Crystal phase transformation of $\alpha$ into $\beta$ phase poly(vinylidene fluoride) via particle formation caused by rapid expansion of supercritical solutions

S. Wolff, F. Jirasek, S. Beuermann and M. Türk

This contribution reports on the impact of the rapid expansion of supercritical solutions (RESS) on poly(vinylidene fluoride) (PVDF) properties in terms of particle size, molar mass distribution, crystal phase and finally piezoelectric behavior. Based on the usage of $\alpha$ phase PVDF powders, submicron particles were obtained involving crystal phase conversion to the $\beta$ form. Moreover, state of the art piezoresponse force microscopy analysis verifies the formation of piezoelectric PVDF particles via RESS.

Introduction

The excellent resistance to chemical, thermal, ultraviolet, weathering and radiation environments has led to the wide-ranging applications of semicrystalline hydrofluorocarbon poly(vinylidene fluoride) (PVDF). Popular items are e.g. coatings, piping equipment, or membranes. PVDF is recognized with at least 5 polymorphs ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\epsilon$ phase) and exhibits unique piezo-, pyro-, as well as ferroelectric properties, particularly in its $\beta$ phase. Since each crystal phase is associated with varying characteristic features, several studies concentrate either on targeted synthesis or conversion of PVDF crystal phases. For example, the crystal phase transformation of $\alpha$ into $\beta$ phase can be achieved by means of drawing, annealing or poling at different temperature and pressure conditions. PVDF applications exploiting piezoelectric properties in special devices like sensors, capacitors or actuators are highly interesting. The emphasis was on the influence of polymer properties such as molar mass, polymer end groups and degree of crystallinity on the obtained particle size. The particle size was shown to decrease 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.

In this contribution we describe the impact of RESS on PVDF properties for a model polymer with a number average molar mass of $M_n = 2000$ g mol$^{-1}$. The end groups are $\text{ClC}_6\text{F}_{12}$ and I originating from the chain transfer agent used in polymer synthesis. RESS is introduced as a promising method to
generate piezoelectric polymer particles by crystal phase transformation from \( \alpha \) into \( \beta \) phase PVDF.

**Experimental**

**Controlled radical polymerization of vinylidene fluoride**

PVDF samples were obtained from solution polymerization of vinylidene fluoride (VDF, 99%, provided by Dyneon GmbH) in \( \text{scCO}_2 \) (grade 4.3, 99.995% Linde AG) at 393 K and 150 MPa with 0.07 mol L\(^{-1} \) di-tert-butyl peroxide (DTBP, 99% AKZO Nobel) as initiator. The VDF concentration is 3.5 mol L\(^{-1} \). To control polymer molar mass 0.23 mol L\(^{-1} \) \( \text{CCl}_2\text{F}_2\text{I} \) (98%, Apollo Scientific Limited) was used as chain transfer agent (CTA). The CTA allows for controlled reversible – deactivation radical polymerization, so-called controlled radical polymerizations, and therefore, the synthesis of low dispersity polymer. Moreover, the controlled radical polymerization of VDF excels robust, solvent- as well as stabilizer-free characteristics. For more details refer to ref. 33 and 34.

**Rapid expansion of supercritical solutions (RESS)**

In a typical RESS experiment, the polymer is dissolved in \( \text{scCO}_2 \) (grade 3.0, 99.90% Linde AG) at 323 K and 20 MPa. The homogeneous supercritical mixture is subsequently rapidly expanded through a heated capillary nozzle (338 K, inner diameter = 50 \( \mu \)m) to atmospheric conditions. As a consequence, spontaneous phase transition occurs and polymer particles are formed. The RESS process is carried out for 45 minutes. Further details on the experimental set-up and the general experimental procedure can be found elsewhere.\(^{40,41} \)

**Analytical methods**

In order to determine the particle size of the obtained polymer particles, scanning electron microscopy (SEM) was performed. The sample preparation included the loading of polycarbonate membranes (What-man®NucleporeTM, 47 mm diameter with a 0.2 \( \mu \)m pore size) within the RESS expansion chamber followed by platinum sputtering (approx. 2 nm). The SEM micrographs (secondary electrons) were taken with the support of the Labo-

**Results and discussion**

In the following section three samples were differentiated: the so-called “raw material” is the PVDF polymer received by controlled radical polymerization in \( \text{scCO}_2 \) prior to RESS. The PVDF fraction which remained in the extractor column of the RESS apparatus and which was thus not micronized, is referred to as “residue”. For the RESS product the term “RESS” is used. At the same time, three colors are utilized in the subsequent graphs: the raw material is represented in grey, the residue in blue and the RESS sample in red.

Fig. 1 and 2 summarize the significant effect of RESS on the polymer powder size. The raw material is a white powder featuring rather large agglomerates/aggregates. One example is demonstrated in Fig. 1a with a diameter of nearly 15 \( \mu \)m.
A typical SEM image of micronized polymer particles is additionally shown below (Fig. 1b). In Fig. 2 the associated PSD with ranging particle sizes from 38 nm ($x_{10}$) to 60 nm ($x_{50}$) is presented. This size distribution is based on the evaluation of approximately 30,000 particles of 35 SEM micrographs, taking into account varying sample collection times and lengths during the RESS experiment. The resulting median particle size ($x_{50}$) is 47 nm which means that the average particle size was reduced by a factor of 300.

It is known that the polymer solubility in CO$_2$ increases with decreasing molar mass.\(^{40}\) Since a sufficient solubility is crucial for the RESS process itself, our present investigation regards comparatively low molar mass PVDF. The number average molar mass ($M_n$) of the raw material is 2000 g mol$^{-1}$ and shows a dispersity ($D$) of 1.3 (cf. Table 1). The MMDs of all samples are depicted in Fig. 3. Compared to the distribution of the raw material, the red line representing the material after micronization is shifted to the left implying that low molar mass species are preferentially extracted due to higher solubility. The polymer which remained in the extractor of the RESS apparatus thus consists of the higher molar mass species of the initial raw material. The dispersity was not changed by RESS. $M_n$ and $D$ data values are listed in Table 1.

Whether RESS is able to change crystal phases of PVDF was investigated applying FTIR in combination with XRD analyses. This procedure is in line with current literature and allows for the correct identification of the phases.\(^{41}\) Fig. 4a demonstrates the FTIR analyses of the three samples. Note, the photoacoustic cell allows for analysis of the solid material without any processing, e.g. as required for ATR. For reasons of clarity just a few representative absorption bands were high-lighted. The raw material exhibits typical absorption band characteristics of the $\alpha$ phase.\(^{11,12,44-46}\)

| Sample    | $M_n$ (g mol$^{-1}$) | $D$ |
|-----------|---------------------|-----|
| Raw material | 2000               | 1.3 |
| Residue   | 2500               | 1.3 |
| RESS      | 1400               | 1.3 |
Fig. 4 Crystal phase characterization of unprocessed PVDF, residue and via RESS micronized particles by (a) FTIR and (b) XRD.

Fig. 5 PFM analysis of PVDF raw material (I), residue (II) and micronized particles (III) described through four columns: respective sample (a) topography, (b) piezoresponse image prior to the application of voltage pulses, (c) localization of the four voltage pulses and (d) piezoresponse after the application of voltage pulses. Note: to avoid saturation of the PFM signal, the sensitivity for (III d) was reduced by a factor of 10 when compared to all other piezoresponse images shown.
While the residue spectrum shows no change in comparison to the raw material, the analysis of the micronized particles is altered. Typical $\alpha$ bands like 615, 760 or 795 cm$^{-1}$ have disappeared and a new strong absorption band has emerged at 840 cm$^{-1}$. This band corresponds either to the $\beta$ or the $\gamma$ phase. Under consideration of some distinguishable FTIR bands of the $\gamma$ phase which cannot be found in Fig. 4a (e.g. 776 and 812 cm$^{-1}$), it is assumed that the particle formation via RESS has led to the formation of $\beta$ phase particles.\textsuperscript{47-49} This assumption was confirmed by XRD.\textsuperscript{47-49} The patterns of raw material and residue are similar featuring characteristic $\alpha$ phase planes: (100), (020), (110) and (021) (cf. Fig. 4b). Consistent with FTIR analysis, the RESS diffractogram distinctly presents the $\beta$ phase in a single peak at 2 theta = 20.26° ((110)/(200)). Both FTIR and XRD measurements were repeated after a period of three months indicating no significant crystal phase change.

To our knowledge, the origin of the PVDF phase transformation is not yet fully understood. Previously, it was reported that treatment of $\alpha$ PVDF films with scCO$_2$ and rather slow controlled depressurization did not result in a phase transformation.\textsuperscript{46} However, successful phase transformation from $\alpha$ into $\beta$ phase PVDF has already been induced by ultra-fast cooling/quenching of the melt.\textsuperscript{41,52-55} The formation of $\beta$ phase PVDF strongly depends on the quenching temperature assuming that the maximum nucleation rate of the $\beta$ phase occurs at lower temperatures than that of the $\alpha$ phase. Thus, in the case of a high cooling rate, $\alpha$ phase nucleation is suppressed and $\beta$ phase formation is preferred. Applying RESS, the phase transformation is suggested to be the result of super-cooling due to the extremely high rate of expansion which triggers the crystallization of the solute.\textsuperscript{48} At the same time, however, it should be noted that further experiments are needed in order to understand cause and mechanism of the phase transformation. This is emphasized by studies on the polymorphic control of pharmaceuticals via RESS. For example, it was found that the crystalline form of the pharmaceuticals barbital, tobutamide and carbamazepine particles depend on the specific extraction conditions of the RESS process.\textsuperscript{54,55}

The piezoelectric properties of the PVDF particles in their $\beta$ form obtained via RESS could be established by PFM measurements. Therefore, three identical data sets investigating the raw material (I), the residue (II) and the micronized particles (III) were recorded (Fig. 5). Each data set consisted of three steps: characterization of the sample (topography (a) and piezoresponse (b)), application of voltage pulses at four positions (c), and again recording topography (not shown) and piezoresponse (d) of the sample. Comparison of the two topographical images confirmed having recorded the same position before and after the application of the voltage pulses. Fig. 5 shows the results of the experiments. Obviously, despite the careful sample preparation, the topography for all three samples showed a roughness of $\sim$1 $\mu$m, which is the maximum corrugation a SFM can handle, leading to long image acquisition times of 20 min per $\times 5 \times 5$ $\mu$m$^2$-scan. Initially, the piezoresponse (b) of all three samples featured no distinct patterns but basically shows an information-free noise image. After the application of voltage pulses, however, only the sample with the micronized particles (III) exhibited locally poled areas, whereas for both, the raw material (I) and the residue (II), no change in the piezoresponse image could be observed. Control experiments at different positions of the samples yielded the same results. The piezoresponse image of the REES sample needs a little more discussion. At first glance, it is striking that (III d) is a lot less noisy when compared to all other piezoresponse images shown. This is due to the fact that the sensitivity of the detection was reduced by a factor of ten, thus preventing saturation of the PFM signal. The amplitude of the piezoresponse is of the order of 10 pm V$^{-1}$. The contrast (black/white dots) meets the expectations from the polarity of the poling voltage pulse. Upon closer view, it can be perceived that the poled areas are not circular dots but exhibit a distinct structure which is most probably caused by the roughness of the sample.

Conclusions

RESS was successfully applied on PVDF ($M_n = 2000 \text{ g mol}^{-1}$) obtained from controlled radical polymerization in scCO$_2$. The rapid expansion of the scCO$_2$-PVDF mixture led to the formation of submicron polymer particles with a median particle size of 47 nm. With regard to the raw material used, particles with a clearly reduced average molar mass were generated which is attributable to the higher solubility of lower molar mass PVDF in scCO$_2$. It was also stated, that the dispersity of the samples was not affected by the extraction. The samples were further analyzed by FTIR and XRD revealing a transformation from $\alpha$ to $\beta$ phase PVDF. An unambiguous proof of the piezoelectric property of the RESS-processed $\beta$ phaseed particles was obtained by means of PFM measurements. Pursuing investigations will focus on the thorough study of the crystal phase transformation and the fascinating electrical properties of the obtained particles.

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