



# Synthesis and powder generation of powder coatings using supercritical carbon dioxide



I. Bochon<sup>a</sup>, S. Kareth<sup>b</sup>, A. Kilzer<sup>b</sup>, M. Petermann<sup>a,\*</sup>

<sup>a</sup> Chair of Particle Technology, Ruhr-University Bochum, 44780 Bochum, Germany

<sup>b</sup> Chair of Process Technology, Ruhr-University Bochum, 44780 Bochum, Germany

## ARTICLE INFO

### Article history:

Received 9 May 2014

Received in revised form

25 September 2014

Accepted 26 September 2014

Available online 5 October 2014

### Keywords:

Continuous polymerization

Copolymerization

Supercritical CO<sub>2</sub>

PGSS

Powder coating

## ABSTRACT

This paper reports an integral continuous process of polymerization and micronization of powder coatings using supercritical CO<sub>2</sub> as solvent. Combining different process steps into one single process, using ultra short production chains, can be one future use of supercritical fluids. This contribution is therefore an example of how such integral processes can be designed and how the development of new products can look like using supercritical fluids. An acrylic resin consisting of glycidyl methacrylate, methyl methacrylate and styrene was chosen as polymer system for use of thermosetting material for acrylic powder coating application. The reaction was performed in a tubular reactor. A monomer conversion of more than 96% was achieved with short reaction times of about 30 min at a temperature of 135 °C and at a pressure of 30 MPa in a homogeneous CO<sub>2</sub> phase. The resulting polymer has a number average molecular weight of about 2500 g/mol with a narrow polydispersity index of 1.6. In this process, the synthesis step in compressed carbon dioxide was followed by a high pressure micronization using the well-known PGSS process. Thus, small particles of about 25 μm were obtained. Simultaneously, residual monomers were removed from the polymer product with the escaping CO<sub>2</sub>-gas, achieving a high purity grade. The process is designed as a straight forward process combining synthesis, micronization and purification of a polymer without depressurization between the unit operations and demonstrates the benefits which supercritical fluid technologies offer for product and process development.

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## 1. Introduction

Conventional processes for the manufacture of powder coatings require technically complex plants which are cost- and energy-intensive. Furthermore, the synthesis of resins of powder coatings is conventionally carried out in the absence of organic solvents such as xylene or toluene, harmful to the environment or human health. After such polymerization the solvent has to be separated and recovered, either by vacuum distillation or by spray drying, both requiring considerable energy input. Organic solvents are applied as diluents to overcome technical challenges of high viscosity and to eliminate exothermic heat from the polymerization reaction [1,2]. An attractive alternative to traditional solvents is a compressed gas, here supercritical CO<sub>2</sub> [3,4]. Homogeneous free radical polymerization of acrylic fluorinated monomers in supercritical CO<sub>2</sub>

has first been described by DeSimone et al. [5,6]. Polymerization of acrylic resin in CO<sub>2</sub> has been thoroughly studied by Buback, Beuermann et al. [7,8]; they realized the homogeneous copolymerization of styrene–methylmethacrylate–glycidylmethacrylate with a high monomer conversion in homogeneous supercritical CO<sub>2</sub> in a tubular reactor.

Applying compressed CO<sub>2</sub> as a solvent for polymerization allows that the compressed gas solution can be immediately serve for powder generation from the gas saturated melt. This spraying process is known as PGSS process (Particles from Gas Saturated Solutions), developed by Weidner, Knez and Novak [9]. Based on the PGSS process, Petermann studied the CPCSP (Continuous Powder Coating Spraying Process) [10,11] in which the main components, namely resin and hardener of the powder coating system, are melted separately to prevent inappropriate early reactions before being mixed. Then, the components are quickly mixed in the presence of compressed CO<sub>2</sub> are subsequently powdered by a fast expansion through a nozzle. The operating parameters temperature, pressure, diameter and type of nozzle and specific fraction of CO<sub>2</sub> affect the particle size and distribution allow to obtain tailored particles. A combination of the synthesis of a powder coating resin and the

\* Corresponding author at: Chair of Particle Technology, Ruhr-University Bochum, Universitaetsstr. 150, IC 3/185, 44801 Bochum, Germany. Tel.: +49 234 32 26442; fax: +49 234 32 14277.

E-mail addresses: [info@fvt.rub.de](mailto:info@fvt.rub.de), [petermann@fvt.rub.de](mailto:petermann@fvt.rub.de) (M. Petermann).

generation of particles with the PGSS technology was published and patented in 2002 [12,13].

In this study, the supercritical CO<sub>2</sub>-based synthesis of a resin of the styrene–methyl-methacrylate–glycidylmethacrylate (S–MMA–GMA) type as a typical main component of acrylic powder coatings is performed in a tubular reactor, following a procedure proposed by Beuermann et al. [7]. For the powder coating application, the following characteristics of the polymer are required: A number average molecular weight of about  $M_n = 2500$  g/mol and a polydispersity index (PID) smaller than 2. The synthesized polymer is micronized to powder particles by the PGSS and CPCSP process, respectively.

A major advantage of using compressed gases is the possibility of carrying out a fast chemical reaction in a homogeneous phase regime of low viscosity. After the polymerization, the solvent CO<sub>2</sub> can be easily and completely separated from the polymer by rapid expansion to ambient pressure. Fig. 1 shows the classical production chain for powder coatings applied in industry since 1965 and being still the major process concept. The crossed out units in Fig. 1 illustrate the steps which can be saved by using supercritical carbon dioxide as an auxiliary medium and show the potential offered by the new CSP<sup>2</sup> (Continuous Synthesis Powder Coating Spray Process). The target of the present work is to realize both steps, the polymerization and the particle micronization in a single and simple continuous process. Organic solvents are replaced by supercritical CO<sub>2</sub>. The mixture of reactants and CO<sub>2</sub> is pressurized and heated up to reaction temperature. After the polymerization of the resin component, a hardener and additives can be added and quickly mixed in a static mixer to form the reactive coating mixture which is fed into the final powderization step.

By the sudden expansion in the spray nozzle the polymer components are cooled down; the polymerization is stopped and the cure of reactive groups is suppressed immediately. At ambient pressure, CO<sub>2</sub> is separated from the particles in a spray tower and in a cyclone, in which the fine powder fractions can be separated. Residual monomers can be extracted from the polymer by entrainment in the emanating gas and can be collected at the end of the process by the condensation.

The new combined process CSP<sup>2</sup> reduces not only the number of process steps and consequently the volume of required investment, but allows moreover for essential energy savings by avoiding repeated melting and solidification of the polymers. The classical manufacturing steps like the formation of sheets, the breaking into chips, the air milling and the sieving can be omitted.

## 2. Materials

The following substances were used for the synthesis of the acrylic resin: Styrene (stabilized with 15–17 ppm 4-*tert*-butylcatechol, MERCK), methyl methacrylate (MMA) (stabilized with 100 ppm hydroquinone, MERCK) and glycidyl methacrylate (GMA), currently commercialized under the name (2,3-epoxypropyl) methacrylate (stabilized with 80–120 ppm hydroquinone, Sigma–Aldrich).

MMA has a boiling point of 101 °C and a relatively high vapor pressure (53 hPa at 20 °C). GMA shows a dual functionality containing methacrylic and epoxy groups. Its boiling point (189 °C) is relatively high and the vapor pressure of 13.3 hPa at 82 °C is rather low. The boiling point of styrene is 145 °C and the vapor pressure at 20 °C is 6 hPa. The initial mole fractions of the monomers are:  $f_S = 0.07$ ,  $f_{MMA} = 0.52$  and  $f_{GMA} = 0.41$ . The reaction is initiated by using di-*tert*-butyl-peroxide (DTBP) from Merck; the molecular weight is controlled by *n*-dodecyl mercaptan (DDM; purum  $\geq 97\%$ , Sigma–Aldrich) as chain transfer agent (CTA). Referring to the monomer mixture, 1 wt.% DTBP (0.07 mol L<sup>-1</sup>) and 7.5 wt.% DDM

(0.37 mol L<sup>-1</sup>) were added to the reaction mixture. The half-life of the initiator DTBP at 140 °C is given to be about 20 min, whereas at 130 °C it is about 1 h [14].

Tetrahydrofuran (THF, Rotisolv,  $\geq 99.9\%$ , Carl Roth) is used as eluent in size exclusion chromatography (SEC) analysis. Carbon dioxide ( $\geq 99.95\%$ ) was supplied by YARA (Germany) and is used as both, reaction and as spraying media. Sudan III (biological stain 98%, Acros Organics, Belgium) is an indicator dye for the determination of the residence time in the reactor. Chloroform and methanol are used for analysis concerning the purification of polymer.

The formulation of the acrylic powder coating was chosen, as proposed by Lu [15] for clear coatings, the hardener component as curing agent and additives, such as leveling agent, light stabilizer are added to the synthesized binder: Referring to the binder, 17 wt.% of a hardener dodecandioic acid (DDDA), 2 wt.% Tinuvin 405 as light stabilizer, 2.3 wt.% modalflow powder III as leveling agent, 1 wt.% Tinuvin 144 as a free radical scavenger and 0.5 wt.% benzoin as degassing agent were added. The chemicals were kindly provided by AkzoNobel, Germany.

For the phase-equilibrium investigations, an additional inhibitor, hydrochinone (MERCK) was added to the monomers MMA and GMA, respectively in a concentration of 600 ppm, in order to prevent polymerization during the experiment.

## 3. Phase-equilibrium investigations of GMA/CO<sub>2</sub>, MMA/CO<sub>2</sub>

Phase-equilibrium investigations give information on the compositions of coexisting phases of the reactants with CO<sub>2</sub> at different thermodynamic parameters pressure and temperature. Compositions of emerging phases depending on pressure and temperature of saturated solutions can be observed. Liquid–vapor phase equilibria have been measured for the main monomers GMA and MMA with CO<sub>2</sub> at the typical polymerization temperature of 135 °C.

### 3.1. Experimental set-up

Measurements of the binary system were carried out in a high pressure view cell with a moveable sapphire piston which can be operated at pressure up to 42 MPa and temperatures up to 200 °C (New Ways of Analytics, Germany) (Fig. 2). The cell volume can be reduced from 57 ml to 24 ml to keep the pressure constant while withdrawing samples. The sapphire piston is moved by a hydraulic press. The hydraulic press is driven by compressed air and adjusted by the control unit which allows keeping the pressure constant within  $\pm 0.3$  MPa. The pressure within the cell is measured by a transducer (S11, Wika, Germany), up to  $p_{max} = 400$  bar with an uncertainty of 0.5% of the maximum value. The temperature is adjusted by two heating rods (for each 350 W), placed along the cell's mantle length. Their heating power is set by a PID control unit with a deviation of  $\pm 1$  °C (2216e, Eurotherm, Germany), receiving the signal from a thermocouple (type K, B+BThermo-Technik, Germany) positioned directly within the cell. An immersed propeller stirrer with magnetic coupling in the cell is driven by an electric motor. Liquid carbon dioxide is taken from the gas cylinder and is compressed to the desired pressure by an air driven pressure transducer (PM-101, New ways of analytics, Germany). The high pressure set-up exhibits a T-piece with a rupture disk (35 MPa at 20 °C, Kramer, Germany) fixed in a safety head (NovaSwiss, Switzerland).

The upper outlet of the cell is used for withdrawing samples from the gas-rich phase; the lower outlet allows taking samples from the liquid-rich phase. Both samples are decompressed to ambient pressure; the liquid components are collected in a glass tube while the escaping CO<sub>2</sub> is determined by a gas flow meter with an accuracy of 99% of the value (Illmer Gasgeräte, Germany).

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