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## The Use of Ultrafine Poly(tetrafluoroethylene) as a Stabilizing Agent for Emulsifying Paraffin and Producing Composite Microparticles in a Supercritical Carbon Dioxide Medium

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Supercritical carbon dioxide has found wide use in the production of microcapsules. Microcapsules are microparticles comprising a core and a shell, whose materials differ in physicochemical properties. Experimental procedures implemented at present use one of two general approaches.

The first approach uses agents that stabilize composite microparticles in a supercritical medium, e.g., fluorine-containing surfactants [1–3] that stabilize water microemulsions in supercritical CO<sub>2</sub>. The aqueous core of such microcapsules can serve as a microreactor for chemical synthesis [4, 5].

The second approach involves the production of composite particles during coprecipitation of components of mixed solutions being injected into an antisolvent medium [6–9]. Here, the solvent–antisolvent pair can be a supercritical medium and a gaseous phase [6] or a liquid solvent and a supercritical medium [7–9]. This approach allowed production of, e.g., polymer-coated drug particles [6] and composite protein [7], magnetic [8], and polymer microparticles with a nar-

row particle size distribution [9]. Note that the use of supercritical CO<sub>2</sub> as a reaction medium has the important advantage that there is no problem of residual solvent.

In this paper, we propose a method for producing composite particles consisting of a paraffin core coated with ultrafine poly(tetrafluoroethylene) in a supercritical carbon dioxide medium. This method is based on the phenomenon of stabilization of a paraffin emulsion in supercritical CO<sub>2</sub> by ultrafine poly(tetrafluoroethylene). Thus, this method follows the first of the above two general approaches; however, unlike a conventional procedure for producing composite particles in supercritical media [1–5], this method uses polymer microparticles rather than a surfactant.

The setup for experiments with supercritical CO<sub>2</sub> was equipped with a hand pressure generator, which could produce pressures up to 60 MPa and was connected through a set of capillaries to a high-pressure stainless-steel reaction cell with a working volume of about 30 mL. The setup included pressure transducers for monitoring the parameters of the supercritical medium; the CO<sub>2</sub> supply into the cell was controlled by a set of valves. Desired temperature conditions were maintained by heaters contacting the cell and by temperature transducers. In the experiments, we used CO<sub>2</sub> of high purity (>99.997%; GOST (State Standard) 8050-85).

With allowance made for the possibility of practically implementing the approaches tested in this study, as the material for the cores of microparticles, paraffin used as the base for Visti ski wax (Russia) was taken. The material for the polymer coating of paraffin particles in the supercritical CO<sub>2</sub> medium was Forum ultrafine poly(tetrafluoroethylene) (Institute of Chemistry, Far East Division, Russian Academy of Sciences, Vladivostok, Russia), which is the product of thermal gas-dynamic destruction of industrial poly(tetrafluoroethylene) (Teflon) waste. Previous IR and NMR spectroscopic studies showed [10] that ultrafine poly(tetra-

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fluoroethylene) contains  $-\text{CF}_2-\text{CF}_3$ ,  $-\text{CF}=\text{CF}_2$ , and  $-\text{CF}_2-\text{CFO}$  terminal groups at concentrations of several percent, which was indicative of structural changes in poly(tetrafluoroethylene) molecules during dispersion [10]. From these data, it was concluded that the Forum ultrafine poly(tetrafluoroethylene) consists of low-molecular-weight and oligomer poly(tetrafluoroethylene) chains comprising, on the average, fewer than 100 monomeric units.

The particle size distribution of ultrafine poly(tetrafluoroethylene) was determined by dynamic light scattering on an ALV experimental setup (Germany). For this purpose, with a Sonorex RK52H ultrasonic disperser (Bandelin, Germany), 1 and 0.2 mg/mL suspensions of ultrafine poly(tetrafluoroethylene) in a number of organic solvents were prepared. It turned out that the highest stability, which was sufficient for dynamic light scattering measurements, was characteristic of suspensions in acetonitrile, acetone, ethanol, hexane, and heptane. Comparative analysis of the dynamic light scattering data showed that the average ultrafine particle diameter in poly(tetrafluoroethylene) suspensions ranged from 300 to 1700 nm, the maximum of the distribution was at 700 nm, and the half-heights of the distribution were at 450 and 1100 nm.

Composite particles in the supercritical  $\text{CO}_2$  medium were produced as follows. Samples of components were weighed on an Ohaus AP250D balance (Ohaus, USA); the paraffin-to-polymer weight ratio was taken to be 10 : 90 to 20 : 80. The reaction cell was usually filled with several grams of paraffin and less than one gram of ultrafine poly(tetrafluoroethylene). The cell containing the components of the mixture and a magnetic stir bar was sealed, and a supercritical  $\text{CO}_2$  medium at pressures of 50–60 MPa and temperatures of 80–100°C was created in it. The reaction mixture in the cell was exposed for 1 h during continuous stirring. Then, the cell was rapidly cooled in water at 10–15°C. After the cell was opened and  $\text{CO}_2$  was released, the product was observed to be paraffin particles coated with ultrafine poly(tetrafluoroethylene); these particles neither coalesced nor adhered to the inner surface of the cell. The particle diameter usually ranged from 50 to 300  $\mu\text{m}$  and depended on the initial ratio between the components of the mixture (specifically, it decreased with increasing fraction of ultrafine poly(tetrafluoroethylene)). A similar procedure in the absence of ultrafine poly(tetrafluoroethylene) failed to produce individual particles: after the cell was opened, the product was found to be a coalescent homogeneous paraffin blob.

The composite particles produced were photographed with a DSM 962 scanning electron microscope (Carl Zeiss, Germany) (figure). As a rule, the particles are spherical. In the electron micrographs at more than 2000-fold magnification, the structure of the surface of composite microcapsules is discernible and individual ultrafine poly(tetrafluoroethylene) particles constituting the polymer coating are seen.

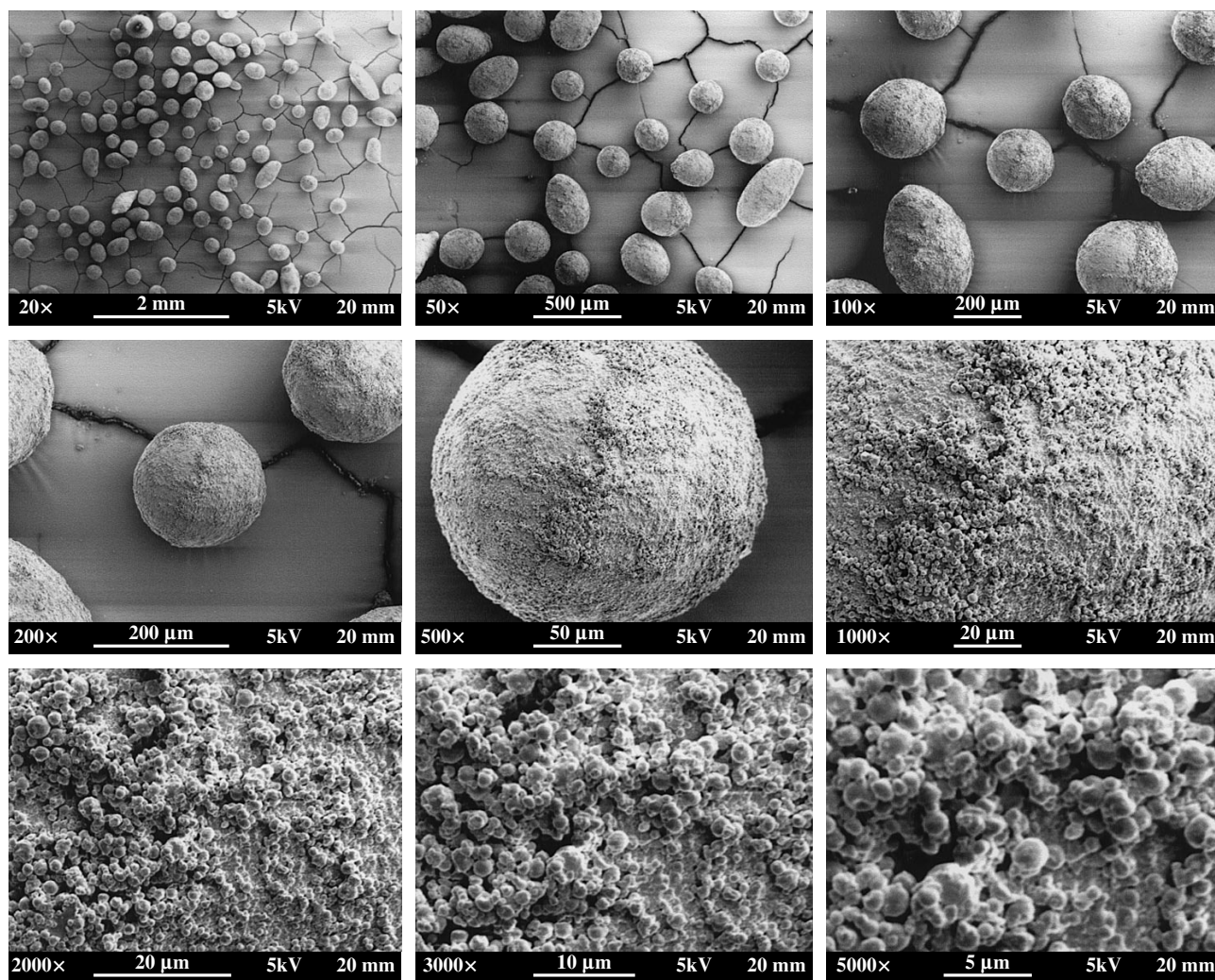
In our opinion, the mechanism of production of composite particles is the following. Under the chosen temperature conditions of exposure, paraffin melts. The solubility of paraffins in supercritical  $\text{CO}_2$  increases with an increase in both pressure and temperature (at pressures above 10 MPa); however, at the chosen thermodynamic parameters of exposure, this solubility is still low: below 0.1 mol % [11]. Intense stirring of the mixture of paraffin and ultrafine poly(tetrafluoroethylene) in the supercritical  $\text{CO}_2$  medium yields a paraffin emulsion in supercritical  $\text{CO}_2$ ; the emulsion is stabilized by ultrafine polymeric material, which prevents particles from coalescing. The phenomenon of stabilization of emulsions by solid colloidal particles is well known [12]. Recently, interest in such systems has considerably increased, in particular, in the context of the possibility of producing selectively permeable capsules—colloidosomes [13].

On rapid cooling, the paraffin emulsion microdroplets coated with the layer of polymer particles solidify; the polymer coating prevents the microdroplets from coalescing and adhering to the cell walls.

The mechanism of stabilization of emulsions by fine-particle materials is related to the fact that, when certain relations for the interfacial energy are valid [12], it is more advantageous for colloidal particles to be located at the interface and stabilize a certain type of emulsion, in this case, an emulsion of paraffin in supercritical  $\text{CO}_2$ . The fluorine-containing polymer layer that coats the paraffin particles decreases the interfacial energy and the adhesive power of the particles. The decrease in the adhesive power of the particles leads, in particular, to the fact that the particles are highly mobile when placed onto a slide. The mentioned relations for the interfacial energy impose no stringent constraints on the choice of the components of the three-phase system [12], which ensures sufficient universality of this stabilization mechanism. This allows one to expect that ultrafine poly(tetrafluoroethylene) can be used to stabilize emulsions of other materials in supercritical  $\text{CO}_2$ .

Under the assumption that the phases of paraffin and ultrafine poly(tetrafluoroethylene) in the particles are completely separated, the polymer coating thickness can be estimated from the weight ratio between the components, their densities, and the average radius of the produced composite particles. The estimated polymer coating thickness is 1–1.5  $\mu\text{m}$ , which corresponds to one or two layers of ultrafine poly(tetrafluoroethylene) particles and is thus indicative of high efficiency of this polymer as a surface stabilizer.

For the system under investigation, we should indicate additional factors that can favor the stability of the polymer interlayer. Preliminary studies showed that at least the lowest-molecular-weight fractions of ultrafine poly(tetrafluoroethylene) can dissolve in supercritical  $\text{CO}_2$  at pressures above 50–60 MPa (high-molecular-weight poly(tetrafluoroethylene) under these conditions is insoluble). Under these conditions, the polymer



Electron micrographs of produced composite particles comprising a paraffin core coated with ultrafine polytetrafluoroethylene. The set of images was obtained under gradually increasing magnification (from  $\times 20$  to  $\times 5000$ ).

interlayer thickness can be expected to decrease to values smaller than 100 nm if the stabilization mechanism presented below takes place.

All the three media—paraffin, the polymer coating, and supercritical  $\text{CO}_2$ —are nonpolar and uncharged. The permittivities and the refractive indices of these media at the thermodynamic parameters of exposure are, respectively, the following [14]: for paraffin, 2.0–2.5 and 1.4–1.5; for the polymer coating, 2.04–2.1 and 1.35–1.38; and, for supercritical  $\text{CO}_2$ , 1.5 and 1.2.

The dielectric parameters for ultrafine poly(tetrafluoroethylene) must be sufficiently close to the corresponding values for poly(tetrafluoroethylene), according to the data on the structure of its molecules [10]. This is also indirectly supported by the fact that, among the most stable of the prepared suspensions of ultrafine poly(tetrafluoroethylene) particles (with a fixed concentration of 0.2 mg/mL), the light scattering intensity is the lowest for suspensions in ethyl acetate ( $n = 1.37$ )

and hexane ( $n = 1.375$ ). This suggests that the refractive index of ultrafine poly(tetrafluoroethylene) is close to the above values.

The presented values show that the dielectric parameters for the polymer interlayer are intermediate, i.e., higher than those for supercritical  $\text{CO}_2$  but lower than those for paraffin. In such a case for two media separated by an interlayer, the dispersion interaction can manifest itself in the emergence of long-range van der Waals repulsive forces [15]. Under these conditions, the derivative of the dispersion component of the disjoining pressure in the interlayer with respect to its thickness is negative, which can meet the condition for stability of thin interlayers [15] (when it is taken into account that all interacting media are nonpolar and uncharged). Note that, as a rule, this stability condition is also met when, instead of paraffin, another nonpolar substance is used.

Thus, we were the first to implement a method for stabilizing an emulsion in a supercritical medium with-

out using a conventional approach involving surfactants; instead, as a stabilizer for particles, we used an ultrafine polymeric material.

The composite whose production was described for the first time in this paper can find wide practical use. The first tests demonstrated that this composite holds promise for a new generation of ski waxes. The proposed method using a supercritical solvent can be relatively readily implemented on a commercial scale.

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