

Research Article

Precipitation of Polypropylene and Polyethylene Terephthalate Powders Using Green Solvents via Temperature and Antisolvent-Induced Phase Separation

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Received 1 March 2023; Revised 20 October 2023; Accepted 1 November 2023; Published 30 November 2023

Academic Editor: Gyorgy Szekely

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Polymer dissolution and precipitation are two common processes for the production of polymer powders, especially for cases where usual means of comminution are not applicable. I investigated six dissolution–precipitation processes based on high-boiling sustainable green organic solvents and antisolvents for the polypropylene and polyethylene terephthalate with respect to apparent particle morphology for a closed loop production scheme. Of the investigated processes two are considered antisolvent-induced precipitations whereas the other four can be considered temperature induced. The applied solvents included p-cymene, dibutoxymethane, ethylbenzoate, γ -valerolactone, ethanol, and hexanol. All processes yielded powders consisting of agglomerated primary particles at a powder dry substance of less than 25% by weight. The produced powders consist in all cases of agglomerates of smaller primary particles.

1. Introduction

In today's world polymers are ever existent, be it in packaging, automotive, clothing, or other consumer products. In 2017 over 14-million tons of different polymers were produced in Germany alone, with polyethylene terephthalate (PET) and polypropylene (PP) making up 6% and 17%, respectively [1].

Virgin polymer is commonly used as pellets in manufacturing, however, processes like powder-based additive manufacturing (laser sintering, 3D printing) or powder coating require other qualities. Ball milling, grinding, and precipitation are usually the way of choice if polymer powders are needed [2]. For commercially available polymer materials like polyamides, processing routes via precipitation exist, though, advances in dissolution and precipitation processes for PET and PP have also been made. Even though some commercial PP and PET powders exist for powder-based additive manufacturing applications, both PP and PET are not yet common materials for additive manufacturing. Hence, the topic of powdering those polymers is more relevant in end-of-life management and recycling. While

powderization is not strictly necessary especially in the context of solvent based recycling, polymer powders as intermediate products offer the possibility of enhanced desolventation and easier addition later on compared to polymer melts.

Due to the polymer's longevity and the ever increasing mass of plastic waste, end-of-life options for plastic waste are drastically needed. End-of-life options may include a secondary use of a polymer as a powder-based coating or as fibers, commonly referred to as downgrading. In theory, any thermoplastic polymer can be melted, pelletized, and reused for another lifecycle. In practice, recycling is more complex, especially with the different polymers in multicomponent materials or filled polymers.

Most commonly, dissolution and precipitation techniques have received relevance through the development of recycling techniques. Such techniques offer the possibility of separating usually inseparable and in thermomechanical recycling incompatible polymer materials by means of selective dissolution. Suitable stocks for such recycling approaches are commonly multilayer light-weight-packaging, often comprised of

polyolefins (mostly PE), barrier polymers (i.e., EVOH), and polyesters (PET) [3–5].

Dissolution and precipitation for polyesters have been an object of research for more than 50 years. For the most part, research on this field was focused on the recovery of PET instead of production of PET powders for specialized applications. With most of the material to be recovered originating from packaging waste, separation of mixed polymers is the most prevalent reason for dissolution technologies in recycling. With the exception of PET material from bottles, PET waste is usually a mixture of either a variety of vastly different and mostly incompatible polymers or in the case of mixed fabrics with natural fibers like cotton. In order to obtain pure PET from such mixed waste streams several approaches were developed.

Many patents were issued for PET dissolution and precipitation processes. While some were only focusing on the dissolution of polyester materials, most also explain methods of precipitation. Generally, two methods exist for a precipitation of a polymer from solution. These two methods are temperature induced phase separation (TIPS), i.e., changing the temperature of the polymer solution in order to decrease solubility of the polymer in the solvent, and antisolvent-induced phase separation. While in theory in TIPS a solvent mixture's temperature could be increased to decrease solubility, this is a seldom practice and usually done by decreasing the temperature [6]. Exceptions to the aforementioned separation methods are, e.g., the addition of primary particles, acting as nucleation sites [7]. In general TIPS as a methodology has been applied to a variety of both polymers and solvents. Especially in recent years with the increasing importance of powder-based additive manufacturing new methods for the precipitation of tailored powders were developed. These covered polymers such as polypropylene, polyamides, polycarbonate, polybutylene terephthalate, polylactic acid, and polyetherimide [8–11]. The particles produced via those process routes are typically described as spherical and semicrystalline.

In the early decades of PET dissolution and precipitation processes many disclosed patents relied on dissolution in petrochemical aromatic organic solvents such as naphthalene or benzene and their respective derivatives [12–14]. Other patents included halogenated, especially chlorinated, organic solvents as well as aliphatic organic solvents [7, 15, 16]. In a minority of patents alkyl sulfones were disclosed, acting as a solvent but also in some instances as antisolvent for the precipitation of polymer [17]. While earlier patents were more focused on the dissolution of PET from pure sources or fabrics containing cotton, true selective dissolution for the separation of PET from other polymers was shown later in [16, 18–20].

In one of the first patents on this topic Siggel and Kleine [12] described a solvent based purification process with a temperature induced phase separation with a solid product at the end of the process. Fuchs [21, 22] further disclosed dissolution processes for PET with a wide range of solvents, most of them based on aromatic alcohols.

Shoemaker et al. [13, 14] patented solvent-based dissolution strategies for the recovery of polyesters from waste

material including colored textiles with varying mixtures of solvents such as naphthalin or benzyl alcohol. Nauman and Lynch [15] disclosed a process for selective dissolution of a variety of polymers by temperature modulation in the same solvent (THF, toluene, xylene) and separation by preferably flash devolatilization. Serad [17] patented a process for the separation of polyester from waste polyester/cotton blends by dissolving the polyester in tetramethylene and precipitation with water. For the separation of PVC and other polymers from PET waste streams Brownscombe et al. [18] designed a process in which the PET parts are selectively solubilized in the high-boiling organic solvents. Similar to the Shoemakers [14] patents a dissolution process using phthalates and toluates as solvents is also published by Everhart et al. [19].

Separating PET from fabrics is still a large issue. A multitude of concepts were developed for exactly this specific case, with all included processes aiming at the physical dissolution of the PET phase rather than the cotton without degrading any of the polymers.

In the last two decades, the approach of Poulakis and Papaspyrides [23] as well as the CreaSolv[®] process of Mäurer et al. [24, 25] received large publicity for their capability of selective dissolution of polyesters in a closed loop with regard to the solvent. Poulakis and Papaspyrides [23] suggested the solvent system of *n*-methylpyrrolidone (NMP) in mixture with *n*-octane as solvent together with *n*-hexane as antisolvent for the selective dissolution of PET from mixed waste and following precipitation as granular product.

Most recently, Pestana et al. [26] covered a novel dissolution approach using natural eutectic solvents to dissolve PET wastes, thus leading the way for more sustainable solvent based processes.

Polypropylene powders are for the most part required as materials for powder coatings and more recently for powder-based 3D printing processes like powder bed fusion. Even though polypropylene powders also do exist as a result of solvent-based recycling technologies, common recycling technologies focus not necessarily on PP alone, but mostly on the polyolefins as a target group. To recover high-quality polypropylene from a mixture of polyolefins, at least one type of polymer has to be dissolved. It is not a novel process to recover polypropylene by dissolution and precipitation since this has been proposed by Poulakis and Papaspyrides [27] and Pappa et al. [28] was shown to be scalable for a pilot plant operation. Later, proposals followed the same idea of separating polyolefin waste material into the respective fractions, though the choice of solvents has not been consistent. Achilias et al. [29–34] used a combination of xylene and methanol for separation, while others proposed the use of a combination of petroleum ether, toluene, benzene, or turpentine with *n*-hexane. Further developments covered not only the recycling of polyolefins as mono-material but also of polypropylene fiber composites, though with the solvent choice falling once again on xylene [35]. Not only the recycling of polypropylene composites has been a topic, but also production of new composite material has been of interest [36]. All currently existing technologies rely heavily on non-

sustainable resources such as fossil fuel derived solvents. For a dissolution/precipitation process to be economically and ecologically viable in the future more sustainable solvents must be chosen.

In this paper I investigate six different solvent based processes for the production of PET and PP powders by means of dissolution and precipitation. All solvents used in this paper can be considered green as they can be obtained from renewable sources, differentiating this work from most other approaches relying mostly on the solvents sourced from fossil sources. A focus was held on the macroscopic and microscopic appearance of produced particles as well as the mass balances.

2. Solvent Selection

For dissolution of polypropylene and polyethylene terephthalate a variety of solvents are available. In case of polyesters, PET is the most common representative of this group with several methods already being investigated and published. Shoemaker et al. [14, 13] patented methods for recovery of polyester as well as decoloration based on precipitation with various solvents including biphenyl, naphthalene, dichloromethane, and benzyl alcohol. Vane and Rodriguez [37] investigated the dissolution and recovery of PET with N-methyl-2-pyrrolidone from bottle waste. Serad disclosed a solvent-based separation process via dissolution and precipitation of polyester with a sulfone-based solvent [17]. Brownscombe et al. [18] patented a process for PET waste separation with solvents ranging from dialkylesters of naphthalates, phthalates, terephthalates, and isophthalates to the cyclic carbonates. Similar solvents were used by Everhart et al. [19] with the addition of methyl-p-toluate as possible solvent. In a different approach Brownscombe et al. [38] disclosed diethyl glutarate, dimethyl succinate, dimethyl sulfoxide, diphenyl sulfone, N-methyl-2-pyrrolidone, and sulfolane as possible solvents for a polyester recovery. In patents of Mäurer et al. [24, 25] PET was dissolved in dibasic esters. Poulakis and Paspapirides [23] followed an approach of antisolvent-induced phase separation with precipitation of PET from N-methyl-2-pyrrolidone and *n*-octane with 1-hexane. Li et al. [39] proposed the use of supercritical CO₂ as an antisolvent for PET precipitation from phenol. Biphenyl–diphenyl was also seen as an alternative solvent for PET, posing the possibility of enhancing postpolymerization of PET in the swollen state and precipitating PET into nanofibrills [40, 41]. Walker [42–44] patented their process for the recycling of PET using a variety of solvents, for instance ethyl benzoate. In further studies the formation of particles in a specific size was investigated [45]. In the latest instance the system γ -valerolactone/water was used as a solvent/antisolvent pair for the precipitation of PET [46].

Most approaches of dissolving polypropylene include solvents of fossil origin, often aromatic compounds and benzene derivatives such as toluene, xylene, and mesitylene. Both have been shown to be suitable solvents for the dissolution and precipitation of polypropylene. Toluene has been shown to be a suitable solvent for solvent targeted recovery and precipitation at already moderate temperatures [47].

Xylene is described as solvent both in recycling processes as well as processes for the preparation of powders for additive manufacturing [23, 27, 34, 48]. Mesitylene, in combination with *n*-hexane and petroleum ether has been shown to be a suitable system for the dissolution and precipitation of polypropylene as well [49]. In an approach to use more environmentally friendly solvents, the system p-cymene with acetone as antisolvent was proven to be viable [50]. Other research investigated the precipitation from p-cymene using antisolvents like ethanol, ethylene sulfite, γ -valerolactone, and terpinol, but with other processing parameters [51]. In the analysis of polyolefins dibutoxymethane is a suitable solvent for size exclusion chromatography, however, no precipitation procedure is described yet [52].

Out of the solvents used in prior publications, several of them were assessed on a theoretical basis with regard to their compatibility based on the Hansen [6] solubility parameters (HSP). The theory behind the HSPs is based on the assumption of like dissolves like. In order to assess the likeness of solvents and solutes the cohesive energy density is used. In contrast to the Hildebrand solubility parameters, the HSP subdivide the cohesive energy density δ^2 into the respective components representing the energy from dispersion forces δ_d^2 , from dipolar intermolecular forces δ_p^2 and from hydrogen bonding between molecules δ_h^2 .

The Hildebrand and Hansen solubility parameters are connected by Equation 1 in which ΔH_V is the latent heat of vaporization, V_m the molecular volume, R the universal gas constant and T the absolute temperature.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 = \frac{\Delta H_V - RT}{V_m} \quad (1)$$

The likeness of solute and solvent is represented by the distance in Hansen space R_a , calculated using Equation 2.

$$R_a^2 = 4(\delta_{D,1} - \delta_{D,2})^2 + (\delta_{P,1} - \delta_{P,2})^2 + (\delta_{H,1} - \delta_{H,2})^2 \quad (2)$$

The resulting distance in Hansen space is then compared to an experimentally determined interaction radius R_0 of the solute, resulting in the relative energy distance (RED) $RED = R_a/R_0$. For a solvent and a solute to be assessed as compatible in this model, a RED of less than 1 is expected. Solvents with a RED just minimally above 1 may induce swelling of the solute, but will very likely not dissolve the solute.

Further criteria like the boiling temperature, commercial availability, and sustainable production lead to the selection of the solvents p-cymene and dibutoxymethane for the dissolution of polypropylene and ethanol as well as 1-hexanol as antisolvent for the precipitation step. Ethyl benzoate and γ -valerolactone were chosen for the dissolution of polyethylene terephthalate with 1-hexanol as antisolvent due to the temperature compatibility. The solubility parameters of the respective solvents and antisolvents are shown in Table 1. RED was calculated using an interaction radius of

TABLE 1: Hansen solubility parameters (HSP) for polyethyleneterephthalate (PET) and polypropylene (PP) and applied solvents.

	δ_D	δ_P	δ_H	RED _{PP}	RED _{PET}
Polypropylene	18	3	3		
p-cymene	16.67	0.35	0	0.60	1.58
Dibutoxymethane	15.7	4	3.9	0.60	0.99
PET	18.2	6.4	6.6		
Ethyl benzoate	17.9	6.2	6.0	0.55	0.11
γ -Valerolactone	16.9	11.5	6.3	1.17	0.94
Water	15.5	16.0	42.3	5.21	6.32
Ethanol	15.8	8.8	19.4	2.24	2.33
1-Hexanol	15.9	5.8	12.5	1.34	1.23

Note: The calculated relative energy differences (RED) for the solutes were calculated with an R_0 of 5.0 and 8.0 for PET and PP, respectively. All parameters were taken from Hansen [6].

$R_{0,PP} = 8 \text{ MPa}^{1/2}$, and $R_{0,PET} = 5.0 \text{ MPa}^{1/2}$ for polypropylene and polyethylene terephthalate, respectively [6].

Additionally, most of the chosen solvents can be considered as green solvents. As it is directly available in a variety of plants, p-cymene has been shown to be producible via processing of α -limonene from citrus waste material [53–55] as well as other sources like eucalyptus oil [56] and perillyl alcohol [57]. Dibutoxymethane, a common additive for biodiesel, can be produced from butanol and formaldehyde [58, 59]. Both platform chemicals can be sourced sustainably with the following procedures. Butanol can be produced via fermentation of lignocellulose or by reduction of volatile fatty acids with hydrogen [60]. Formaldehyde is commonly produced from syngas, a mixture of hydrogen and carbon monoxide using a catalyst [61]. Ethyl benzoate cannot—in high amounts—be directly sourced from any agricultural produce or other sustainable resources. Its precursor benzoic acid can be prepared in a recycling process from polystyrene, though commonly it is produced by oxidation of toluene and is therefore mostly a petrochemical product [62, 63]. γ -Valerolactone on the other hand is a platform chemical based on lignocellulosic biomass which can be produced either directly from the lignocellulosic biomass or from decomposition products like levulinic acid [64, 65]. Hexanol, a common short chain aliphatic alcohol, can beside the common route as a byproduct of the fossil industry also be produced from renewable resources using cellulose as a platform [66].

3. Materials

Polypropylene polymers chosen for this study were Borealis PP SD233CF (PP_R) and LyondellBasell HP570M (PP_M). Both PP types were received as ellipsoidal granules with diameters of 3.5–3.6 mm and 2.9 mm height. The polymers were chosen based on similarities in the area of application as both PP types are used in film applications and possess similar melt flow rate (MFR) values with 7 g/10 min for PP_R and 7.5 g/10 min for PP_H. [67, 68] The mass weighted molecular weights (M_w) of the polypropylene types were measured as $401.6 \text{ kg mol}^{-1}$ and $384.6 \text{ kg mol}^{-1}$ for PP_H and PP_R,

respectively. Considering similar MFR values, similar molecular chain lengths are expected. Due to the unknown composition of the random copolymer (PP_R) no clear assessment of the chain length can be made despite the known molecular weights.

Invista Polyclear[®] Refresh PET 1101 with a mass weighted molecular weight average at $M_w = 61.2 \text{ kg mol}^{-1}$ was chosen for PET as model polymer. PET was received as cylindrical granules of a diameter of 2.3 mm and a height of 2.2 mm. The PET type was chosen based on its wide range of applications and could therefore pose as a good model polymer. Typical applications for this PET-type are packaging applications for (carbonated) drinks, both alcoholic and nonalcoholic, food and oil as well as for pharmaceutical use and consumer goods [69].

Solvents dibutoxymethane ($\geq 99\%$) and ethyl benzoate ($> 99.9\%$) were obtained from CarlRoth Germany; p-cymene (95%) from Alfa Aesar; γ -valerolactone (BioRenewable, $\geq 99\%$, ReagentPlus[®]) from Sigma Aldrich. 1,2,4-Trichlorobenzene ($\geq 99\%$, ReagentPlus[®]) was ordered from Merck Germany.

4. Methods

All powder preparations were conducted using a similar experimental setup consisting of a high 250 mL glass beaker with a stirrer bar on a temperature regulated magnetic stirring plate. Every experiment was performed with a 5 wt% solution obtained by dissolving 2.5 g of polymer in 47.5 g of solvent. Precipitation was performed at 250 rpm in the same beaker without transfer of the solution. Prior to precipitation the stirred solutions were allowed to cool down while covered with aluminum foil to prevent contamination with potential nucleation seeds and to minimize loss of solvent from evaporation. Cooling was performed without active cooling only by ambient heat exchange. Separation of the produced powders was performed in a vacuum assisted filtration with a Whatman ashless filtration paper with $22 \mu\text{m}$ porosity in a 72 mm Büchner funnel.

4.1. Precipitation of Polypropylene from Dibutoxymethane with Ethanol (PP_I). Upon addition of polymer granules to preheated solvent the setup was held at dissolution temperature for 30 min to guarantee complete dissolution of granules. PP_R was dissolved at 130°C , whereas PP_H required a temperature of 145°C . The solution was then allowed to cool down to a temperature of 100°C before addition of an aqueous solution of 50 wt% ethanol. Up to this point the solutions remained clear, indicating the absence of primary crystals prior to the addition of the antisolvent. For the initial precipitation, 23.75 g of antisolvent were added for both the random copolymer and the homopolymer, resulting in a ratio of antisolvent to solvent of 0.5.

The resulting primary suspension was allowed to stir at the resulting temperature of 70°C for 10-min before further addition of ethanol to agglomerate primary particles and increase processability of the suspension and yield. For secondary precipitation 11.87 g of technical ethanol was added for PP_R and PP_H, resulting in an addition ratio of 0.75. The

resulting secondary suspension was then further stirred for 10 min at 60°C prior to vacuum assisted filtration.

4.2. Precipitation of Polypropylene from *p*-Cymene with Ethanol (PP₂). PP_R and PP_H were dissolved in *p*-cymene following the same procedure as PP₁ at temperatures of 120°C and 135°C for PP_R and PP_H, respectively. The obtained solution was then allowed to cool down to 100°C prior to the addition of antisolvent. For PP_R, 47.50 g of 50 wt% ethanol was added, for PP_H 47.50 g of 75 wt% ethanol. After stirring at 70°C for 10 min, further 23.75 g ethanol was added to the primary suspension of PP_R, for PP_H 35.60 g of technical ethanol. The secondary solution was allowed to stir for 10 min before particles were separated by vacuum assisted filtration.

4.3. Precipitation of Polypropylene from *p*-Cymene and 1-Hexanol (PP₃). PP_H was dissolved completely in a mixture of 44 wt% *p*-cymene and 56 wt% 1-hexanol at a temperature of 140°C within 70 min. The solution was then allowed to cool to 100°C at which the solution became cloudy, indicating the start of the precipitation. The solution was held for 10 min at 100°C while being stirred to allow formation of larger particles before separation by vacuum assisted filtration was performed.

4.4. Precipitation of Polypropylene from Dibutoxymethane and 1-Hexanol (PP₄). PP_H was dissolved completely in a mixture of 77 wt% dibutoxymethane and 23 wt% 1-hexanol at a temperature of 140°C within 70 min. The solution was then cooled to 100°C at which the solution turned cloudy, indicating the start of precipitation. The solution was then held for 10 min at 100°C while being stirred to allow formation of larger particles before separation by vacuum assisted filtration was performed.

4.5. Precipitation of Polyethylene Terephthalate from Ethyl Benzoate with 1-Hexanol (PET₁). PET was dissolved in ethyl benzoate at 200°C within 20 min. The solution was cooled to 150°C before 47.5 g of 1-hexanol, preheated to 145°C, was added to aid precipitation, resulting in an antisolvent to solvent ratio of 1:1. At this point precipitation had already begun, determined by the cloudiness of the solution. After 10 minutes of stirring at 150°C, the precipitate was separated from the solution by vacuum assisted filtration. The particles were then redispersed in 50% aqueous ethanol to a slurry before further deionized water was added to agglomerate the particles. The final particles were then again separated by filtration.

4.6. Precipitation of Polyethylene Terephthalate from γ -Valerolactone with 1-Hexanol (PET₂). PET was dissolved in γ -valerolactone at 190°C over the course of 11 min. The solution was then cooled while stirring to a temperature of 150°C, at which particle formation started. Precipitation was performed by adding 47.5 g of preheated (145°C) 1-hexanol, resulting in an antisolvent to solvent ratio of 1:1. After 10 min of stirring at 150°C, the particles were separated using vacuum assisted filtration.

4.7. Dry Substance Measurement. Dry substance was determined from a sample size of 1–2 g by thermogravimetric measurements at 160°C for 70 min using a Sartorius MA35 drying scale. Using the dry substance, the yield of the precipitation was calculated.

4.8. Scanning Electron Microscopy (SEM). SEM pictures were taken with a JEOL JSM-7200F scanning electron microscope (JEOL Germany GmbH) with 5-kV acceleration voltage and a secondary electron detector. Prior to imaging, the samples were sputtered for 30 s to deposit a gold layer on the particles.

4.9. Size Exclusion Chromatography (HFIP-SEC). Virgin PET dissolved in hexafluoroisopropanol (HFIP) was measured using size exclusion chromatography with a refractive index detector against poly(methyl metacrylat) (PMMA) references. HFIP was used as mobile phase and a PSS PFG Linear XL column with 7- μ m particle size (Polymer Standards Service (PSS), Germany) as stationary phase. Parameters for HFIP-SEC were 1 mL min⁻¹ for flow rate and 40°C for column temperature.

4.10. High -Temperature Size Exclusion Chromatography (HT-SEC): virgin polypropylene dissolved in 1,2,4-trichlorobenzene ($\geq 99\%$, ReagentPlus[®] grade, Merck Germany) at 160°C was measured by high-temperature size exclusion chromatography with infrared detection using a GPC-IR (PolymerChar, Spain) against polystyrene standards. 1,2,4-Trichlorobenzene was used as mobile phase with a guard column (Polefin Guard, 8 \times 50 mm, 10 μ m) (Polymer Standards service PSS, Germany) and three Polefin XL columns (Polymer Standards Service (PSS), Germany) containing modified styrene-divinylbenzene copolymer with 10 μ m particle size as stationary phase. Parameters for HT-SEC were 1 mL min⁻¹ for flow rate and 150°C for column temperature.

5. Results and Discussion

Using the abovementioned preparation, it was possible to produce polymer particles from the solution by means of precipitation. While macroscopically, the polymer appears to be precipitated as large particle agglomerates, those macroscopic particles consist of smaller, more regular primary particles.

5.1. Processing. Following the proposed processes I was able to produce powders both of PP and PET. Processes PP₁ and PP₂ proved to be unreliable in producing powders, whereas the proposed processes PP₃ and PP₄ on the other hand can provide a much smoother and reliable precipitation at similar conditions. This can be traced back to a combination of the low boiling point of the antisolvent used in PP₁ and PP₂, an aqueous diluted ethanol solution, and the temperature at which the antisolvent is added to the solution. Since the initial temperature for the precipitation is higher than the boiling point of the antisolvent, the solution boils instantaneously, often leading to formation of large scale formation of lumps. In PP₃ and PP₄ no additional antisolvent is added to precipitate the polymer, resulting in an easy processing.

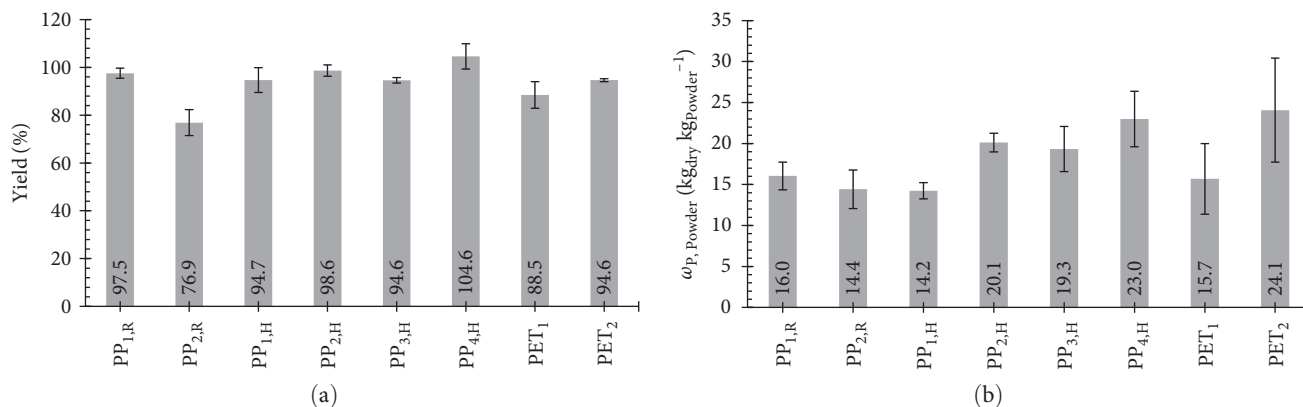


FIGURE 1: Polymer recovery: yield of all process routes (a) and dry substance of the recovered polymer powders (b).

PET₁ and PET₂ proved to be easily processable, both in dissolution and precipitation. Both processes require high temperatures to dissolve PET, resulting in high-thermal load on both the polymer and the solvent, visible in PP₄ by discoloration of the solvent γ -valerolactone.

Since precipitation is initiated by cooling of the solution to a temperature below the boiling point of the antisolvent prior to its addition, processing during precipitation proved to be uncomplicated.

5.2. Synthesis Yield. Yields were calculated according to Equation 3, comparing the recovered polymer as product of the recovered powder mass (m_{powder}) and its dry substance ($\omega_{p, \text{powder}}$) to the initial polymer mass. The measured dry content and resulting yields as means of three samples are shown in Figure 1.

$$Y = \frac{m_{\text{powder, dry}}}{m_{p,0}} = \frac{\omega_{p, \text{powder}} m_{\text{powder}}}{m_{p,0}} \quad (3)$$

I could achieve yields of 97% and 95% for the preparation using dibutoxymethane (PP₁), while the yields for the precipitation from p-cymene (PP₂) were calculated to be 77% and 99% for PP_R and PP_H, respectively. Precipitation of PET resulted in a recovery rate of 89% and 95% with ethyl benzoate (PET₁) and γ -valerolactone (PET₂), respectively.

While the recovery rates are high, some process routes (PP_{2,R}, PET₁) are far from full recovery of the material. This could be the result of several reasons including an incomplete precipitation from solution and material losses due to systematic errors during sample preparation. In order to prove (in) complete precipitation, further antisolvent was added to the filtrate and then was allowed to cool down to room temperature. This did not instantaneously result in further precipitate, indicating a mostly complete precipitation of the polymer. However, for both dibutoxymethane and p-cymene based routes with ethanol as antisolvent (PP₁, PP₂), a precipitate formation was observed after several days at room temperature. It was not possible to separate the formed precipitate from solution by filtration due to their size being smaller than the porosity of the available filter media and, therefore, not possible to include into the mass balance.

Incomplete precipitation is a very likely source of low recovery rates as shown above. Similarly to the PP processes some PET cannot be recovered even at significantly lower temperatures, determined by the yield being below 1. In order to circumvent this issue, process conditions should be adapted. Adaptations should aim for increasing the super saturation in the solution in order to enhance particle formation. Possible adaptations include a change in the amount of added precipitant or the addition of a secondary, stronger precipitant to the already precipitated solution.

Looking at the solution parameters, all solutions at the point of precipitation are far from the solubility limit defined by the Hansen parameters. Figure 2 shows the dependence of the RED of the solvent mixtures with respect to the 1-hexanol composition.

In general, further addition of 1-hexanol as primary precipitant appears to be a suitable process adaptation for the PET precipitations, even though the dissolved polymer began precipitating before addition of precipitant to the solution. Alternatively, the addition of a secondary precipitant after the initial precipitation appears more sensible. Possible candidates are low-molecular weight aliphatic alcohols such as ethanol, 1-propanol, or butanol, though other organic low molecular weight compounds may be suitable as well. A limitation to the choice of secondary precipitant is miscibility with the already established solvent mixture.

For PP precipitations the addition of a surplus of 1-hexanol during precipitation does appear as a sensible option as the calculated RED is not close to the calculated RED=1 line. But earlier experiments concluded that the addition of further 1-hexanol to the precipitation often results in increased agglomeration of the produced particles.

As already established with PP₁ and PP₂, the addition of a strong antisolvent to a cooled solvent mixture after filtration of the precipitated solution is not advantageous in increasing the yield in a suitable timeframe. As such, the addition of a different, secondary antisolvent to the precipitated solution may prove to be more suitable since crystallization can occur at already existing polymer surfaces.

Another parameter for increasing the super saturation is the precipitation temperature and the temperature between precipitation and filtration. The current precipitation temperatures of

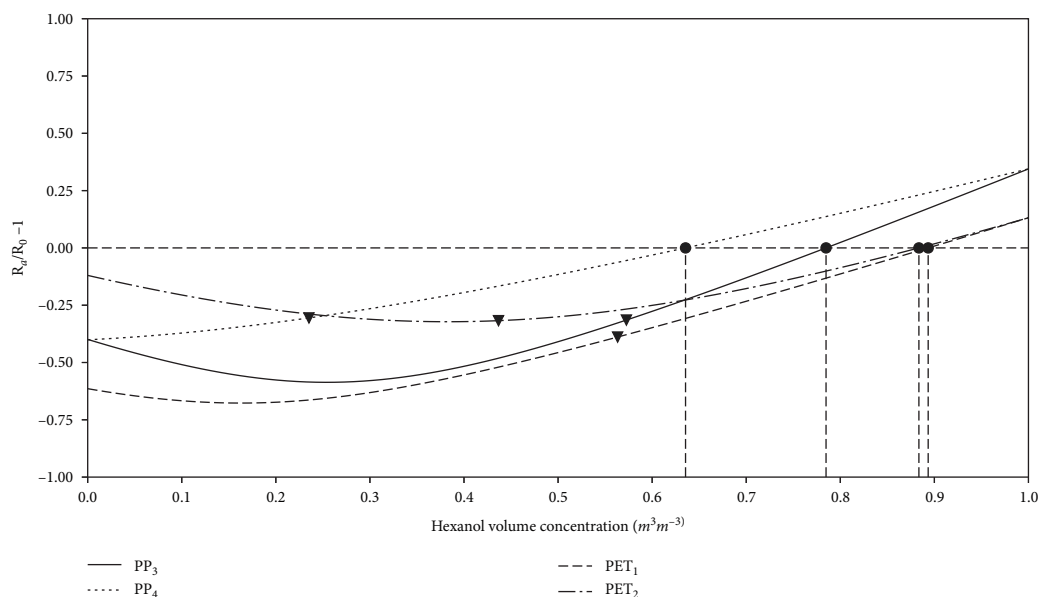


FIGURE 2: Solubility parameters of solvent mixtures at standard conditions in dependence of 1-hexanol concentration in solvent. Triangles depict the current state of the solution at the point of precipitation and circles the concentration where RED = 1. Calculated with HSP at standard conditions.

PP_{3|4} and PET_{1|2} were chosen as low as possible since at those temperatures precipitation begins, resulting in precipitation temperature being an unavailable process parameter. Both the temperature between precipitation and filtration and the respective time frame between each step on the other hand are available process parameters. A decreasing temperature ramp over a sufficiently long timeframe after the initial precipitation may prove to be a suitable measure for increasing super saturation in the remaining solution, resulting in enhanced particle formation and thus increasing the overall yield.

5.3. Particle Morphology. All particles produced by the described method possess a macroscopically irregular shape with a rough surface. Particle shapes vary in dependence on stirring rate and type of baffle used during precipitation. Particles produced with a comparably small baffle tend to possess a more pronounced elongated shape since the polymer is more likely to precipitate along the stream lines of the solution due to lower turbulence. Particles produced with a larger baffle typically possess a rounder shape.

Figure 3 depicts SEM pictures of the precipitated polymer powders. The produced macroscopic particles appear to consist of smaller particles and are therefore agglomerates. Polypropylene particles produced via the route of precipitation from p-cymene with ethanol appear to consist of two different types of primary particles. Particles of PP_H appear to consist of spherical shaped particles in a matrix of elongated, string like particles almost reminiscent of a web while PP_R particles possess a less pronounced granular structure. Yet PP_R particles possess a very rough shape as well;

including apparent steps and particle borders, further indicating an agglomeration of the primary particles.

PP_H particles precipitated from dibutoxymethane with ethanol possess a plate-like structure, resulting in a macroscopically open structure in the agglomerates. Similar shapes can be seen in the PP_R particles from the dibutoxymethane-ethanol precipitation, though the plate-like structure is considerably less pronounced. Yet, on a macroscopic level the resulting agglomerates possess a similar open appearance compared to the aforementioned PP_H particles. Compared to the particles produced in PP₂, the PP_H particles produced using the dibutoxymethane-hexanol precipitation possess less plate-like structure but instead appear more three dimensional, yet irregular shapes remain. This variety of shapes of the primary particles results in a denser appearance of the agglomerates. PP_H particles produced via the p-cymene hexanol precipitation possess less of a single particle structure and instead appear to consist of larger agglomerate. On the surface of the agglomerates single particles are visible; indicating that the larger agglomerate may still consist of smaller primary particles beyond the apparent smooth surface.

Both PET particle types possess a granular structure resulting from agglomeration of the primary particles. Particles precipitated from GVL appear considerably larger with spherical primary particles discernible already at low magnifications. Particulates precipitated from ethyl benzoate show an irregular shape with agglomerates consisting of very small primary particles possessing rough edges and plate-like appearance.

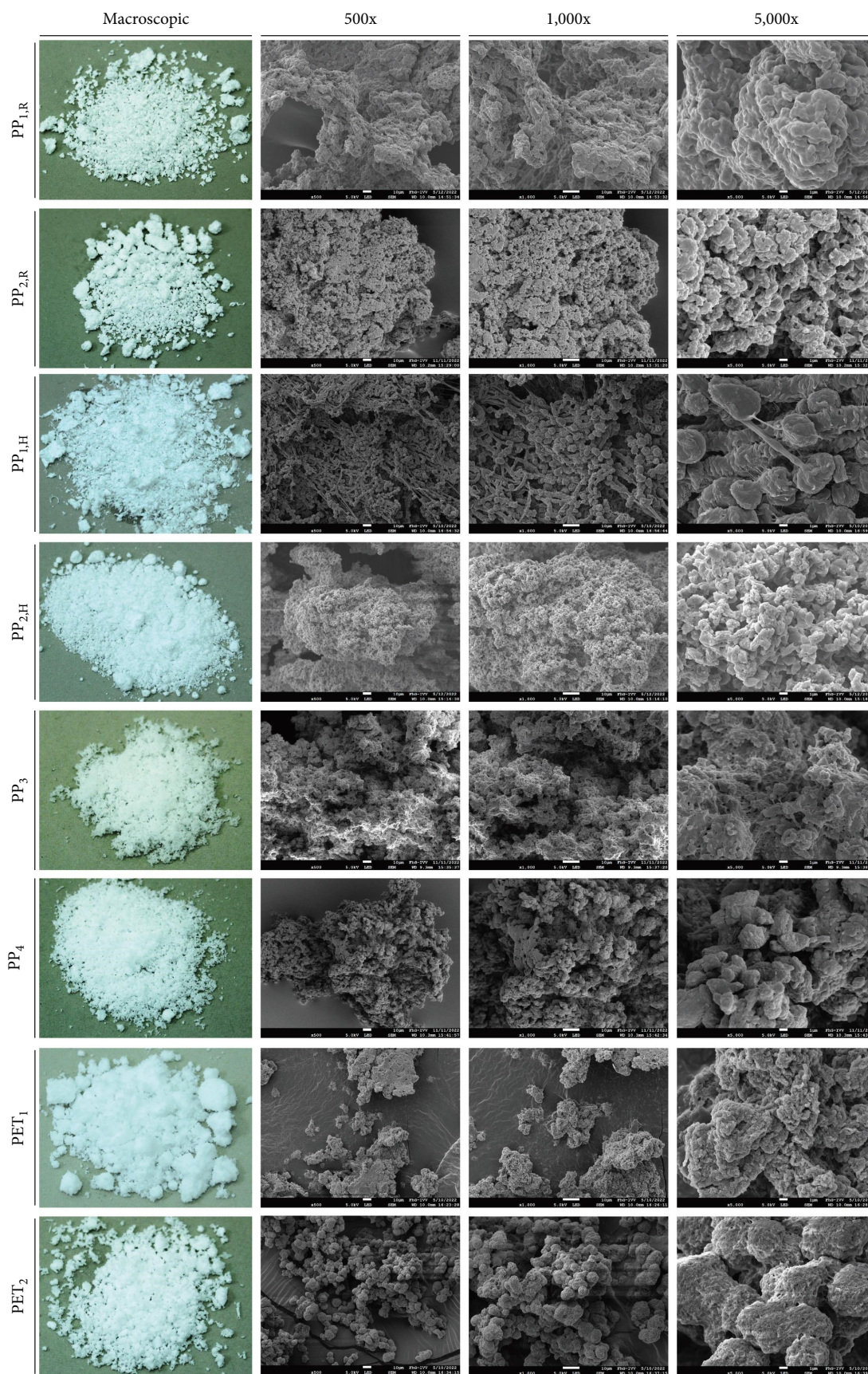


FIGURE 3: SEM photographs of the produced powders both macroscopically and microscopically. From left to right: macroscopic appearance, magnifications of 500, 1,000, and 5,000.

6. Conclusion

The proposed dissolution and precipitation technologies offer new possibilities for easy and reliable polymer powder preparation, especially in cases where comminution of polymer material is unfavorable. The proposed technologies are based on the dissolution of polypropylene and polyethylene terephthalate in sustainable green solvents and in two cases further precipitation using short chain aliphatic alcohols of which both are commodity chemicals. Four of the proposed techniques are considered temperature induced phase separation due to precipitation without addition of antisolvent. Due to the low-technological requirements the technologies are promising especially in fields such as solvent based recycling where cost-effectiveness is a decisive factor.

The produced powders from all proposed processes consist of agglomerates of the primary particles in the wet state. It is yet to be investigated how the powders perform once the residual solvent content is reduced, which will be investigated in the future projects. With powder preparation routes established, desolventation of produced polymer powders is yet to be investigated. This will be further investigated in a following publication. Possible desolventation routes include but are not limited to convective drying in an inert atmosphere or air as well as contact drying. Desolventation will be required in order to receive suitable mechanical properties and to enable the use of the produced polymers for either powder-based processing or in case of recycling for the substitution of virgin material.

Symbols

V_m :	Molar volume, $\text{m}^3 \text{mol}^{-1}$
T:	Temperature, K
δ^2 :	Cohesive energy density, MPa
R_a :	Distance in Hansen Space, $\text{MPa}^{1/2}$
R_0 :	Empiric interaction radius, $\text{MPa}^{1/2}$
R:	Universal gas constant, $\text{kJ kg}^{-1} \text{K}^{-1}$
RED:	Relative energy difference
Y:	Yield
m_{Powder} :	Mass powder, kg
m_p :	Mass polymer, kg
m_s :	Mass solvent, kg
m_{AS} :	Mass antisolvent, kg
ω_p :	Solid content
PP:	Polypropylene
PET:	Polyethylene terephthalate.

Data Availability

The yield and solid content data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The study was funded in completion by Fraunhofer IVV as part of the author's dissertation and open access funding enabled and organized by Projekt Deal.

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