MAKING OF METAL-POLYMERIC COMPOSITES VIA SUPERCRITICAL CARBON DIOXIDE AND METAL-VAPOR SYNTHESIS

L.Nikitin[1]*, A.Vasilkov[1,2], Yu.Vopilov[3], V.Bouznik[4], A.Khokhlov[1]

[1]*Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St., 28, Moscow, 119991 Russia, lnik@ineos.ac.ru*
[2]*Department of Chemistry, Lomonosov Moscow State University, Leninskie gory, Moscow, 119992 Russia* [3]*Department of Physics, Lomonosov Moscow State University, Leninskie gory, Moscow, 119992 Russia*
[4]*Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Leninskii prospect, 49, Moscow, 119991 Russia*

Abstract

Fixation of metals on the polymeric surfaces for making of composite materials which possess a set of required properties is a non-trivial problem. Modification of semicrystalline polymers such as polyethylene, polypropylene, polytetrafluoroethylene etc. in supercritical carbon dioxide (SC-CO_2) is complicated by the low values of swelling coefficients that makes it impossible to introduce the required amount of metal nanoparticles into polymer. The usage of metal-vapor synthesis (MVS) for making of metal-polymeric nanocomposites requires porous materials. Therefore, an effective solution of this problem is to use ultrafine materials with developed surface which is enough to stabilize significant amount of metal nanoparticles. The method of porous structure forming in polymers from SC-CO_2 could be used to increase active surface of composites. MVS method might be effectively used for production of nanosized hybrid materials.

The rapid growth of interest in fluorinated materials has initiated development of new forms of PTFE. Ones of these materials are ultrafine polytetrafluoroethylenes (UPTFE) "FORUM"® (**F**luoro**OR**ganic **U**ltra-dispersed **M**aterial, Russia). This UPTFE combines all the general properties of PTFE with wider solubility region. In this study we for the first time propose an original method for production of composite "core-shell" nanomaterials on the example of using ultrafine particles of polytetrafluoroethylene by Method of Impulse Modification in SC-CO_2 (MIM) and MVS. The solubilities of low molecular mass cuts of UPTFE in SC-CO_2 have been measured at temperatures of 318, 333, 348, 363 and 383 K in the pressure range of 10-70 MPa. The solubilities of UPTFE in SC-CO_2 increases with temperature while showing different trends at different pressures. At 10-25 MPa the solubility increases with temperature up to 350 K and then a plateau is observed. At 25–70 MPa the solubility are increased almost linearly and no plateau is observed.

Introduction

Metal immobilization on block polymers for manufacturing composites with a set of definite properties is a complex task. Modification of some partially crystalline polymers (polyethylene, polypropylene, polytetrafluoroethylene, and others) in SC-CO_2 is complicated by low degrees of swelling and the associated impossibility of doping polymers with sufficient metal levels. The use of MVS for design of metal–polymer composites requires porous substrates. Therefore, an efficient solution in metal–polymer composite design is to use ultradisperse materials whose surfaces are developed sufficiently for stabilizing considerable amounts of metal nanoparticles. One way to increase the specific surface area is to generate a pore structure in a polymer by treating it with SC-CO_2 [1, 2]. The particular pore-structure morphology can be created by varying the pressure and temperature of SC-CO_2, exposure time, and depressurization rate. Metal–polymer systems can be generated as follows: metal

nanoparticles prepared by rapid thermodestruction of metal compounds in solution melts of polymers in oils [3] or by MVS can be introduced. Metal vapor synthesis can be efficient for manufacturing nanosized hybrid materials [4]. For example, a magnetic metal–polymer composite with high construction and dielectric parameters was prepared by modifying poly(arene sulfides) by MVS synthesized iron nanoparticles [5]. This ecosafe synthetic approach offers a means for preparing mono- and bimetallic nanoparticles of various compositions and structures, which can be stabilized on the surface of oxide or polymer supports [6, 7]. In this work we report an original process for manufacturing hybrid core/shell nanomaterials implemented for UPTFE with the use of SC-CO_2 and MVS.

Experimental

Ultradispersed polytetrafluoroethylene "FORUM"$^®$ was chosen as the main polymer. This commercial material is the product of the thermal gas dynamic destruction of commercial polytetrafluoroethylene and consists of a mixture of low molecular weight and oligomeric perfluorinated linear chains, (–CF_2–)$_n$ [8]. High purity CO_2 (Linde Gas Rus, Russia, 99.995%) was transformed into the supercritical state using a high-pressure unit. The unit which was described elsewhere [9], consists of reaction cell for the exposure of substrate, liquid thermostat for the stabilization of the temperature regime of exposure, valve system, capillary lines and manometers for the supply of SC-CO_2 to the cell, manual pressure generator for the transformation of CO_2 into the supercritical state, and cylinder with CO_2. The experiments described here differ from previous ones in that UPTFE was treated with SC-CO_2 in an extraction container to keep polymer particles from penetrating the capillary system during depressurization of the autoclave.

Ultrafine PTFE was modified with SC-CO_2 as follows: an extraction container with a polymer sample (3–5 g) was placed into an autoclave 12 cm^3 in capacity, which was purged with carbon dioxide for 120 s to remove air and water vapor and then made airtight. After being made airtight, the autoclave was thermostated at 70°C, and the CO_2 pressure was increased to 75 MPa. After 2-h exposure of the polymer, the autoclave was rapidly depressurized; the CO_2 release rate was 5 cm^3/s. The above conditions can efficiently generate a certain pore-structure morphology in hydrocarbon polymers [10]. The MIM of polymers with SC-CO_2 with abrupt CO_2 release was performed periodically one, two, or four times. Metal–polymer nanocomposites were manufactured by impregnating SC-CO_2-treated UPTFE particles with copper, gold or silver organosols, prepared using MVS, in isopropanol or toluene as described in [11]. The metal was vaporized from a tungsten bar in vacuo (10^{-2} Pa). In a representative experiment, the metal and solvent were condensed on the liquid nitrogen–cooled walls of a glass reactor 5 L in capacity with the metal: solvent ratio 1:300. Then, the cocondensate was heated to melting, and the resulting copper organosol was used to impregnate UPTFE particles inside a Schlenk vessel. The excess organosol was removed; the support was dried in vacuo (1 Pa) at 90° C. Before synthesis, the ultrafine PTFE used to prepare metal–polymer nanocomposites was heated in vacuo (1 Pa) at 90° C for 1 h.

Thermogravimetric heating curves for UPTFE and metal–polymer composites were recorded on an MOM Q derivatograph in air at 10 K/min; the sample size was ~20 mg. Adsorption characteristics were measured on a Quantachrome NOVA 2200e instrument. Before analysis, test samples were degassed in vacuo for 8 h at 60° C. The working gas was nitrogen. Measurements were carried out within the linearity range of the Brunauer–Emmett–Teller (BET) equations for relative pressures from 0.05 to 0.8. Microscopic experiments were performed on a Zeiss LEO 1420 scanning electron microscope equipped with an Oxford Instruments INCA Energy 300 energy dispersive spectrometer and on a Zeiss LEO 912AB OMEGA transmission electron microscope. Thin (10–100 nm) current-conducting metallic (Au/Pd) coatings were sputtered using a Sputter Coater Polaron SC 7640 SEM instrument.

Results and Discussion

Our experiments to study the effect of SC-CO$_2$ on block Teflon showed that the polymer only insignificantly swells in the supercritical medium and rapidly expels CO$_2$ after pressure release without increasing its surface area. It is feasible to generate coated particles in which the core is paraffin and the shell contains UPTFE particles [12]. Here, we propose to use the MIM of powder polymer materials with SC-CO$_2$ for this purpose. Analysis of differential pore-size distribution curves showed that most pores in the starting UPTFE had diameters of about 10.8 nm. Having studied UPTFE particles before and after MIM, we showed that the BET surface area S_{BET} increased 2.1-fold in going from one to four SC-CO$_2$ treatments. The ratio between the micro- and mesoporosity also changed considerably: the pore surface with pore sizes up to 6 nm (S_{micro}) decreased 1.7-fold, whereas the pore surface with sizes between 6 and 100 nm (S_{meso}) increased 3.8-fold (Table 1).

Table 1. Some characteristics of ultrafine PTFE before and after modification with SC-CO$_2$.

Number of PMs	S_{BET}, m^2/g	K_{BET}	S_{micro}, m^2/g	S_{meso}, m^2/g	K_t	D, nm
–	0.74	0.9961	0.390	0.35	0.9980	10.85
One	1.20	0.9922	0.333	0.863	0.9986	5.96
Two	1.45	0.9958	0.313	1.134	0.9988	3.96
Four	1.57	0.9994	0.228	1.338	0.9991	3.32

Note: K_{BET}, correlation coefficient for the BET surface areas; K_t, correlation coefficient for the t test, used to calculate some parameters of micropores; and D, pore diameter derived from the differential volume pore distribution curve.

(a) 2 μm

(b) 2 μm

(c) 2 μm
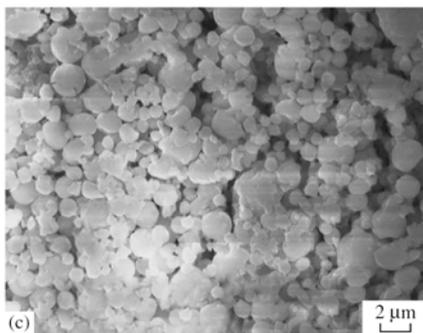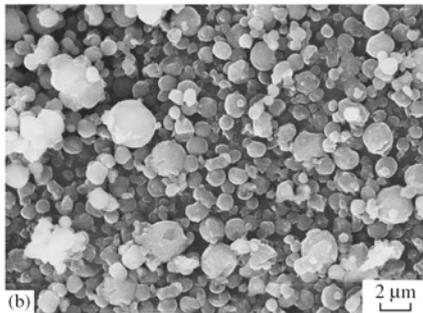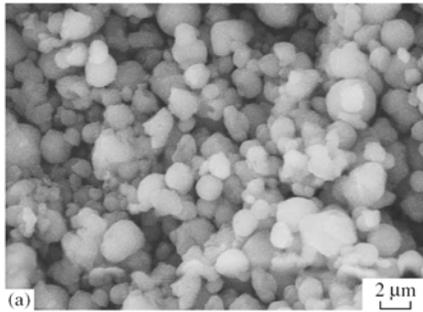
Thus, SC-CO$_2$ increased the proportion of mesopores in UPTFE particles, which was responsible for the efficiency of MVS in manufacturing metal–polymer composites. Scanning electron microscopy (SEM) showed that a single MIM decreased the average particle size of UPTFE from 1.34±0.11 to 0.88±0.04 μm (Figs. 1a, 1b). Fourfold SC-CO$_2$ treatment considerably altered the shape of UPTFE particles, which now were combined into druses and conglomerates (Fig. 1c).

The particle-size distribution became bimodal: along with an increasing proportion of fine particles with sizes of 0.78±0.03 μm, coarse formations were observed with an average size of 2.17±0.23 m. A likely explanation is that MIM, along with removing the low-molecular-weight fluorinated fraction, gives rise to fragmentation of PTFE particles; this can signify the block structure of PTFE in accordance with atomic force microscopy data. The coarse-size mode can apparently arise from the agglomeration of fine swollen particles on the surfaces of coarser fragments during supercritical treatment. Ultrafine PTFE samples with different histories were studied thermogravimetrically. The thermostability of ultrafine PTFE became 30° C higher after SC-CO2 treatment (the 5% weight loss temperature became 202 instead of 172° C). The observed change in thermostability can arise from the elimination of low-molecularweight fluorooligomers from the precursor ultrafine PTFE during SC-CO$_2$ modification. Metal vapor synthesis was used to prepare a copper–toluene organosol, which was then used to treat unmodified UPTFE samples and samples after one or four MIMs.

Fig. 1. SEM images for ultrafine PTFE samples (a) before MIM and after (b) one and (c) four MIMs.

Electron probe microanalysis performed on a scanning electron microscope showed that the copper nanoparticle–modified polymer was a heterogeneous mixture of ultrafine PTFE particles and metal aggregates. One MIM of UPTFE yielded a graygreen substance in which copper concentrations were 2–4%. The use of MVS for the material treated four times with SC-CO_2 yielded a greenish material. The copper concentration in the near-surface layer was 0.16–0.37%, and the copper particle size was 20–60 nm (Fig. 2). This small scatter in copper concentrations in the near-surface layers of nanocomposites is likely because of the different sorption capacities associated with the pore distribution over the surface area of SC-CO_2-modified UPTFE particles.
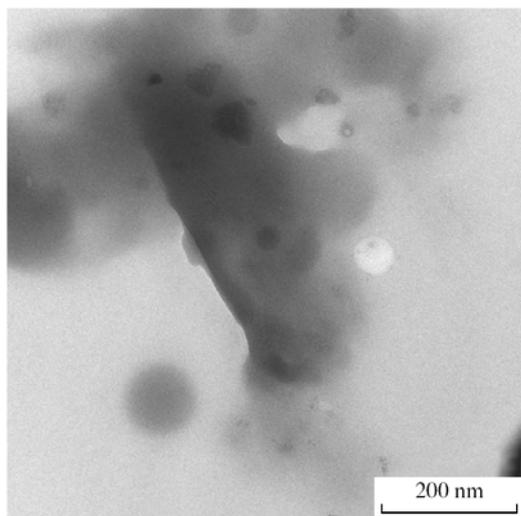

Fig. 2. TEM image for a metal–polymer composite. Copper particle sizes are from 20 to 60 nm.

On the whole, the metal surface distribution was rather uniform recorded from different regions of the nanomaterial. Doping ultrafine PTFE with copper nanoparticles brought about a 50° C increase in thermostability (up to 222° C), probably because of the ability of transition metals to enter radical reactions (which occur in polymers at high temperatures) and either initiate or inhibit thermooxidative transformations depending on the situation [13].

The solubility of low molecular mass cuts of UPTFE in SC-CO_2 have also been measured using static method at temperatures of 318, 333, 348, 363 and 383 K in the pressure range of 10-70 MPa. The solubility isotherms follow the typical and expected behavior of a solid/SCF system, with the solubility increase with pressure, due to the increase of scCO_2 density and, consequently, to the SC-CO_2 dissolving power. The solubility data were correlated by three different density-based models proposed by Bartle, Chrastil and Mendez-Santiago. The parameters of all the models considered were fitted to the solubility data by using the least square method. Experimental data are better explained by the Bartle equation and Mendez – Santiago equation at temperature range of 318– 383K and pressure range of 10-70 MPa.

Conclusion

In summary, we have developed the first process for manufacturing metal–polymer nanocomposites on the basis of ultrafine PTFE, combining the modification of powdered polymers with supercritical carbon dioxide and their doping with metal nanoparticles with the use of metal vapor synthesis.

Acknowledgments

List of Publications

[1]. Yang, K. Ozisik, R., *J. Supercrit. Fluids*, 2008, vol. 43, pp. 515–523.
[2]. Naumkin, A.V., Krasnov, A.P., Said-Galiev, E.E., et al., *Dokl. Phys. Chem.*, 2008, vol. 419, part 2, pp. 68–72.
[3]. Gubin, S.P., Korobov, M.S., Yurkov, G.Yu., et al., *Dokl. Chem.*, 2003, vol. 388, nos. 4–6, pp. 44–46.

[4]. Klabunde, K.J., *Free Atoms, Clusters and Nanosized Particles*, San Diego, etc.: Academic Press, 1994.

[5]. Vasil'kov, A.Yu., Zachernyuk, B.A., Karpikov, Z.N., et al., *Zh. Prikl. Khim. (S.-Peterburg)*, 2007, vol. 80, no. 12, pp. 2058–2063.

[6]. Vasil'kov, A.Yu., Nikolaev, S.A., Smirnov, V.V., et al., *Mendeleev Commun.*, 2007, vol. 17, no. 5, pp. 268–270.

[7]. Suzdalev, I.P., Maksimov, Yu.V., Vasil'kov, A.Yu., et al., *Ross. Nanotekhnol.*, 2008, vol. 3, no. 1/2, pp. 76–81.

[8]. RF Patent No. 1775419 (1992).

[9]. Gallyamov, M.O., Nikitin, L.N., Nikolaev, A.Yu., et al., *Kolloidn. Zh.*, 2007, vol. 69, no. 4, pp. 448–462.

[10]. Nikitin, L.N., Nikolaev, A.Yu., Said-Galiev, E.E., et al., *Sverkhkrit. Flyuidy. Teor. Prakt.*, 2006, vol. 1, no. 1, pp. 77–88.

[11]. Vasil'kov A.Yu., Olenin A.Yu., Titova E.F., Sergeev V.A., *J. Colloid Interface Sci.*, 1995, vol. 169, pp. 356–360.

[12]. Gallyamov, M.O., Buznik, V.M., Tsvetnikov, A.K., et al., *Dokl. Phys. Chem.*, 2003, vol. 392, nos. 1–3, pp. 217–220.

[13]. Camacho, W. and Karlsson, S., *Polym. Degrad. Stab.*, 2002, vol. 78, pp. 385–391.