THE STRUCTURE AND MORPHOLOGY OF METAL-POLYMER NANOCOMPOSITES MADE IN SUPERCRITICAL CARBON DIOXIDE

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The method of organometallic compounds impregnation into polymer matrices assisted by supercritical carbon dioxide (SC CO_2), reduction of metals and metal-polymer nano composites formation are considered. The organometallic include Pd, Pt, Ag-complexes. Metal-polymer nanocomposites structure investigation by SAXS, SEM and some other methods are presented.

INTRODUCTION

Impregnation of metal-organic compounds into polymer matrices is one of important development line of "green chemistry" in supercritical carbon dioxide (SC CO_2). Metal-polymer composites made by impregnation of SC CO_2 solution of metalloorganic compounds into polymer matrices are interesting as catalytic, conductive, antifriction, biotribological and other materials. The articles published last years were devoted to impregnation of COD Pt $(CH_3)_2$ into poly(4-methylpentene and PTFE [1], Fe $(hfacac)_3$ into LDPE [2], COD Ag [hfacac] into PI [3], Cu $(hfacac)_2$ and Fe $(hfacac)_3$ into polyarylate(PAR) [4], Cu(II)-, Co(II) -, Ni(II)-, Fe$(hfdi)_3$, ferrocene, COD Pt $(CH_3)_2$, Pd $(acac)_2$, COD Ag [hfacac] into PAR, PTFE, PET, PC, PS [5] and COD Ag (tetraglim) into UHMPE [6].

The work deals with synthesis of Pt / PAR, Pd / PAR and Ag / PAR composites and investigation of their structure and morphology.

I - MATERIALS AND METHODS

Commercial complexes COD Pt $(CH_3)_2$, Pd $(acac)_2$, COD Ag [hfacac] were received from Aldrich. Polyarylate on the base of bis-phenol A and tere (iso-) phthalic acids (1:1), M_w= 80 10^{3} , M_w / M_n = 2.4, amorphous, T_g == 220- 230° C was purchased as a film with a depth of 39± 2 μm on "Polymersynthesis", Russa. Impregnation of metalloorganic compounds from SC CO_2 solutions into polymer matrix and subsequent reduction of the metal in Ar, CO_2 or H_2 medium were applied as a method of metal particles immobilization in polymer matrices. Analysis technique included: gravimetry, UV-VIS-spectrophotometry, SEM-, SAXS- and RFA. Construction of the reactor is given below.

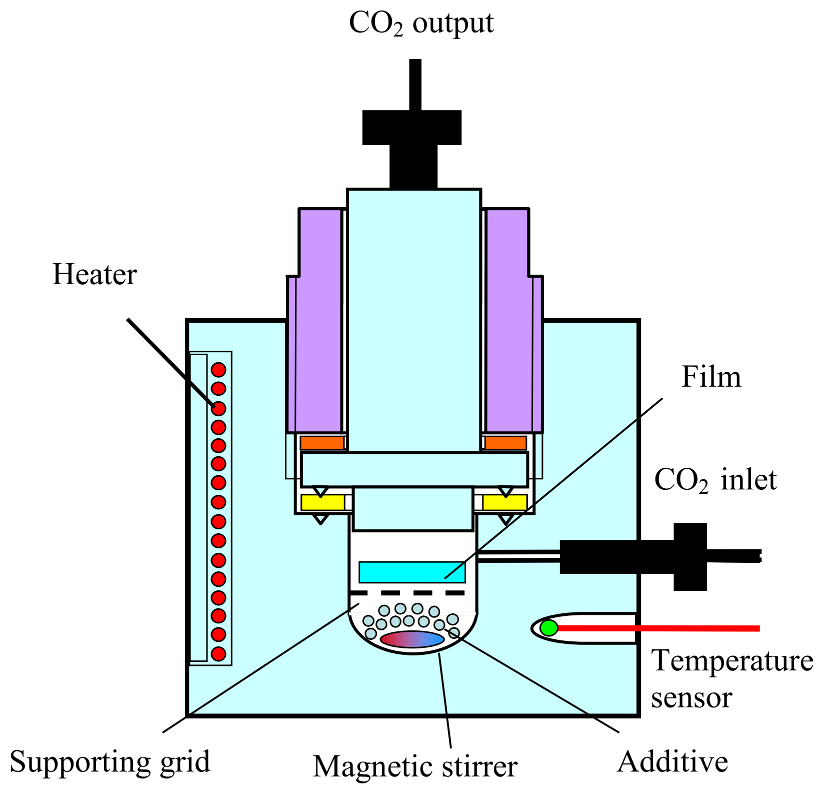


Figure 1. Reactor construction.

II - RESULTS AND DISCUSSION

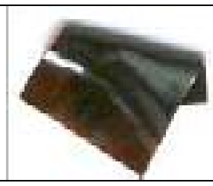
Conditions and results of experiments are cited in the following tables:

Table 1. PAR impregnation conditions

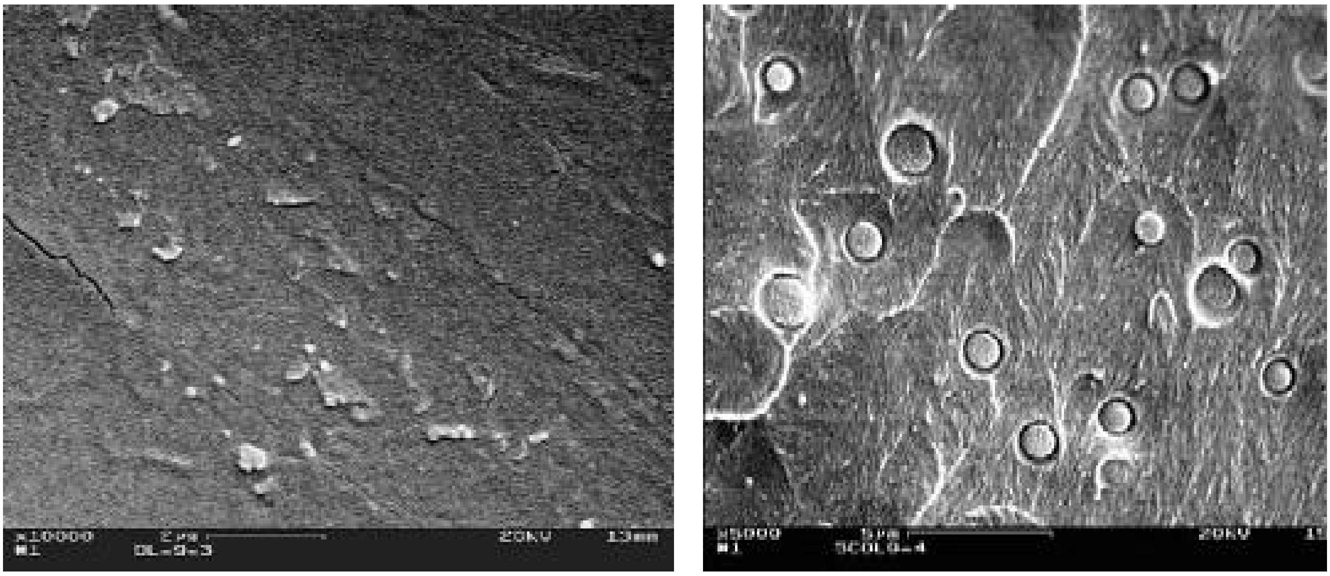
Complex	**T, ^{o}C**	**P, bar**	**t, hrs**	**Complex conc., %**	**Metal concentration (calculation and RFA data)**	**Film appearance**
PAR initial	100	200	2.0	0	0	Transparent, colorless
COD Pt $(CH_3)_2$	100 90	200 100	2.0 1.0	27.2	18.0	Transparent
Pd $(acac)_2$	90 110	200 100	1.4 1.0	5.0	1.8	
COD Ag (hfacac)	105 110	150 100	3 1.3	12.1	3.4	

It is seen from the table that Pt and Ag-complexes are impregnated into PAR-film more efficiently. Pd is impregnated weaker that may be explained by its lower solubility in SC CO_2. Two-step impregnation was used for increasing of the partition coefficient.

Table 2. Metal reduction conditions

Complex	T, ^{o} C	P, bar	Time, hrs	Medium	Film appearance
COD Pt $(CH_3)_2$	a/210 b/60	1 70	2.5 7.7	Ar H_2	
Pd $(acac)_2$ COD Ag(hfacac)	225 205	1 1	3.0 2.0	Ar air	

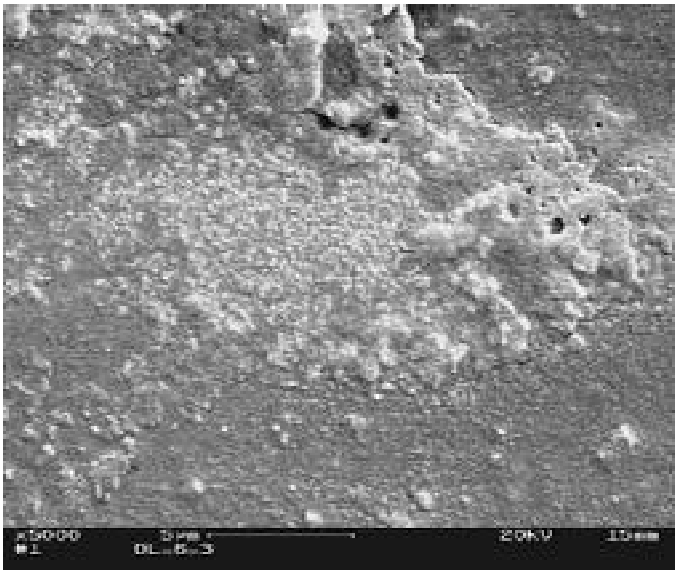
A thermal reduction may proceed in different atmosphere. Utilization of H_2 lets to decrease appreciably the temperature of the metal reduction. After reduction of the metal polymer films lose their solubility in volatile organic solvents.

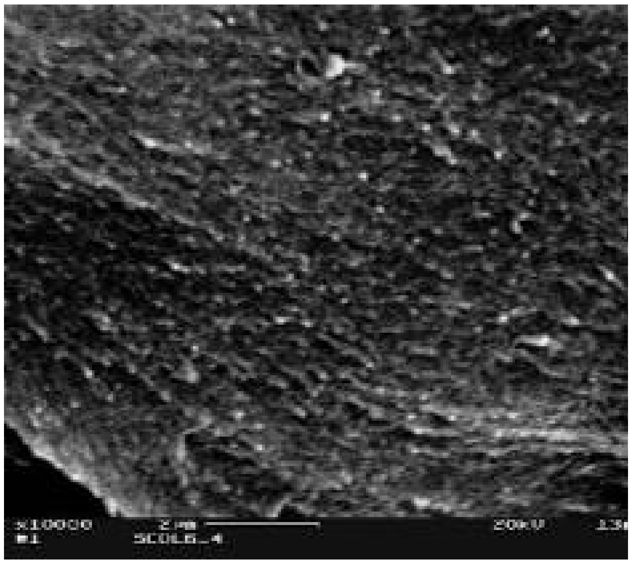


a) b)

Figure 2. SEM-photomicrography of Pt / PAR composite: **a)** - surface, **b)** - cross-cutting

Some quantity of Pt locates on the film surface. One can see huge clusters with the size 1-15 μm consisting of large quantity of small particles on the cross-cutting surface

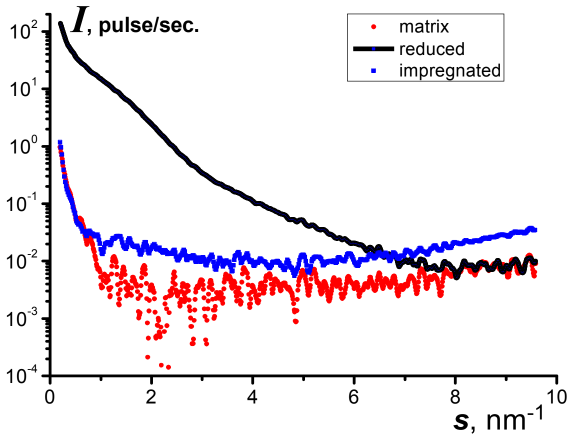


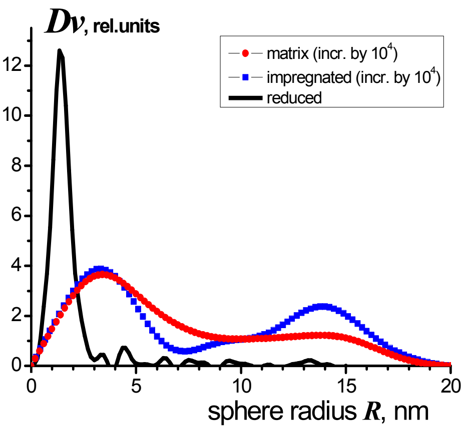


a) **b)**

Figure 3. SEM-photomicrography of Pd / PAR film: **a)** - surface, **b)** - cross-cutting.

It is seen many metal particles on the film surface and a low one on the cross-cutting surface but this may be due their small size and therefore low visibility

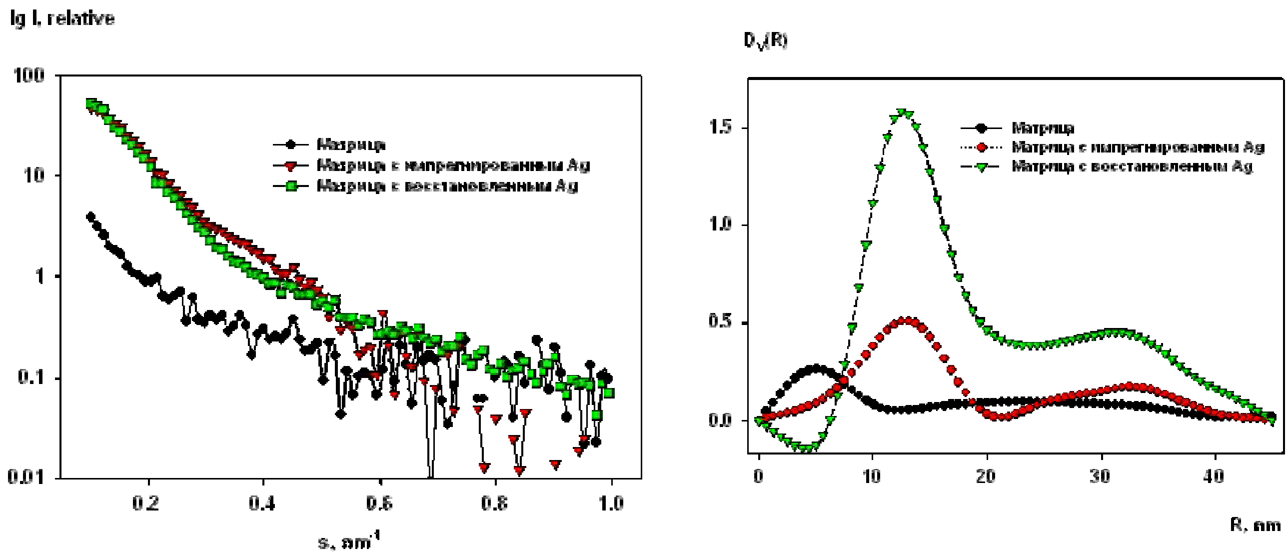




a) **b)**

Figure 4. SAXS-curves of PAR film with Pt-particles: a- scattering, b- cluster size distribution

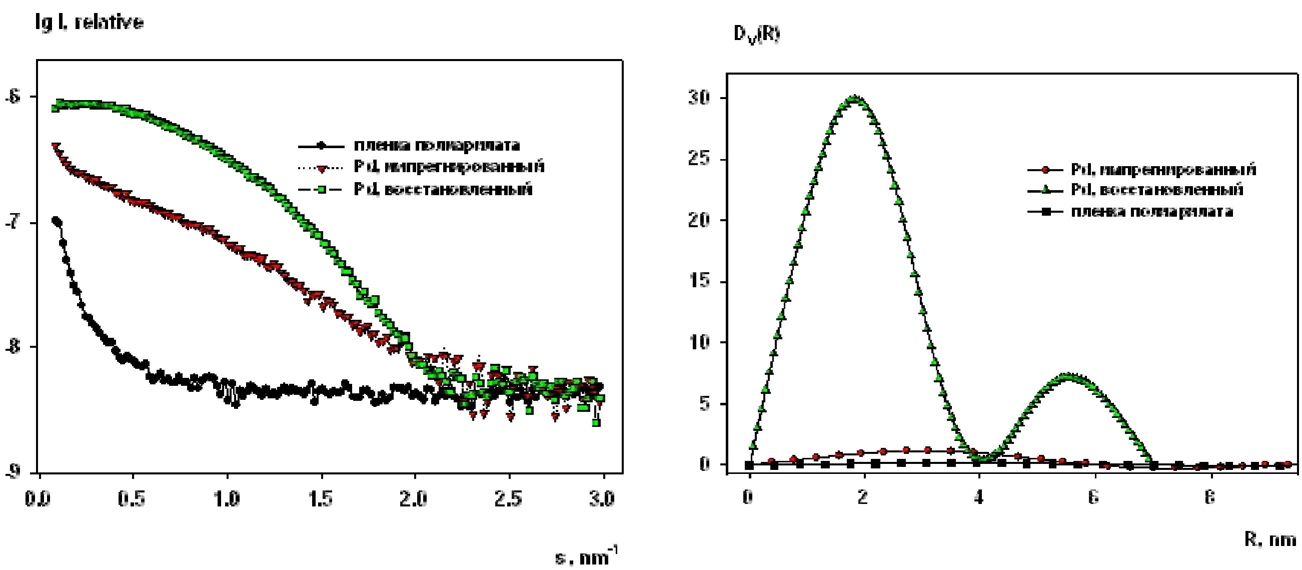
Initial and impregnated films have low difference in scattering (4a). A scattering from reduced specimen is substantial and corresponds to nanoparticles system with narrow particles size distribution. Pt- nanoparticles volume distribution calculated by means of Fourier-analysis program “Gnom” supposing sphere form of the particles is shown on fig.4b. It is shown that after reducing by H_2 Pt-atoms formate clasters with average size $\sim$ 1.5 nm (11 atoms)



a) **b)**

Figure 5. SAXS-data of Ag / PAR composite: a- scattering, b- cluster size distribution

SAXS curves of PAR film impregnated by silver complex (a) and after metal reduction (b) are shown on the figure. It is seen that amplitudes of all three specimens are sufficiently large that points to presence of the nanoscale scattering heterogeneities. Their size distribution is presented on (b). Amplitude of initial film is multiplied by five for a compare. All distribution curves have bimodal character. After impregnation Ag-complex and the metal reduction the size distribution is characterized by two peaks 13 nm (90 atoms) and 32 nm (222 atoms). Because amplitude of curve distribution maximum increased in three times after heat treatment it can be concluded that Ag reduction has taken place. At the same time metal clusters generated from Ag-complex have the same size because common character and fraction relation didn't change after thermal treatment. However a structure of the sample has been felt some transformations that follows from curves in the angle field from 0.25-0.5 nm. A coincidence of main sizes of scattering particles follows from coincidence of SAXS curves in lower angles.



a) **b)**

Figure 6. SAXS-data of Pd/PAR composite: a- scattering, b- cluster size distribution

One can suppose on the base of SAXS-curves character that a new structure is generated at the Pd-complexe impregnation. The last has transformed into another one at a subsequent reduction. The size distribution for reduced Pd- particles is very narrow and corresponds to their small sizes. An average radius of particles is equal to 2 nm (14 atoms). Besides it can be supposed that the metal was reduced completely because the distribution function amplitude for reduced metal is more intensive than for impregnated complex. The metal particles form was calculated using "DAMMIN" program and is given further.

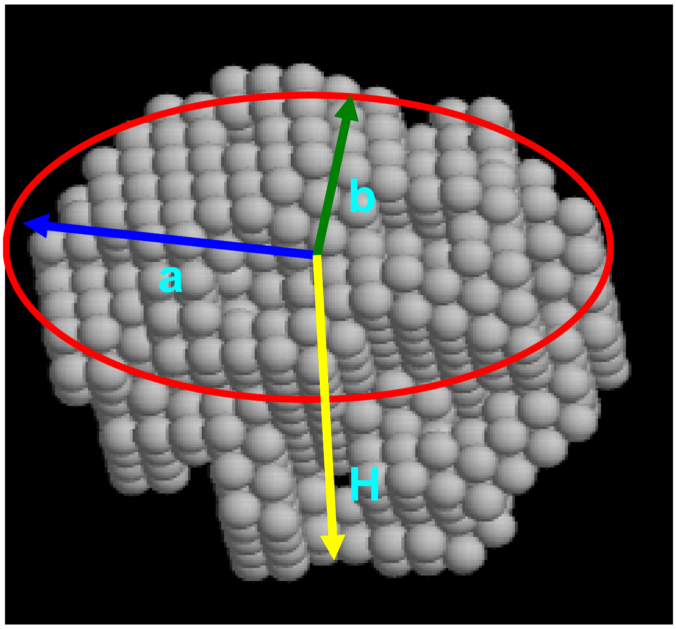


Figure 7. Geometric form of Pd-particle

Scattering curve profile of PAR film after metal reduction is typical for monodisperse compounds. Therefore we made an attempt to calculate scattering particles form. Simulation methods by simple bodies and by spheres have shown that the particles have elliptic cylinder form (with semi-axis sizes: a = 2.4 nm, b = 1.9 nm, and H = 2.3 nm).

CONCLUSION

1. Metal-polymer composites Pt/PAR, Pd/PAR and Ag/PAR have been synthesized in SC CO2 and their structure and morphology have been investigated
2. It was shown that the composites by metal particles size correspond to nanoscale, in particular maximum of clusters size distribution conforms to 2 nm (14 atoms) for Pd, 1.5 nm(11 atoms) for Pt and 13 nm(90 atoms) for Ag that is very suitable for heterogeneous catalysis
3. Pd-nanoparticles have a geometry of elliptic cylinder with semi-axis sizes a = 2.4 nm, b = 1.9 nm, and H = 2.3 nm according to calculations using "DAMMIN" software
4. PAR films lose their solubility in volatile organic solvents after a metal thermal reduction.

ACKNOULEDGMENTS

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