire-mesh. Then, the cell was closed and pressurized up to 5-6 MPa, heated up to desired temperature and pressurized to working pressure. The runs were carried out in two temperature-pressure steps: the first step is solvation of the complex in sc CO_2 and second one is the impregnation of polymer matrix. After completion of a run the cell was decompressed and the film was weighed on OHAUS AP250D electronic balance (the accuracy of 10^{-5} g).

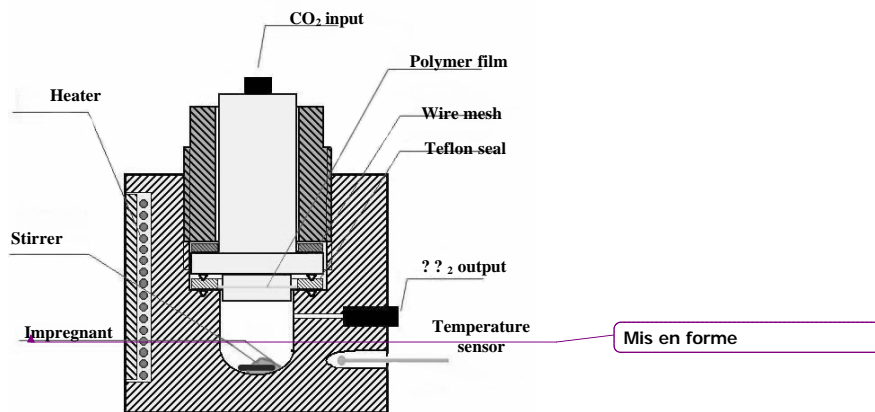


Figure 1. Experimental cell

Reduction of metal

Reduction of a metal was carried out under Ar- or CO_2 - atmosphere in the cuvette at the temperature of $140\text{-}220 \text{ }^\circ\text{C}$ for 2-4 hours or in a horizontal furnace at a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ to $230 \text{ }^\circ\text{C}$ and keeping at this temperature for 30 min. After that they were cooled, weighed and placed into an ampule filled with argon to prevent any subsequent chemical processes.

Spectral Measurements

The FT-IR spectra were recorded on a “Nicolet” Magna 750 and “Carl Zeiss” SPECORD 71IR spectrometers. The size distribution of metal particles in films was determined using an automated small-angle X-ray diffractometer Amur-K (Cu K_α radiation, $\lambda = 1.54 \text{ \AA}$), operating at the accelerating potential of 30 kV and the anode current of 30 mA. EPMA analysis was carried out on LSM-U3 JEOL scanning electron microscope at an accelerating voltage 25kV. X-ray photons emitted from the sample were detected by a KEVEX-5100 X-ray energy dispersive spectrometer (EDS mode) at take off angle 30° . SEM investigations were proceeded on “Zeiss” DSM 962 scanning electron microscope by standard technique. TEM-images were made on “Philips” EM 400 T transmission electron microscope.

II - RESULTS AND DISCUSSION

Results of impregnation are given in the following tables:

Table 1. Impregnation conditions and results for metal diiminates

Complex	Polymer	T, °C	P, MPa	Time, h	[C] _{complex} , %	[C] _{metal} , %
Cu(II)-HFPDI	PAR	90	12.0	2.0	50.0	10.9
			9.0	1.0		
	PS	45	9.0	1.6	1.92	0.24
			9.0	1.0	4.36	0.56
	PC	75	14.0	1.0		
			9.0	1.0		
PTFE	75	14.0	1.0	0.25	0.03	
		9.0	1.0			
Co(II)-HFPDI	PAR	110	12.0	2.0	11.2	1.45
			9.0	1.0		
	PC	110	18.0	2.4	19.8	2.80
			10.0	1.6		
	PTFE	110	12.0	2.0	12.5	1.70
			9.0	1.0		
PMMA	45	12.0	1.6	29.0	4.80	
		9.0	1.6			
Ni(II)-HFPDI	PAR	110	12.0	2.0	25.5	3.80
			9.0	1.0		
	PC	100	12.0	2.0	17.8	2.45
			9.0	1.0		
	PTFE	100	9.0	1.0	1.45	0.17
			12.0	2.0		
Fe(III)-HFPDI	PAR	100	21.0	2.2	6.75	0.55
			9.0	2.0		
	PC	100	21.0	2.2	9.60	0.80
			9.0	2.0		

As seen from the table the copper complex among diiminate ones possess a maximum impregnation ability. The reason may be a better solubility in sc CO₂ and a more compact conformation in a solution. The iron diiminate has a minimum impregnation ability, perhaps due to a larger size of molecule. Ni-diiminate penetrates into PAR better than Co- one. The impregnation effectivity depends also on swelling ability of polymer matrix (10 wt % for PAR and 18 wt % for PMMA, at 38 °C, 12.5 MPa).

The results of impregnation and reduction (200 °C, 2.15 h, air) of copper diiminate in PAR film are shown on Fig.1. As seen from the location of imine group band a reduction of copper proceeds completely. Considerable shifts of NH bands in impregnated complexes (Table 2) may be attributed to the interaction with a polymeric system and change of complexes conformations.

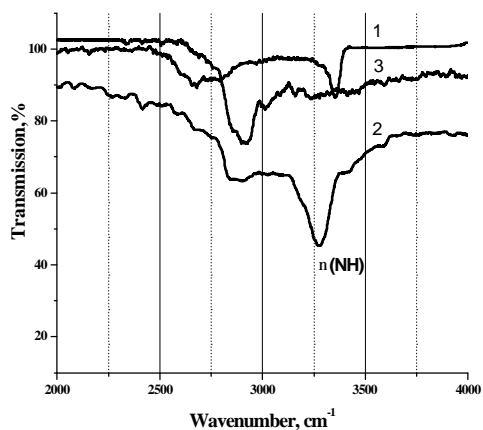


Figure 1. 1- Cu(II)HFPDI in n-hexan, 2- PAR film after impregnation, 3- PAR film after impregnation and metal reduction.

Table 2. List of "red" shift in wave number of IR absorption peaks due to interaction between the PAR and the incorporated complex

Complex	Functionel group	
	N-H	C=O
Cu(II)-HFPDI	41 cm ⁻¹	6 cm ⁻¹
Fe(III)-HFPDI	26 cm ⁻¹	1 cm ⁻¹
Ni(II)-HFPDI		1 cm ⁻¹
Co(II)-HFPDI	35 cm ⁻¹	3 cm ⁻¹ *
(Ferrocene)	37 cm ⁻¹	3 cm ⁻¹ *

* "blue" shift.

Table 3. Impregnation conditions and results

Complex	Polymer	T, °C	P, MPa	Time, hs	[C] _{complex} , %	[C] _{metal} , %
Fe(C ₅ H ₅) ₂	PAR	110	12.0	2.0	25.9	9.5
			9.0	1.0		
	PC	100	9.0	1.0	11.7	3.8
			13.0	1.8	0.07	0.02
			13.0	1.8	2.8	0.85
(COD) Pt(CH ₃) ₂	PAR	100	22.0	2.25	27.20	18.0
			10.0	1.00		
	PTFE	120	35.0	3.25	0.34	0.20
			10.0	1.50		
			25.0	3.70	14.1	8.8
	PS	100	22.0	2.25	destr.	
			10.0	0.80		
PMMA	90	10.0	10.0	1.0	8.3	5.0
Pd(acac) ₂	PAR	120	15.0	1.70	4.80	1.70
			15.0	1.70	8.30	3.05
	PC	120	9.0	0.75	0.25	0.09
			20.0	2.25	destr.	
			9.0	1.75		
[Ag(COD) (hfacac)] ₂	PAR	100	20.0	2.20	27.10	8.70
			9.0	2.00		
	PC	100	20.0	2.20	4.74	1.25
			9.0	1.25		

*Percent of impregnated complex: $C_{\%} = \frac{M_I}{M_I + M_P} \cdot 100\% = \frac{M_{IP} - M_P}{M_{IP}} \cdot 100\%$, where M_P is initial mass

of the polymer sample, M_I is the mass of impregnated complex and M_{IP} is the mass of the impregnated polymer sample after desorption of CO_2 .

**Percent of impregnated metal if the complex is decomposed and only the pure metal is left in the polymer sample:

$$M_{\%} = \frac{\frac{AW}{FW} \cdot (M_{IP} - M_P)}{\frac{AW}{FW} \cdot (M_{IP} - M_P) + M_P} \cdot 100\% = \frac{AW \cdot (M_{IP} - M_P)}{AW(M_{IP} - M_P) + FW \cdot M_P} \cdot 100\%$$

, where AW is the molar mass of the metal and FW is the molar mass of the whole complex.

As seen from the tables near all of runs were made on two step mode for an increase of metal complex partition coefficient [5]. The Pt, Ag - complexes and Ferrocene are very effective impregnants may be due their good solubility in sc CO_2 .

Pt-complex is characterized with nonuniform distribution along the film depth and concentrates mainly near the surfaces (Fig. 3).

At the same time the distribution for copper complex was found to be uniform.

The Pt particles are not seen on the surface but the picture of cross-cut is unexpected. Large spherical metal aggregates (up to 1.5 μm in diameter), which consist of lower size particles are seen. The sample was unstable in the beam and we could not obtain higher magnification.

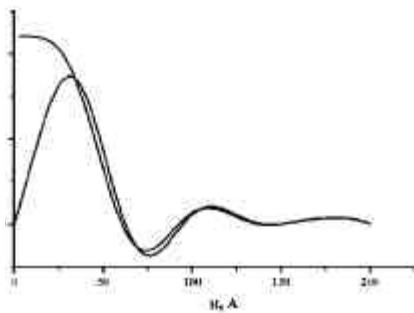


Figure 4. Size distribution of Pt-particles in PAR (reduction conditions: 210 °C, 2.75 h, Ar).

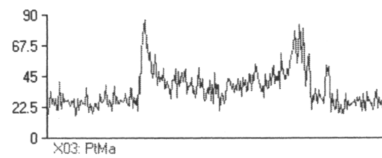


Figure 3. EMPA scan through PAR film cut for Pt content. Film thickness is $39 \pm 2 \mu\text{m}$.

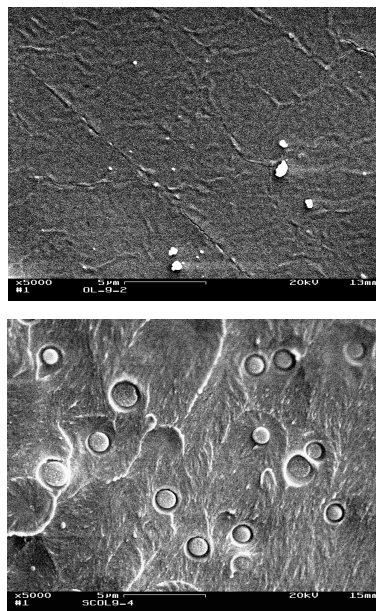


Figure 5. SEM-images of the surface (top) and cross-cut (bottom) of PAR film after platinum reduction.

PAR films impregnated with Pd- and Fe-complexes after metal reduction were investigated by TEM. Particle sizes were 2-12 nm for palladium and 3-5 nm for iron. We also tested some electrical and catalytic properties of our metal-polymer composites.

Table 4. Some electrical characteristics of PAR film samples impregnated with Ag-complex and reduced in argon flow

Sample	Capacity, pF	Dielectric loss tangent	Specific resistance, $\Omega \cdot \text{cm}$
1, initial	18.9	0.0035	$1.48 \cdot 10^{14}$
2, impregnated (12% of the complex) and reduced (230 °C, 2h)	10.2	0.0095	$7.4 \cdot 10^{11}$
3, impregnated (4.4% of the complexes) and reduced (205 °C, 2h)	17.7	0.0047	$1.8 \cdot 10^{13}$

As can be seen from the Table 4 the composite after reduction is nearly the same as dielectric properties, though the specific resistance can decrease by the orders of magnitude. The reflectance of the sample 3 was higher as compared with 2, but its electrical properties differ little from the initial sample. This means that the main part of metal concentrates in a surface layer. Verification of catalytic properties has shown that PS film, containing Cu particles (0.15 wt. %) catalyzes the reaction of hydroquinone - quinone oxidation.

CONCLUSION

The conditions of copper-, nickel-, cobalt-, iron hexafluorodiiminates, ferrocene, palladium(II) acetylacetonate, (1,5-cyclooctadiene) dimethyl platinum(II) and (1,5-cyclooctadiene)(hexafluoroacetylacetonato)silver(I) impregnation into polyarylate, PC, PET, PS and PMMA have been found. The structure and morphology, electrical and catalytic properties for some of them have been studied.

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REFERENCES:

- [1] DARR, J.,A., POLIAKOFF, M., Chem. Rev., Vol. 99, **1999**, p.495
- [2] KAZARIAN S., G., Polymer Science, Ser. C, Vol.42, **2000**, p.78
- [3] SAID-GALIYEV, E., NIKITIN, L., VINOKUR, R., GALLIAMOV, M., KURYKIN, M., PETROVA, O., LOKSHIN, B., VOLKOV, V., KHOKHLOV, A.,SCHAUMBURG, K., Ind. Eng. Chem. Res., Vol.39, **2000**, p.4891
- [4] HOWDLE, S., M., QUN, L., POPOV, V., K., BAGRATASHVILY, V., N., SOBOL, E.N.,The 4th Int. Symp. on Supercritical Fluids, Japan, May 11-14, 1997: ISASI, Nancy, France **1997**, p.250.