J. of Supercritical Fluids 117 (2016) 18–25

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Impact of rapid expansion of supercritical solution process conditions on the crystallinity of poly(vinylidene fluoride) nanoparticles

Simone Wolff[a], Sabine Beuermann[b], Michael Türk[a,*]

[a] Institute for Technical Thermodynamics and Refrigeration, Karlsruhe Institute of Technology (KIT), Engler-Bunte-Ring 21, D-76131 Karlsruhe, Germany
[b] Institute of Technical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Straße 4, D-38678 Clausthal-Zellerfeld, Germany

ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form 15 July 2016
Accepted 18 July 2016
Available online 19 July 2016

Keywords:
$scCO_2$
Rapid expansion of supercritical solutions
PVDF
Crystal phase transformation

ABSTRACT

The rapid expansion of supercritical solution (RESS) process was used to produce poly(vinylidene fluoride) (PVDF) nanoparticles. PVDF was chosen since five different crystal phases ($\alpha, \beta, \gamma, \delta, \varepsilon$) have been reported in literature. The experiments were performed with a low molar mass polymer ($M_n = 1500\,g\,mol^{-1}$) that consists exclusively of α phase. The main objectives of this study were to examine the influence of process parameters, i.e. inner nozzle diameter, pre-expansion temperature and pressure on polymer crystallinity and crystal phase properties. Before and after micronization, the polymer was characterized by scanning electron microscopy, size-exclusion chromatography, differential scanning calorimetry and X-ray diffraction.

The findings of our investigations clearly show that RESS enables the formation of submicron particles. Furthermore, under certain process conditions, i.e. higher expansion and cooling rates and thus small nozzle diameters, RESS induces a crystal phase transformation from α to the desired β phase. In opposite thereto, simple static treatment with $scCO_2$ does not induce crystal phase transformation. Furthermore, average molar mass, dispersity and crystallinity of the RESS product was reduced due to the preferred extraction of low molar mass fractions.

1. Introduction

Poly(vinylidene fluoride), denoted PVDF, is a semicrystalline highly versatile polymer, exhibiting an extraordinary crystal phase behavior [1–3]. Apart from the most common phases, α and β, at least three other crystal phases ($\gamma, \delta, \varepsilon$ phase) are known. Each crystal phase is featured by different properties, however the β phase holds an exceptional position due to its unique piezo-, pyro- and pyroelectric properties [4–6]. Aiming the targeted production of a polymer with specific features, several studies focus either on synthesis strategies or the conversion of PVDF crystal phases [7–11]. For instance, the transformation of α into β PVDF may be achieved by drawing of polymer films. In general, crystal phase transformation is influenced by a large number of different parameters, such as temperature variations or the application of mechanical stress.

Nowadays, there is a growing interest in the development of supercritical fluid (SCF) based processes since the use of SCFs requires less energy, is environmentally friendly and offers the possibility to obtain new products with special characteristics. For example, the crystal phase transition of isotactic poly-1-butene as well as syndiotactic polystyrene polymers could be affected using supercritical CO_2 ($scCO_2$) [12,13]. However, most published works deal with pharmaceutical ingredients like carbamazepine or budesonide [14,15]. Among the different experimental approaches investigated, the rapid expansion of supercritical solutions (RESS) is one of the most promising techniques to control phase transformation. Applying RESS, the substance of interest is dissolved in a supercritical fluid and subsequently rapidly expanded through a capillary nozzle to ambient conditions. Due to ultrafast depressurization of the homogeneous supercritical mixture, precipitation of the solute is induced leading to the formation of small uniform particles. Already investigated pharmaceuticals include e.g. carbamazepine, flufenamic acid, phenylbutazone and tolbutamide [16–22]. The results of various investigations show that processing parameters such as operating temperature and pressure, depressurization temperature and pressure, as well as depressurization rate influence the final particle size, size distribution, and morphology of the produced particles [23]. The exact cause of the observed phase transformation is often difficult to define and cannot be explained with certainty so far.

Apart from the micronization of pharmaceuticals, RESS has also been applied to different polymers. Comprehensive reviews

---

* Corresponding author.
E-mail address: tuerk@kit.edu (M. Türk).

http://dx.doi.org/10.1016/j.supflu.2016.07.013
0896-8446/

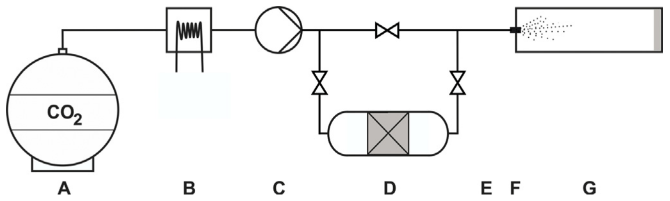

Fig. 1. Schematic diagram of the RESS apparatus: (A) CO_2 supply, (B) chiller, (C) diaphragm pump, (D) extraction column, (E) pre-expansion unit, (F) capillary nozzle, (G) expansion chamber.

especially focused on the formation and modification of polymer particles with SCFs have been published by Yeo and Kiran in 2005, by Reverchon et al. in 2009 and recently by Kiran in 2016 [24–26]. Previous works reported that RESS produced polymer (e.g. polycaprolactone, poly(methyl methacrylate), poly(heptadecafluorodecyl acrylate), poly(L-lactide), fluorinated tetraphenylporphyrin and PVDF) particles are in the range from a few ten nanometers up to some microns [27–37]. While the vast majority of the above mentioned activities is focused on basic questions such as process feasibility and optimization, formation of polymer—drug delivery systems as well as size and shape of the submicron particles, only a few investigations are focused on RESS-induced modification of the crystal phase properties. Thus, there is an increasing need for examination the possibility of using the RESS process to produce submicron polymer particles and to control the formation of the desired crystal phase of these polymer particles. Results of a former investigation show that the particle size can be decreased either by increasing molar mass, in case of identical polymer end groups, or by increasing the degree of crystallinity, in case of similar molar mass and different end groups [34]. Recently we reported that RESS [37]:

a) Leads to PVDF particles with a mean particle size 47 nm and
b) Induces a phase transformation from α to the desired β phase.

Hence the main objectives of this study were to examine the influence of the expansion processing conditions, i.e. inner nozzle diameter, pre-expansion temperature and pressure on polymer crystallinity and crystal phase properties. Thus, the present work intends to contribute to an improved understanding of the basic principles of crystal phase transformation caused by RESS.

2. Experimental

2.1. Materials

In all RESS experiments, CO_2 (99.9%, Linde AG) was used as solvent. PVDF samples with a number average molar mass (M_n) of 1500 g mol^{-1} featuring C_6F_{13} and I end groups were obtained from solution polymerization of 37 mol dm^{-3} vinylidene fluoride (VDF, 99%, provided by Dyneon GmbH) in $scCO_2$ [38,39] at 408 K and 150 MPa using 0.32 mol dm^{-3} di-*tert*-butyl peroxide (99% AkzoNobel) as initiator. In order to control polymer molar mass, 23.21 mol dm^{-3} perfluoro-*N*-hexyl iodide (98 %, Fluorochem) was used as chain transfer agent. The comparatively low molar mass was intentionally chosen to allow sufficient solubility of the polymer in $scCO_2$ to ensure feasibility of the RESS process.

2.2. RESS

In order to micronize PVDF, a laboratory scale RESS apparatus was used. The basic concept of the process is depicted in Fig. 1. Gaseous CO_2 is initially passed through a chiller and subsequently compressed to required pressure conditions with the aid of a diaphragm pump. After temperature setting, $scCO_2$ flows through an extractor column (T_E, p_E) containing polymer powder. The polymer is dissolved in $scCO_2$, and then the homogeneous supercritical mixture passes through a high pressure vessel (T_0, p_0) and is finally rapidly expanded through a capillary nozzle (T_N) into the expansion chamber to atmospheric conditions. Therefore, high supersaturation is induced, which leads to precipitation and the formation of small and uniform polymer particles. More details on the general experimental procedure are given in former publications [34,37].

Due to the laboratory scale apparatus design, maximal pressure and temperature conditions in the system where limited to 25 MPa and 343 K. Within the framework of this work, the following process conditions were adjusted: extractor column $T_E = 313$ K or 323 K, $p_E = 10$–20 MPa, high- pressure vessel (i.e. pre-expansion unit) $T_0 = T_E + 10$ K, $p_0 = p_E$, nozzle: $T_N = T_0 + 5$ K. In addition to the variation of temperature and pressure, the influence of the inner nozzle diameter ($d_N = 35$, 50 and 75 μm) on the properties of micronized PVDF was investigated. As a rule 450 mg polymer were used for each RESS experiment and the duration of the experiments was fixed to 45 min.

Furthermore, the apparatus was used to perform additional experiments without the expansion step, in which the impact of sole $scCO_2$ treatment on the properties of PVDF powders was investigated. For this purpose polymer samples were stored in the extraction column under $scCO_2$ atmosphere at $T_E = 323$ K and $p_E = 20$ MPa for different periods of time.

2.3. Characterization

For visual characterization of the unprocessed and processed PVDF, scanning electron micrographs (SEMs) were prepared with a LEO 1530 scanning electron microscope (Carl Zeiss AG). For this purpose, polycarbonate membranes (Whatman® Nuclepore™, pore size 0.2 μm) were loaded during the RESS experiments and subsequently sputtered with platinum.

Size-exclusion chromatography (SEC) was applied to determine molar mass distributions of the polymer samples. The SEC apparatus was calibrated using low dispersity polystyrene standards. *N*,*N*-dimethyl acetamide (99%, Acros) containing 0.1% LiBr (99%, Riedel-de-Haën) served as eluent. Further details on the SEC set-up are available elsewhere [38].

The melting behavior of PVDF was characterized by differential scanning calorimetry (DSC, DSC 1–Mettler Toledo). Using a heating rate of 10 K min^{-1}, the temperature was varied from 193 K to 473 K under a nitrogen flow of 50 ml min^{-1}. In order to estimate the degree of polymer crystallinity, *X*, the heat of fusion obtained by integration of the first heating run was related to the heat of fusion of 100 % crystalline PVDF, 104.7 J g^{-1}. This approach is commonly applied in literature [34,39–43]. Nevertheless, the authors would like to note that the previously given 100% value is based on measurements on pure α PVDF [44]. As a consequence, all given crystallinity values are determined under the assumption that the heat of fusion is independent from the actual crystal phase or phase composition of the PVDF sample.

The different crystal phases were identified by X-ray powder diffraction (XRD), because α and β phase have been shown to be indistinguishable in DSC measurements [45]. Both crystal forms melt in similar temperature ranges between 440 K and 445 K. A detailed comparison of literature data is scarcely realizable, because given values originate from the investigation of high molecular weight polymers. As opposed to that, our current investigation addresses low molar masses leading to melting peaks at lower temperature ranges. XRD analyses were performed by a STADI-MP diffractometer (Stoe & Cie. GmbH) with