

Development of Functional Polymer Coatings Using Supercritical Fluids: Technologies, Markets, and Prospects

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Abstract—This review analyzes the studies and developments of technologies based on the use of supercritical fluids for the micronization of polymer particles and the formation of efficient powder polymer coatings. Potential advantages of supercritical fluid technologies which combine different stages of formation of powder coatings in a unified flowsheet are considered. Possible further trends in scientific and engineering research are identified. A growth in the global market of powder coatings by 2020 is forecasted.

Keywords: supercritical fluids, micronization, polymerization, polymer microparticles, functional powder coatings, market forecast

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INTRODUCTION

Polymer coatings based on polyolefins, fluoropolymers, polyamides, and biocompatible polymers possess high durability; strength; and resistance to atmospheric precipitation, sunlight, temperature, aggressive chemical substances, etc. [1]. The leading segments of the market of polymer coatings are the production of consumer goods, automobile engineering, architecture and construction, instrument engineering, aviation, the furniture industry, electronics, telecommunications, the defense industry, and other newly emerging science-driven sectors of economy. Polymer coatings are also widespread on the market of medical products, where they are successfully utilized in surgical equipment and armarium, cardiologic, optic, endoscopic, and radiologic instruments, etc.

The industrial methods for the application of protective polymer coatings based on liquid paints and varnishes are currently being successfully replaced by powder coating techniques. This is to a large extent due to the constantly tightening environmental standards limiting the emission of toxic and harmful substances to the environment, which becomes a major problem in the case of using traditional coatings based on organic solvents [2]. However, such a replacement is associated not only with environmental restrictions, but also with a series of technological problems encountered when using paints and varnishes (non-uniform application of the coating, significant overconsumption of materials, instability, short lifetime, etc.). The technique of polymer powder coating involves the application of a dry powder with specific

morphology and fractional composition, prepared in advance, onto the surface of the material, followed by the heat treatment of the product, during which a durable uniform coating is formed. However, in this case, traditional methods for the formation of the polymer powders themselves also involve the use of organic solvents.

Supercritical fluids (SCFs), which made it possible to perform the microencapsulation and microdispersion of polymer materials to obtain micron-, submicron-, and nanoscale particles, as well as to create environmentally friendly technologies based on the use of supercritical fluids, constituted a viable alternative to toxic organic solvents in the processes of production and processing of polymers [3, 4]. Their emergence made it possible to address the disadvantages intrinsic to the traditional methods for the preparation of powders, which substantially improved the performance characteristics of the polymer coatings being formed [5, 6].

The leading role as the environmentally friendly solvent in supercritical fluid technologies (SCFTs) belongs to carbon dioxide due to its inertness, nontoxicity, fire and explosion safety, inexpensiveness, availability, and possibility for its relatively easy transition to the supercritical (SC) state [7]. SC-CO₂ is a good solvent for many nonpolar and some polar substances with a low molecular weight; however, it is a poor solvent for many polymers with a high molecular weight. Here, it should be noted that, although the solubility of most polymers in SC-CO₂ is extremely low, nevertheless, the solubility of CO₂ itself in many polymers is very significant, which can lead to a considerable

decrease in both their glass transition points and melt viscosity at very moderate pressures [8, 9].

Despite the relatively short existence of SCFTs which began to be widely used only in the 1980s, they have been currently rapidly developed and implemented into the world industrial practice, which is evidenced by the constantly growing number of scientific publications and patents in this field.

The aim of this review is to consider the developments on the use of the potential of supercritical fluid technologies in the micronization of polymer substances and production of modern multifunctional powder polymer coatings, as well as to analyze the condition and prospects for the development of the global market for such products.

THE ROLE OF SCFTS IN THE MICRONIZATION OF POLYMER PARTICLES AND THE FORMATION OF COATINGS ON THEIR BASIS

Traditional methods for the dispersion of polymer materials are based on mechanical action (crushing, cutting, grinding, etc.), as well as on the preparation of powders from solutions or melts; however, substantial disadvantages are intrinsic to these operations. For instance, mechanical action leads to the formation of powders with significant polydispersity, nonuniform morphology, and contamination with particles of the grinding charge, as well as to the mechanical destruction of the polymer. Powders formed from solutions contain traces of toxic solvents, while the preparation of powders from melts is complicated by their high viscosity and inevitable thermal destruction of the polymer.

Possible application of technologies based on SCFTs has become one way to solve the problem of efficient microparticles preparation. They can be divided into three large groups, depending on the role played by the supercritical fluid [10]:

(i) the SCF is the solvent for the substance being atomized (RESS, PGSS, RESOLV, RESAS, and DELOS processes);

(ii) the SCF serves as the medium for the sedimentation of the substance from a different solvent (GAS, ASES, PCA, SAS, ASAIS, and SEDS processes); and

(iii) the SCF acts as the atomizing agent (CAN-BD and SAA processes).

Among the wide variety of SCFTs and their modifications, a number of fundamental methods, most widely and successfully used for the micronization of polymer particles in scientific research and industrial practice, can be highlighted [1, 10, 11]:

(i) RESS (Rapid Expansion of Supercritical Solution);

(ii) GAS (Gas AntiSolvent);

(iii) SAS (Supercritical AntiSolvent); and

(iv) PGSS (Particles from Gas Saturated Solution).

The RESS Method

The RESS method was the first to be proposed for the preparation of microparticles using SCFs as the solvent. Currently, it is one of the most common and employed in practice micronization methods utilizing SCFs. In the case of micronization using this method, the solution of the substance being dispersed in an SCF passes through a capillary nozzle, in which depressurization from a high pressure at the inlet to a low pressure at the outlet occurs. The sharp decompression leads to the separation of phases with a characteristic time of 10^{-5} – 10^{-6} s and fast nucleation of the solid phase. The advantages of the RESS method are its simplicity, possibility for the reuse of the SC solvent in the case of a continuous cyclic process, the absence of traces of the residual solvent in the particles being formed, and the possibility for application for the dispersion of multicomponent systems. However, the disadvantages of the RESS method should be noted as well, the most significant of which is, as it was noted above, the poor solubility of most polymer materials in SC-CO₂, which severely restricts the possibilities for the application of the method.

The RESS process is based on two key steps: (a) the dissolution of the substance being dispersed in an SCF (e.g., carbon dioxide) and (b) the formation of microparticles from a supersaturated solution formed during depressurization.

First, the dissolution or extraction of a solid substance with the SCF is performed in a high-pressure chamber, and then the solution passes through a nozzle or a capillary to a low-pressure chamber (Fig. 1) [10]. Here, the substance of the SCF undergoes a transition to the state of conventional gas and adiabatically expands, which leads to a fast drop in temperature and pressure and formation of microdrops or particles of the substance directly in the expansion device. Particles with a narrow size distribution can be obtained by controlling the conditions of the process (this process can also sometimes be called a Supercritical Fluid Nucleation (SFN) process).

The RESS method is characterized by the substantial influence of the conditions of the process on the characteristics of the particles being obtained *before* and *after* the moment of expansion. Temperature, pressure, raw materials, structure of the substance being dissolved (crystalline or amorphous; mixed or pure), and solvent are the former parameters (before expansion), while the temperature of the nozzle and its geometry, sizes, distance, and surface impact angle are the latter (after expansion).

The method is attractive due to its simplicity and relative ease of implementation, at least in the case of small-scale production, when only one nozzle is used. When the RESS process is scaled up upwards, either the use of a system consisting of multiple nozzles operating in parallel or the use of porous materials with a narrow pore size distribution is required. The insuffi-

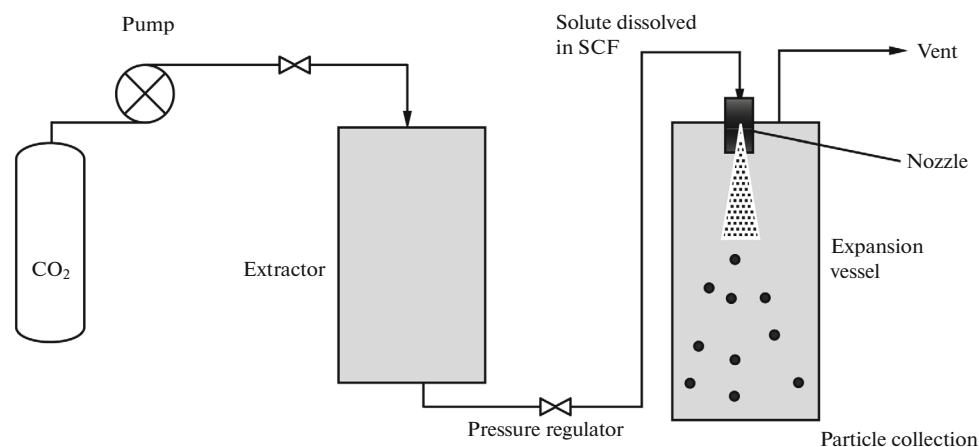


Fig. 1. RESS equipment concept [10].

cient solubility of a large number of compounds in SCFs, which prevents the formation of fair prices for the products in many cases, still remains one of the limitations for the use of the RESS process in practice [12]. The implementation of the RESS process on a commercial scale is possible only when the solubility of the initial compound in SC-CO₂ at acceptable pressures is not too low and is $\geq 10^{-3}$ kg/kg [10].

It was shown that, in the RESS process, durable uniform films with a vast scope of applications can be formed from a suspension of poly-2-ethylhexylacrylate in SC-CO₂ with an average size of the drops of ~ 70 μm in the case of spraying from a nozzle with a diameter of 30–100 μm [13]. The characteristic feature of the process was a significant decrease in viscosity due to the dissolution of CO₂ in the polymer phase; here, the suspension of the polymer after depressurization and repeated increase in the pressure consisted of larger drops in comparison with the initial suspension.

A process for the preparation of coatings from polymer microparticles was proposed, all the operations during which are performed in an SCF (preferably, CO₂) at any pressure above critical and temperatures above the critical temperature up to 190°C [14]. The influence of the solubility of the polymer in the SCF on the size of the particles being obtained, as well as the possibility for controlling the particle size distribution via a step-by-step decrease in the temperature and depressurization in the mixing chamber, was shown. The authors managed to solve a series of practically important tasks: they decreased the number of stages of the technological process and improved their compatibility, provided a homogeneous mixing of the components, and improved the appearance and mechanical strength of the powder coating being formed.

In order to study the formation of the particles of low-molecular-weight perfluoropolyether diamide in a SC-CO₂ medium via the RESS method, the mathematical modeling of the process was performed [15,

16]. The interrelation between the characteristics of the drops and splashes formed in a system consisting of low-molecular-weight perfluoropolyether diamide dissolved in CO₂ and conditions of the RESS process (temperature, concentration of the solution, and shape of the nozzle) was determined. The investigation of the process of sedimentation of the polymer included the following:

- (a) modeling of the hydrodynamics of the process;
- (b) modeling of the dynamics of the movement of the aerosol; and
- (c) analysis of the solvent/dissolved substance phase equilibrium.

Pressures at which cloud points were reached, as well as the compositions of thermodynamically equilibrium compositions in different solvent/dissolved substance systems, were determined and served as the base for the development of a multidimensional mathematical model for the movement of the aerosol, which shows good agreement with the experimental data and makes it possible to predict the formation of microscale polymer drops under the set conditions. The fluorine-containing polymer studied by the authors can be used as an effective coating in architecture and construction for the protection of stone buildings and structures from degradation. Such coatings are resistant to acids, high temperatures, UV radiation, and oxidizing agents; they are clear, colorless, and make it possible to preserve the natural appearance of natural stone for a long period of time.

Using state-of-the-art research procedures, a group of scientists investigated the properties of water-soluble epoxide coatings with the additions of polyaniline nanoparticles synthesized in a medium of SC-CO₂ [17, 18]. It was shown that the additions of such nanostructured polyaniline make it possible to substantially improve the anticorrosive properties of the epoxide coating being formed.

To improve the hydrophobicity of moisture-sensitive biodegradable materials, a polymer coating based on nanoparticles of poly(trifluoroethyl methacrylate) obtained via the RESS method in a SC-CO₂ medium, as well as a mixture of thermoplastic starch with poly(butylene adipate terephthalate), were used as the substrate [19]. The influence of the process conditions (temperature, pressure, and concentration of poly(trifluoroethyl methacrylate)) on the surface morphology and hydrophobicity of the polymer coating based on particles with a size from 30 nm to several micrometers being obtained was studied; the optimum process parameters making it possible to obtain stable hydrophobic polymer coatings were determined.

The use of water-free methods of application of polymer coatings in the paper industry can provide substantial savings due to the decrease in the consumption of water and energy, in comparison with wet application methods traditionally employed in the sector. Thus, to study the process of application of a coating onto paper, a dry method of formation of powder coatings based on poly(methyl methacrylate) with the addition of modified calcium carbonate and an inorganic pigment in a SC-CO₂ medium was utilized and tested, which can be successfully applied in the stationary industry [20]. Also, an in situ study of the polymerization of methyl methacrylate on paper under water-free conditions in SC-CO₂ in the presence of kaoline was conducted [21]. The investigation of the monomer, initiator, and stabilizer concentration influence on the molecular weight and morphology of poly(methyl methacrylate) being formed using gel permeation chromatography, scanning electron microscopy, IR spectroscopy, and thermogravimetric analysis showed that the characteristics of poly(methyl methacrylate) as a film-forming agent with respect to the molecular weight distribution correspond to the traditional methods of application of the coating under conditions when the concentration of the monomer in the solvent is ~10 wt %, while the concentration of the initiator is 1.0–1.5 wt % and that of the stabilizer is ~10 wt % relative to the monomer. It was found that the polymer coatings being produced in this case possess good operational characteristics and stability. It was concluded that it is possible to efficiently use powder coatings based on a poly(methyl methacrylate)/kaoline composition for the application of protective coatings onto a paper base via a dry method under industrial conditions.

The SAS Method

The SAS method is used for the micronization of substances which are insoluble or low-soluble in a supercritical fluid, which is characteristic for many polymer compounds [22]. In this method, the solution of a substance in a conventional liquid solvent is injected through a nozzle into a vessel containing an SC antisolvent, where the substance sediments in the

form of solid particles. Depending on the conditions for conducting the process via the SAS method, the following structures can be obtained by varying the shape of the nozzle and initial materials [23]:

- (i) microspheres (500–5000 nm) or nanospheres (50–200 nm);
- (ii) hollow spheres (5–50 μm) formed from nanoparticles; and
- (iii) microfiber structures and hollow microfibers with a diameter of ≥0.01 μm.

The advantages of the SAS method include the possibility for the use of lower pressures and more concentrated solutions, while its main disadvantages include the use of traditional liquid solvents, toxic organic solvents in particular, which contaminate the finished product and make this method not as popular as the RESS.

A process for the preparation of polymer coatings on the basis of nanoparticles with the use of the SAS process with an SC antisolvent was developed [24]. The coating application process occurs at the moment when the SC solvent (e.g., CO₂) and a suspension containing nanoparticles are mixed, which leads to the sedimentation of the suspended nanoparticles in the form of nanocoatings. The optimum parameters of the process which improve the efficiency of the SAS method, as well as a procedure and system for the control over the polymer coating application process, were determined. The know-how of the authors can be widely applied in the pharmaceutical, cosmetic, food, chemical, and agricultural industries and the production of pesticides and catalysts.

The SAS method was also applied in pharmaceutical studies during the investigation of the process of application and encapsulation of ultrafine particles of a polymer [25]. Synthesized silica particles were chosen as the application objects, while a poly(lactide-co-glycolide) biodegradable polymer used for the controllable unblocking of drugs at a desired point in the body was chosen as the material of the coating. In the SAS process, a suspension of particles of silica in an acetone–polymer solution was sprayed through a capillary nozzle into SC-CO₂, which acted as the antisolvent of acetone. The fast interdiffusion of SC-CO₂ and acetone induced supersaturation of the polymer solution, thus leading to the nucleation and sedimentation of the polymer encapsulated in the substrate particles. It was found during the study of the influence of different conditions of the SAS process (polymer/particle weight ratio, concentration of the polymer, temperature, pressure, flow rate of the solution of the polymer, and additions of a surface active substance soluble in SC-CO₂) that the polymer/particle ratio and concentration of the polymer are the critical parameters for the successful encapsulation of the silica particles with their minimum agglomeration, while the remaining parameters have little if any influence on the SAS process.

An efficient process of application of polymer coatings onto agglomerates of nanoparticles in a fluid bed was developed using SAS [26]. Titanium dioxide (TiO_2) particles and a solution of a Pluronic F-127 polymer in ethanol were chosen as the model objects. The process parameters, which can promote an increase in the yield and settling of a unimodal particle size distribution with a small increase in their average size relative to initial TiO_2 , were studied. It was shown that the solution feeding speed (it should be low) and concentration of the solution (low concentrations are preferable) affect the yield of the product the most. The sizes of the particles being obtained, which vary from 0.60 to 3.00 μm , strongly depend on the polymer/particle weight ratio. As for the morphology of the coating being formed, the polymer being introduced distributes over the whole surface of the agglomerate, while the bulk density of the suspension linearly increases with an increase in the polymer/particle weight ratio. The results showed that the process with the use of SAS proposed by the authors could have become a good alternative to the traditional methods of polymer coatings application.

The GAS Method

The GAS method is also applicable to substances insoluble in SCFs. The GAS method is based on a decrease in the dissolving capacity of a liquid towards a target substance in the case of its saturation with a gas (from a gas or supercritical fluid phase). Here, due to the speed of feeding of the antisolvent, the degree of supersaturation of the solution can be finely tuned, and the morphology of the coating being formed can be controlled (from microparticles to large crystals).

In [27], GAS and Precipitation from Compressed Antisolvent (PCA) methods were used for the polymer coating of aerogel-like particles filled with a pharmaceutical product. The first of them was used for relatively large particles (300 nm) when the coating was applied during the mixing of a suspension of the aerogel particles in acetone with a polymer dissolved in it with compressed CO_2 ; for the coating of smaller particles (65 nm), the suspension was injected into a continuous flow of CO_2 . All the coatings were applied without any preliminary functionalization of the aerogel particles surface. The results of the studies showed that porous particles of the submicron- and nanoscale substrate used in the experiments are successfully covered with the polymer to form weakly bound agglomerates. It is noted that the proposed method can be applied for preparing pharmaceutical products and microparticles with a core-shell structure with a narrow size distribution.

Note that the special attractiveness of GAS and SAS processes is remarkable particularly in the case of creating expensive products obtained on small production facilities (from units to several hundreds of

kilograms per day), in particular, for the production of pharmaceutical products, cosmetics, superconducting materials, etc. [12].

The PGSS Method

The PGSS method is often applied in the case of preparing polymer particles with a complex composition. The process is intended for the formation of microparticles from materials which adsorb the substance of an SCF well. The procedure has vast prospects for the production of polymer powder coatings on an industrial scale [1].

In the PGSS process, the substance from the SCF phase dissolves in a melt or suspension of a polymer and then the mixture is sprayed through a nozzle under high pressure. The advantages of the PGSS process include the following: there is no need to dissolve the substance in SC-CO_2 [28]; it is possible to form microparticles from suspensions of polymers; the consumption of the fluid and pressure created in the reactor are lower in comparison with the RESS method; and, hence, smaller investments will be required in the case of commercialization of the PGSS process [29].

Processes of preparation of micro- and nanoscale particles on the basis of PGSS have already been implemented on a relatively large scale. The advantages of the PGSS method are especially efficiently and most often used in the pharmaceutical industry during the development of targeted drug delivery systems [30–32]. Here, the simplicity of the PGSS method, which results in relatively small investments, provides the possibility for further expansion of the fields of its practical application, including for the formation of polymer microparticles [28].

Advantages and Disadvantages of SCFTs

Due to the above-discussed RESS, SAS, GAS, and PGSS processes, which are different versions of implementing SCFTs, it became possible to form microscale and nanoscale polymer particles which can be then used for application onto various substrates as multifunctional powder coatings with good consumer qualities.

As opposed to the already traditional techniques of preparing powder coatings, such as application in a fluid bed and electrostatic spraying, the formation of powder paint and varnish coatings by using SC-CO_2 -based spraying systems is characterized by the following advantages [33]:

(a) economic (a decrease in capital, energy, and operating costs and consumption savings of the material to be applied);

(b) environmental (a decrease in the emission of toxic organic compounds of up to 85%, with the potential of up to 100% in the case of industrial production; a decrease in the amount of harmful environ-

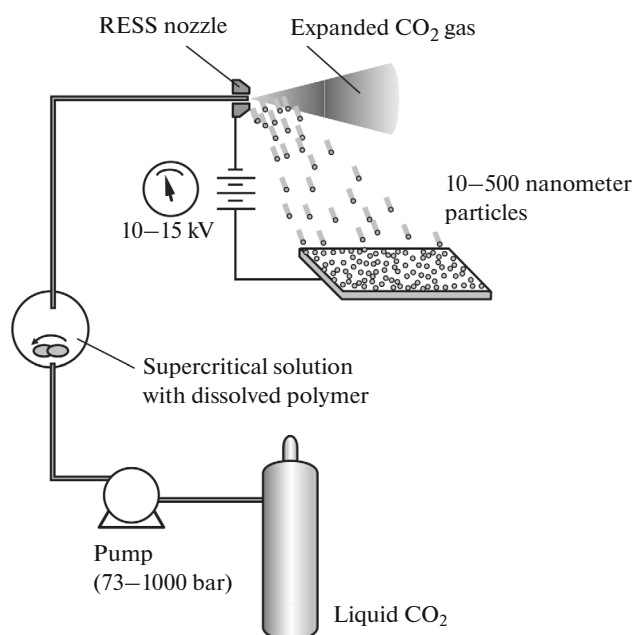


Fig. 2. Schematic of device for electrostatically charging particles in a RESS expansion and then depositing them onto a substrate in a strong electric field (the combined RESS–ED method) [34].

ment pollutants and solid wastes (up to 100%); and the exclusion of flammable solvents); and

(c) technological (the formation of high-quality film coatings, simplified application technique (e.g., in the form of sprays), the possibility for controlling the thickness of the coating, and enhanced corrosion resistance).

Overall, it can be noted that all the functional polymer powder coatings obtained using SCFTs possess a whole range of undeniable market advantages:

- (i) the use of environmentally safe supercritical fluids;
- (ii) the possibility for the formation of micro- and nanoscale particles of the materials being applied with a narrow size distribution, which promotes the formation of uniform high-strength functional coatings;
- (iii) the combination of the properties of gases (low viscosity and high diffusion coefficient) and liquids (significant density and high dissolving capacity) provides fast mass transfer throughout the volume of the polymer material;
- (iv) the easy removal of the solvent due to the transition to the gas phase during the depressurization.

As for the disadvantages of SCFTs, these technologies are associated with high investments in the commercial development in the first place, which substantially limits their wide practical application. Generally, the organization of industrial SCFT production facilities for the formation of polymer powder coatings is efficient only when the production of high-demand

expensive products which cannot be otherwise obtained is required.

To change the situation in terms of this aspect, years of intensive research aimed at increasing the efficiency of SCFTs and decreasing their capital intensity will be needed; here, the range of commercial products with applied polymer powder coatings will have to be substantially expanded as well. This, in particular, can be promoted by the integration of different stages of coatings formation in a single SCFT manufacturing process.

COMBINING DIFFERENT STAGES OF COATINGS PRODUCTION IN A SINGLE SCFT PROCESS CHAIN

Technologies for the preparation of polymer powder coatings should first and foremost solve two relevant tasks:

- (i) the formation of micro- and nanoscale particles with a specified morphology and
- (ii) the application of the obtained particles onto a surface to form a powder coating with appropriate operating characteristics.

The possibility for combining different stages of supercritical fluid technologies and integrating them into a single continuous process chain is of great practical interest. This refers to, in particular, the possible options during the organization of the production of powder polymer coatings presented below.

Combining Processes of Micronization of Particles and Application of Coatings

In most cases, a modified RESS–ED method, which is a combination of the RESS process with the ED (Electrostatic Deposition) process, is used for these purposes.

Such a combined RESS–ED method was used, in particular, in [34]. Figure 2 presents the scheme of the process of formation of thin films and coatings due to the sedimentation of particles of three different fluorine-containing polymers obtained via the fast expansion of solutions in supercritical CO₂ onto metallic and semiconductive substrates in a strong electric field. At the first stage, nanoscale polymer particles were obtained via the RESS method, which were then charged in a high-voltage electrostatic field applied to the nozzle. The particles sedimented onto a solid surface to form a uniform coating with a thickness from tens of nanometers to several micrometers.

The RESS–ED method was also used for preparing a superhydrophobic polymer coating [35]. The synthesized polymer, poly(vinyl acetate)–poly(vinyl trimethyl acetate), was dissolved in a mixture of SC-CO₂ and acetone and then sprayed. A difference of potentials of 8 kV was maintained between the nozzle and the substrate, onto which the coating was sedimented.

To find the optimum parameters of spraying, the distance between the nozzle and the substrate (3, 6, and 9 cm) and the concentration of the polymer were varied. The use of RESS–ED at a spraying distance of 9 cm led to obtaining high contact angles of above 150° and roll-off angles of 11° throughout the range of the studied concentrations of the polymer. Spraying at a distance of 6 cm was an exception where the formation of superhydrophobic surfaces was only observed at specific concentrations of the polymer.

Combining Polymerization and Micronization Processes

Generally, a traditional approach to the direct synthesis of polymer particles is emulsion polymerization, which can be successfully carried out in an SCF medium [36]. However, the poor solubility of surfactants, which are generally used in emulsion polymerization in liquid media, in CO_2 forces the use of special expensive fluorine-containing and siloxane stabilizers soluble in CO_2 .

In connection with this, the development of efficient supercritical fluid technologies integrating the processes of polymerization and micronization in a single process are of great interest.

Thus, in a series of works [37, 38], data on the combination of the processes of polymerization in SC solvents and the formation of microparticles via the PGSS method are presented. One distinctive feature of such an approach is the possibility for the development of modified polymer systems, in which intrinsic physicochemical properties of the polymer are capable of providing the formation of particles with specified operating characteristics. Thus, e.g., copolymers of acrylonitrile with methyl methacrylate and 2-chlorostyrene were obtained in SC- CO_2 , and the possibility for controlling the glass transition point of the polymer when varying the conditions of its synthesis was demonstrated [39].

An original technology for the preparation of polymer coatings using SC- CO_2 is currently at the stage of development by experts at the Institute of Problems of Chemical Physics, Russian Academy of Sciences. The combined method being developed makes it possible to apply coatings based on polymer microparticles including composite materials onto the surface of products made of different materials and is based on the joint use of the following three individually well-proven techniques in a single continuous process chain:

(a) the conduct of nonisothermal (frontal) polymerization in a sub- and supercritical fluid medium [40–43];

(b) the synthesis of polymer composite materials via polymerization filling [44]; and

(c) the atomization of the reaction product due to the fast decompression through a capillary nozzle.

One important feature of the combined approach under consideration is the fact that particles of the filler are present in the medium being polymerized; here, some polymer macroradicals recombine on the surface of these particles, forming a strong chemical bond between the polymer and the filler. Another part of polymer macroradicals is also preserved in the process of atomization and spraying of the polymer composite obtained in this way onto a substrate, which provides high adhesion of the coating being applied to the surface of the substrate. Depending on the nature of the coating material, the method makes it possible to obtain functional various-purpose layers, as well as to combine these layers during their successive deposition according to their required composition. The schematic diagram of the laboratory setup for the implementation of the combined technological process under development is presented in Fig. 3.

The initial monomer with functional additives introduced into it (an initiator, dyes, antipyrenes, etc.) from vessel 3 and CO_2 from cylinder 1 are fed using high-pressure plunger pumps 6 and 7 to mixer 8 equipped with a stirrer, in which they are mixed with a dispersed filler preliminarily introduced into it. Then the initial reaction mixture is fed at a specified flow rate under pressure to tubular reactor 11 for nonisothermal polymerization, where the process of transformation of the monomer to the polymer proceeds. The microparticles of the polymer composite formed during the throttling of the mixture of the polymer with the fillers, residual monomer, and CO_2 are sprayed onto the surface in chamber 16; here, CO_2 , which underwent a transition to the gas phase, entrains the residual monomer as well, which makes it possible to obtain a high-purity final polymer. The item with the applied powder layer is then sent to heat treatment, during which the particles are sintered and form a uniform polymer coating.

Therefore, almost the entire process (except for the heat treatment), starting from the initial monomer and ending with a finished product, is performed in a single closed process chain, which promotes a decrease in the cost of production due to the exclusion of the operations of transportation, storage, and preparation of intermediate products, as well as a decrease in the emission of harmful and toxic substances to the environment.

In [45], a continuous combined process integrating polymerization and micronization in an SC- CO_2 medium was studied as well. An acryl resin consisting of glycidyl methacrylate, methacrylate, and styrene was chosen as the base for the formation of thermosetting powder coatings. Carrying out the reaction in a tube reactor showed that, over a quite short time (~ 30 min) at 135°C and 30 MPa in the homogeneous phase, the conversion of monomers could exceed 96%; here, a polymer with a molecular weight of ~ 2500 g/mol and a narrow molecular weight distribution (a polydisper-

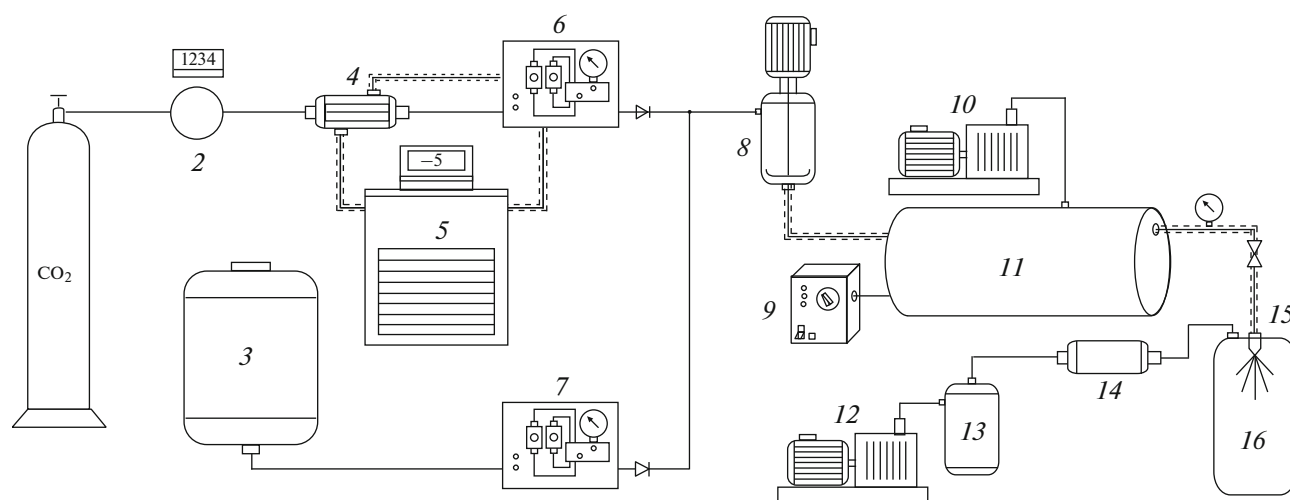


Fig. 3. Schematic diagram of the laboratory setup for the combined preparation of polymer microparticles and products on their basis using an SCF: (1) CO₂ cylinder, (2) Coriolis mass flow meter, (3) vessel with the initial monomer, (4) heat exchanger, (5) cryothermostat, (6, 7) high-pressure plunger pump, (8) high-pressure mixer (saturator), (9) temperature controller, (10, 12) vacuum pump, (11) tubular reactor, (13) cryogenic trap, (14) filter, (15) atomizing device, and (16) protective shield (chamber).

sity index of 1.6) was formed. After the stage of synthesis, micronization using the PGSS process was performed. Together with the formation of microparticles, the residual monomer was removed from the polymer product with CO₂, which underwent a transition to the gas phase as well, which made it possible to reach a high degree of purity of the product being obtained. Therefore, the authors managed to join the stages of synthesis, micronization, and purification of the polymer in a single more effective process.

Composite particles of titanium oxide with a shell of poly(methyl methacrylate) with a size of ~5 μm were obtained via “pseudodispersion polymerization” [46]. In this case, the particles of the filler themselves, the surface of which was modified with 3-(trimethoxysilyl)propyl methacrylate, served as the stabilizer. SiO₂–polystyrene composite particles with a diameter of 2–3 μm, which possessed higher mechanical properties in comparison with the pure polymer, were obtained via a similar method [47]. In addition, the presence of an inorganic oxide filler is also capable of modifying the thermomechanical, optic, electric, and magnetic properties of a composite polymer material obtained using a supercritical solvent.

ESTIMATION OF THE CAPITAL COSTS OF THE INDUSTRIAL DEVELOPMENT OF SCFTS

There are still no published reliable estimates of the cost of investments in industrial production based on SCFTs.

A priori it can be said (and many companies in the appropriate field adhere to this opinion) that the planned production with the use of supercritical fluid

technologies is extremely expensive in the first place. First of all, this is associated with very high investments in special equipment operating under high pressures when compared to equipment for medium and low operating pressures. Because of this, many experts tend to believe that, although SCFTs can lead to the manufacturing of commercially viable high-quality products, their use should still be limited and applied only in the case when there is no alternative way for their production.

Based on the long-term experience of operation of pilot and industrial units of various capacities, experts from SEPAREX performed preliminary economic calculations of the cost of investments in key-ready production based on SCFTs [23]. The calculations took into account all the equipment within the unit such as extractors and/or columns, reactors, dispersion chambers, etc., with a total volume V_T , as well as pipelines, various vessels for storage, one vessel for the storage of CO₂, one pump for feeding CO₂ at different speeds of feeding from 30 to 100% of the specified feeding speed of the solvent, heat exchangers, condensers, necessary tooling and instruments, full connections, automation facilities, etc. The results are presented in Fig. 4, where the dimensionless cost parameter (CP) is presented in the form of a logarithmic dependence on the productivity indices of the unit Q . The dependence of the value of CP on the parameters of the unit turned out to be close to the power law dependence with a power coefficient of 0.24:

$$CP = A(V_T Q)^{0.24},$$

where CP is the cost parameter of the unit; A is the correction factor; V_T is the total volume of the equipment, L; and Q is the productivity, kg/h.

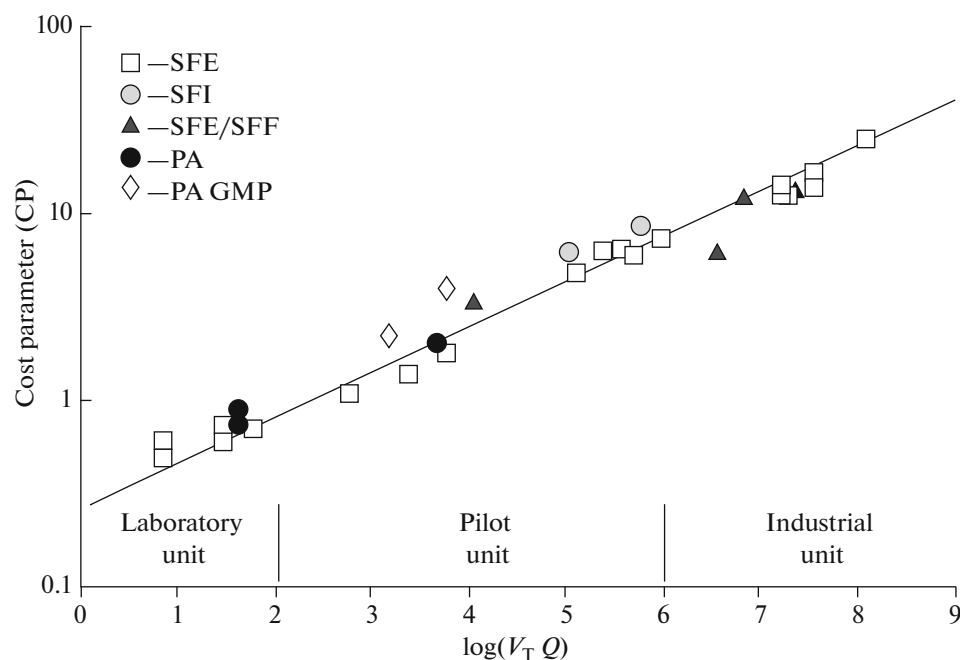


Fig. 4. Cost of different-purpose SCFT units depending on productivity (according to estimations of SEPAREx) [23] (SFE is supercritical extraction, SFI is supercritical impregnation, SFE/SFF is supercritical extraction/fractionation, PA is atomization of particles, and PA GMP is atomization of particles in accordance with the GMP requirements).

For similar units, productivity Q is proportionate to the total volume V_T of all extractors + the volume of the column, and this means that the cost of units for the implementation of SCFTs in practice increases approximately proportionately to the square root of their productivity. Here it should be taken into account that the range of productivities can be very wide, from 0.5-L autoclaves to industrial 500-L autoclaves. It also follows from the data of Fig. 4 that the cost of investments substantially increases when the use of special equipment is needed, e.g., for a combination of SCF extraction with SCF extraction impregnation, or for construction of a unit for the atomization of particles in accordance with international Good Manufacturing Practice (GMP) requirements.

It is noted that capital costs sharply decrease with increasing productivity of the unit to certain limits. Therefore, when possible, only high-capacity plant should be constructed instead of several low-capacity units.

Indeed, investments have a close relationship with the type of processes performed on SCFT units. Generally, the operating costs of the maintenance of units for SCF extraction processes are associated with high labor costs, especially when process operations cannot be automated. As for processes with the use of SCFs for fractionation, the labor costs are much lower in this case, because their maintenance facilities can work in a continuous mode for a long time in the case of automated control over process parameters. Anyway, despite the high investments in industrial implemen-

tation and still not very high efficiency of SCFTs, some companies use them for the production of specific (especially pharmaceutical) commercially viable products.

According to the expert estimations of SEPAREx [23], the operating costs of producing a unit of various types of commercial products which take into account the return of capital gain in the case of the commercialization of large-scale SCFT units are as follows:

- (i) food ingredients: 1–10 euro/kg;
- (ii) metallurgy/recycle of mechanical wastes: 0.3–1.0 euro/kg;
- (iii) polymers/powder dyes: 1–5 euro/kg;
- (iv) aerosol drying: 2–10 euro/kg; and
- (v) pharmaceutical powders: 100–2000 (!) euro/kg and above—the most capital-intensive production.

POSITION OF POLYMER POWDER COATINGS ON THE GLOBAL MARKET

Operational Characteristics of Commercial Products

The main requirements for the operating characteristics of powder coatings are as follows:

- (i) mechanical strength;
- (ii) uniformity of the thickness of application;
- (iii) high adhesion to the surface;
- (iv) durability;
- (v) resistance to temperature swings and exposure to aggressive media and solar radiation;

(vi) stability of operating characteristics while in operation;

(vii) easiness of application in hard-to-reach places;

(viii) possibility for the practically complete removal of the coating material if required;

(ix) good aesthetic properties of coatings, etc.

The morphology and sizes of the particles of the powder have the largest influence on the characteristics of the coatings being formed.

Factors Preventing the Development of the Market

The resistance of the market to abandoning traditional paint and varnish coatings based on organic solvents and the slow adaptation of more effective SCFTs are often associated with the insufficient awareness of many manufacturing companies about the advantages of SCFTs, high investments in conversion of the existing production facilities to work with micro- and nanoscale powders, the need for using high pressures and temperatures for the sintering of powders, difficulties in the change of the color of the coating being applied and the introduction of additives, etc. Unfortunately, it should be noted that many of these problems remain unsolved.

Nevertheless, despite the specified constraining factors, polymer powder coatings have already managed to gain sufficient popularity on the market. Thus, in addition to the increased number of end consumers, the market of these coatings, due to the development of new materials and compositions, new-generation process equipment, and the implementation of new and modernization of already known processes, has been demonstrating stable growth during all these years, and this should continue in the nearest future [48].

Market Peculiarities and Forecast for Market Development

The greatest growth in the global market of polymer powder coatings was observed in the 1980s in Europe, followed by North America and Japan. By the early 2000s, the global sales on the market exceeded 1 billion dollars; however, even at that time, despite the rapidly rising demand, coatings based on polymer powders still lagged too far behind traditional solid coatings applied using traditional organic solvents with respect to consumption [3].

Nevertheless, in 2010, the global market of powder coatings was already 5.8 billion dollars and grew at a rate of ~6% per year in 2011–2015 [49]. The field of high technologies and telecommunications that emerged during this period became a new sector in the powder coatings market, where high-quality protective coatings for electronic devices and instruments are in great demand.

Currently, the market of functional polymer coatings is led by four global companies: AkzoNobel N.V. (Netherlands), PPG Industries Inc. (United States), Sherwin-Williams (United States), and Dupont (United States). More than 30% of the global market was accounted for by these companies in total in 2013. Other companies known in the market include Asian Paint Limited (India), Axalta Coating Systems LLC (United States), BASF SE (Germany), Valspar (United States), Nippon Paint (Japan), Kansai Paints Company Limited (Japan), Jotun A.S. (Norway), Tikkurila Oyj (Finland), PHASEX (United States), Bradford Particle Design (BPD) (Great Britain), etc.

The development of the market noticeably accelerated with the development and production of high-technology laboratory, pilot, and industrial SCF equipment. The acknowledged global leaders in this field are THAR Technologies Inc. (United States) [50]; Supercritical Fluid Technologies, Inc. (United States) [51]; SEPAREX (France) [52]; LEWA GmbH (Germany) [53]; and NATEX Prozesstechnologie GesmbH (Austria) [54].

Experts from three leading American analytics companies, namely, MarketsandMarkets [55]; Frost & Sullivan [56]; and Grand View Research, Inc. [57], which have representative offices in many countries, agree that the volume of the market of powder coatings should increase by almost 5 billion dollars in 6 years, starting from 2014, and reach 12.5 billion dollars by 2020. Currently, the leading segment of the global market of polymer powder coatings is the production of consumer goods. The automotive segment will be the most rapidly growing (at an average rate of 7.7% per year) on the market during 2014–2020.

The substantial growth on the market of polymer powder coatings during 2015–2023 will be demonstrated by the sector of hydrophobic materials as well, which will be promoted by an increased demand for them from the electronic, aerospace, and medical industries of the developed countries [58]. The leading manufacturers in this sector are companies such as Aculon, Inc. (United States); Autus Lab Pvt. Ltd (India); DryWired (United States); Hydrobead (United States); NeverWet LLC (United States); NEI Corporation (United States), NTT Advanced Technology (NTT-AT) Corporation (Japan); P2i Ltd. (Great Britain); Surfactis Technologies (France); and UltraTech International, Inc. (United States). It is reported that, by 2021, the sector of hydrophobic coatings on the basis of microparticles should reach 1.8 billion dollars [59].

According to forecasts, the global market of medical powder coatings will increase at a rate of 6.5% per year during 2014–2019 [60]. The major players on the market of medical coatings include companies such as DSM Biomedical (Netherlands) and Hydromer (United States).

Currently, the Asia–Pacific Region (APR) is the largest consumer of powder coatings due to the fast development of the automotive and electronic indus-

tries, as well as launching of new large production facilities (in 2013, 45.8% of the total volume of the global market was accounted for by the APR). During 2014–2020, the rate of the growth in the market of powder coatings in the APR will exceed the worldwide index and will be ~8.5% per year. Here, the long-established markets of North America and Europe may lose their significance due to the transfer of the main production facilities from these regions to countries of Asia and Latin America with booming economies [61].

The field of scientific research (R&D) will remain one of the key factors affecting the development of the polymer powder coatings market. The largest global companies invest hugely in R&D on the creation of innovation processes and modernization of already existing technologies for the production of powder polymer coatings, while simultaneously searching for new potential areas of application of their products.

CONCLUSIONS

In recent years, scientific and applied research on the development of technologies associated with the micronization of polymer substances with the use of supercritical fluids, which possess a series of undeniable advantages in comparison with traditional techniques for the production of polymer powders, has noticeably intensified. SCF technologies have already been tested for the production of many sought-after products, especially in the field of pharmacology, and are successfully applied in practice on a relatively large scale.

The demand for powder coatings grows, thus leading to the appearance of new fields of their practical application. Nevertheless, the implementation of many processes for the production of functional powder polymer coatings based on SCFTs is still associated with overcoming a series of technical, in particular, engineering difficulties. Works aimed at eliminating the limitations existing in this field continue to be very relevant. A deeper understanding of the physical and chemical nature of the processes which form the basis for these technologies should help in the development of fresh scientific and technical and engineering solutions, which will make it possible, in particular, to decrease the still high cost of SCFT production facilities and make them more efficient and attractive.

The creation of more efficient SCFTs for the production of durable polymer coatings and improved external characteristics, lower temperatures of sintering, and faster process of curing should become the main objectives of future R&D. It will be necessary to provide good flow properties, coagulation, and the possibility of varying the properties of the coating being obtained at lower temperatures while creating conditions for the fast formation of intermolecular bonds keeping their operation characteristics and ensuring their stability under storage conditions. Note

that the specified requirements should be met in their entirety.

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