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Direct melt extrusion of polyhydroxyalkanoate solvent-rich gels after polymer extraction and melt processing with integrated solvent recovery

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ABSTRACT

Melt extrusion was evaluated for polyhydroxyalkanoate (PHA)-solvent gels. Gels in 2-butanol were produced with polyhydroxybutyrate (PHB) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) co-polymer blends. Gels were formed by extracting PHA from dried biomass, or by dissolving it in 2-butanol, at up to 135 °C followed by cooling the solutions to room temperature. Excess solvent was pressed from the gel to make a compact gel cake. Cakes with less than 95 wt% 2-butanol were grated into a granulate that could then be consistently fed and melt-processed in a twin-screw extruder. Gels showed significantly reduced PHA melt temperatures. For example, PHB melting temperature was reduced from 180 °C (neat polymer) to 115 °C in a 60 wt% 2-butanol gel. The PHA molecular weight decomposition rates were independent of 2-butanol presence, and they were reduced 6-fold from 180 to 160 °C. Gel extrusion accomplishes polymer drying, solvent recovery, and melt processing altogether. More than 98 wt% solvent removal with 77 wt% solvent recovery was achieved using a vacuum pump and condenser attached to one extruder vent port. Extrudate quality was consistent, but it was influenced by the selected die temperature and barrel conditions that controlled gel residual solvent content at the die. PHA gel extrusion was characterized, and experiments are reported herein. Process efficiencies (solvent recovery and specific mechanical energy), and extrudate qualities were assessed. Insights were gained with thermogravimetry, differential scanning calorimetry, rheology and microscopy. The outcomes suggest benefits from directly combining solvent-based PHA recovery from biomass with gel-based PHA formulation and melt-processing into bioplastic articles.

1. Introduction

Polyhydroxyalkanoates (PHA) are a class of semi-crystalline biopolyesters that are accumulated as intracellular granules by many different bacterial species (Pagliano et al., 2021). Technical feasibility to produce PHAs advances steadily (Koller, 2020) and markets are evolving along with societal and regulatory demands for alternatives to fossil oil-based plastics (Ahmadi et al., 2023). Many applications exist for PHAs, especially for those where biodegradability and the current levels of capacity for PHA supply make sense (Bauchmüller et al., 2021). Needed increase in the generic supply of PHAs will demand robust methods for recovery and ways for efficient economically viable processing of purified PHA into products from a wide range of possible sources of PHA-rich biomass (Estevez-Alonso et al., 2021).

The technical feasibility to produce PHA, starting from regional waste organic residuals and even from municipal sludge sources, has been repeatedly demonstrated in the research literature (Estevez-Alonso et al., 2021; Valentino et al., 2021). However, PHA supply chains still face uphill challenges to establish and to reach the market notwithstanding this demonstrated opportunity for production volumes using regionally available organic waste as renewable substrates. Challenges are due to cost competitiveness with respect to the conventional fossil derived alternatives, uncertainties with production scale polymer quality and property specifications, and no widely established industrial scale supply chains that can broaden market developments. Relatively speaking, current traditional plastic supply and recycling chains are efficient and entrenched in society. This status of entrenchment also needs to come to PHAs, as well as to other renewable biobased

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engineering materials.

PHA production methods using wastes as feedstocks and open mixed microbial cultures (MMCs) are advancing (Estevez-Alonso et al., 2021; Pei et al., 2022), but bottlenecks persist in the steps of polymer recovery, purification, and processing. Non-chlorinated, so-called PHA-poor, solvents are well known for PHA extraction (Kurian and Das, 2021; Liddell, 1996; Vermeer et al., 2022). Methods for PHA extraction from MMCs with 2-butanol for commercial grade polymers have been demonstrated (Pei et al., 2025; Werker et al., 2020, 2023). Solvent recovery was found to be a significant component of cost for both economic (CAPEX and/or OPEX) as well as environmental performances (Bengtsson et al., 2017). Approximately 5000 ton-PHA/yr is anticipated to be a lower limit in economies of scale necessary for economic viability with the green solvent recovery approach (Bengtsson et al., 2017). The distributed capacity for producing PHA-rich biomass using organic residuals and wastes as feedstocks exists in scales from 100s to 1000s of tons of PHA contained in dried PHA-rich biomass per location and year. The PHA content of PHA-rich biomass is expected to be typically between 35 and 70 wt% PHA. Dried PHA-rich biomass is stable over years (Werker et al., 2020) and can be a tradable, transportable, value-added raw material. Thus, distributed PHA-rich biomass production sites may support well-placed economically viable centralized recovery facilities. Efficient ways to process PHAs at such centralized facilities, starting from blended masterbatches of dried PHA-rich biomass, and all the way to formulated bioplastics and/or final articles, need to be developed. In this context of centralized PHA recovery, PHAs can be extracted from dried biomass using a solvent like 2-butanol (Werker et al., 2023). PHA extraction solutions are formed in 2-butanol at temperatures up to 140 °C. Upon cooling to room temperature, the polymer-solvent blend becomes a semi-solid gel. Since solvent recovery is important to the technoeconomic performance of the extraction process, a goal is to make this step more effective and, if possible, also contribute to value generation.

In this research we challenged the need of solvent recovery just for drying the purified PHAs after extraction and before melt processing. Direct processing of extracted PHA-gels in steps of formulation and melt processing into plastic articles, with integrally combined steps of extraction solvent recovery, has to our knowledge not been previously explored. Skipping energy intensive steps of drying for just solvent removal avoids also air drying the polymers to remove adsorbed moisture before melt processing (Gigante et al., 2020). The working hypothesis was that gel-processing directly through to melt processing could be a way to improve the overall recovery and production process economic efficiencies while enabling effective methods for polymer and production quality control. Since an evaluation of the technical feasibility for PHA gel-processing was not found in the research literature, this became the focus of the present investigation.

Polymers are traditionally formulated starting from dried materials into plastics by blending the polymers with additives at sufficiently high temperatures to melt the polymer and to achieve a homogeneously blended mixture (Molenveld et al., 2022). Temperatures are maintained sufficiently high to ensure consistent polymer melt flowability while blending, and with extrusion through a die to form a solidified article after cooling (Gigante et al., 2020). Formulation is often essential to obtain well-defined and reproducible bioplastic property specifications. Processing must also accommodate the fact that the polymer degrades to some extent during the melt processing (Montano-Herrera et al., 2014). Decomposition rates may be influenced by chemical reactions promoted due to the high temperature blending conditions, shear stresses, and added formulation compounds and/or presence of impurities (Palmeiro-Sánchez et al., 2016).

Research has addressed challenges involved with efficient processing of PHA, PHA based blends, and/or PHA composite materials (Bugnicourt et al., 2014; Chan et al., 2019; Collet et al., 2022; Gogolewski et al., 1993; Krishnaswamy RK et al., 2009; Montano-Herrera et al., 2014; Pachekoski et al., 2013; Puppi et al., 2019; Vandi et al.,

2019; Zhang et al., 2004). All these works begin with the PHA supplied as a dried starting material. However, solid gels can instead be the starting purified crude material to use for downstream “cold” formulation and processing directly after PHA extraction from a biomass using PHA-poor solvents like 2-butanol. The present study objective was to evaluate the feasibility of this approach for both the PHA processing and the solvent recovery.

A comprehensive set of gel extrusion and characterization experiments were performed on poly (3-hydroxybutyrate) (PHB) and PHBV (poly (3-hydroxybutyrate-co-3-hydroxyvalerate)) gels formed with 2-butanol. 2-Butanol was used as the example solvent for the study due to an infrastructure that was already established with considerations of the solvent specific risks and safety management. The principles for the method developments were determined from gel samples generated at 100 µL, 10 mL and 10 L process scales. Practical experiments were conducted using twin-screw melt extrusion with mass balances and monitoring of process conditions for extruding a filament. Samples were characterized with measurements including thermal gravimetric analysis, intrinsic viscosity (solution rheology), melt rheology, differential scanning calorimetry, pyrolysis gas-chromatography with mass spectroscopy, and microscopy. Strategies for achieving consistent quality and morphology in the extruded PHA filaments were developed and are discussed herein. The study goal was to establish technical feasibility of linking PHA extraction from biomass to solvent recovery during concurrent gel and melt processing for making bioplastic articles. It was found that intermediate drying of the polymer should not be necessary after PHA extraction for a commercial endpoint of producing valued melt processed articles. Consideration was made of extrusion factors including extruder barrel residence time, temperature zones, and feeding rates to yield bioplastic extrudates with consistent properties.

2. Materials and methods

The starting point for evaluating PHA-gel extrusion was a granulate of gel comprising a PHA and 2-butanol. The gel granulate was obtained after forming solutions of the PHAs in 2-butanol. Established methods of PHA extraction were applied in this study with 2-butanol to form such solutions. These methods have been previously described in detail with results of process yields and polymer quality (Bengtsson et al., 2017; Pei et al., 2025; Werker et al., 2020). In the present study, gel transport in the extruder feeder and barrel were characterized alongside solvent removal rates as a function of temperature and screw speeds. Melting temperatures of PHA in the gel were studied as a function of the solvent content. The influence of the solvent on the polymer decomposition rate was tested. Then extrusion experiments were undertaken to evaluate the operating conditions and the outcomes for the extrudate quality. Periods of extended steady state extrusion operations were performed for making overall mass balances for the process including the solvent recovery.

2.1. PHA sources and raw materials

Commercial grade polyhydroxybutyrate (PHB) powder (Biomer, Germany) was used as a reference PHA. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, was sourced from an in-house inventory of dried PHBV-rich biomass. The PHBV-rich biomass was produced in campaigns conducted at pilot (Pei et al., 2022) and demonstration (Pei et al., 2025) scales during two EU projects (SCALIBUR - ID: 817788 and Agro2Circular - ID: 101036838). Production campaigns used municipal waste activated sludge that accumulated PHBV in fed-batch bioreactors using volatile fatty acid rich feedstocks and methods as previously reported (Pei et al., 2022). In those PHBV production campaigns, the post accumulation bioprocess PHA-rich biomass suspended solids were settled by gravity. The concentrated mixed liquor suspended solids (MLSS) were then acidified (pH 2–2.5) by sulphuric acid addition to induce a maximal possible polymer thermal decomposition temperature as previously described (Werker et al., 2013). MLSS were then

dewatered and oven dried. Dried biomass solids were milled to form a PHBV-rich dried granulate (Pei et al., 2025). Dried solids with nominally 3 % residual moisture content were extracted with 2-butanol as described below to produce PHBV-gel for the experiments reported herein. PHA qualities were assessed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), solution rheology, and pyrolysis with gas chromatography combined with mass spectroscopy (PyGCMS), as previously reported in detail (Werker et al., 2023).

Low density polyethylene powder (LDPE, 500- μ m average particle size, ThermoFischer Scientific Chemicals) was used for the extruder characterization. Solvents, dimethyl carbonate (99 % pure, ThermoFischer Scientific Chemicals) and 2-butanol (EMSURE®, VWR chemicals) were used as received.

2.2. Production of PHA-solvent gel granulates

PHA was extracted at up to 50 g-PHA/L in 2-butanol from dried PHA-rich biomass granulate following previously reported methods (Werker et al., 2020). Methods included heating to above and below a thermo-reversible gelation temperature for the polymer-solvent solutions. Gelation temperatures were determined by differential scanning calorimetry as described in previous work (Werker et al., 2023). A 3 step workflow with (1) extraction, (2) gel processing, and (3) gel extrusion, was applied (Fig. 1) to facilitate this study as follows:

1. Dried PHA-rich biomass granulate extraction at pilot scale (10 L vessel) in 2-butanol at up to 135 °C,
2. Separation of spent biomass particulate by filtration above the solution gelation temperature,
3. Formation of a polymer-solvent gel by cooling the solution to room temperature,
4. Exuding excess solvent to form a cake by mechanical compression, with or without solvent rinsing,
5. Shredding the cake mechanically on a grater to produce a gel granulate,
6. Controlled vacuum drying of the gel to reach lower solvent contents for experiments.

For the purposes of this investigation, a PHBV co-polymer blend with average 34 % wt. (31 mol. %) 3HV was extracted according to the methods of Fig. 1 from the PHBV-rich biomass. The source biomass comprised 30 % g-PHA/g-TS (total dried solids) and 37 g-PHA/g-VS (volatile solids). The extracted 2-butanol-PHBV solution becomes a gel upon cooling to room temperature. The gel was pressed into a cake to

remove excess solvent containing soluble co-extracted residues from the biomass. Pressing was performed at up to 2.3 bar in a custom dead-end press with a 129 mm \varnothing \times 50 μ m gap wedgewire filter (Trislot, Belgium) using a double action pneumatic piston (IMI Norgren, Germany). This cake was mechanically grated with a common household metal cheese grater to produce a gel granulate. The dried solids in this gel granulate was 98.4 % pure PHBV. A more crystalline commercially available PHB (Biomer, Germany) was also used. The higher crystallinity makes PHB generally harder to dissolve in solvents like 2-butanol. It requires higher dissolution temperatures (Werker et al., 2023). PHB gel-granulate was generated by means of the same workflow wherein the PHB powder was introduced into the same 10 L extraction reactor instead of a PHA-rich biomass. In all cases, a gel-granulate with between 85 and 90 wt% solvent content was produced after steps of extraction and mechanically pressing the freshly formed gel to remove excess solvent.

2.3. PHA-gel granulate extrusion

Melt extrusion of solvent-rich PHA gel granulate was carried out according to the workflow of Fig. 1. A twin screw horizontal extruder (10 mm 40D, Rondol Industries SAS, Nancy France) was equipped with eight heating zones. The zone 1 temperature setpoint was 25 °C and it was cooled by constant tap water flow. Zones 2 to 8 and the die were set to selected temperatures as outlined below. The co-rotating, inter-meshing, self-wiping screws were contiguous (constant pitch 5.6 mm), without mixing elements, and could be operated at up to 300 rpm. The extrusion process line (Fig. 2) included a feeder (Rondol single screw pellet or twin screw powder feeder), one open vent, a strand die, a water bath, a filament puller, and a Rondol pelletiser. Evaporating solvent vapours were drawn out from one opened vent on the extruder barrel by a diaphragm vacuum pump (250–500 mmHg applied, KNF LABOPORT® N 820 F T.18). The second last of the four available vent positions was used. Solvent vapours were drawn through the port to a standard Rondol aluminium cup condenser. Solvent condensate was drained by gravity from the cup to a collection flask.

Soft gel granulate particles of nominally 0.5–3 mm diameter were fed into the extruder barrel, and the filament extrudate was quenched by pulling it through a water bath maintained nominally at 25 °C with continuous tap water flow. The filament puller (20 \varnothing mm polypropylene spring compression loaded counter-rotating drums) draw rate was set via pulse-width modulation control. Extrudate dimensional consistency and surface finish qualities were analysed by optical microscope (LEICA MZ 95 with 9.5:1 zoom ratio and magnifications up to 480x with LEI-CADFC320, with illuminated base).

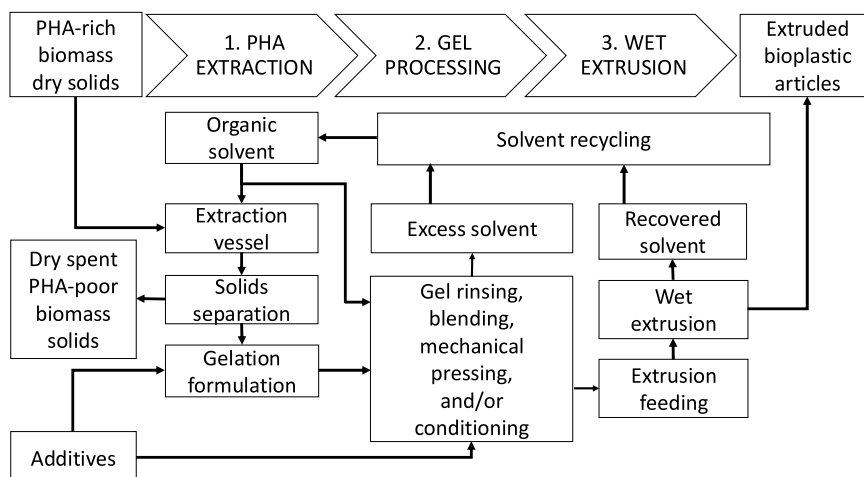


Fig. 1. The applied 3 step PHA workflow including steps of extraction, gel processing and wet extrusion.

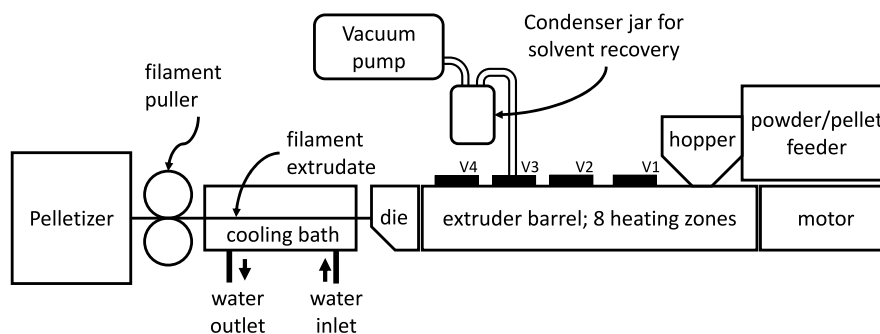


Fig. 2. The extrusion process configuration shown with ancillary unit steps, where V1, V2, V3, and V4 were the available vent port positions on the barrel downstream of the hopper. Only V3 was open and connected to the vacuum pump with condenser.

2.4. PHA thermal decomposition rate experiments

PHA decomposition rates, with and without the presence of 65 wt% 2-butanol, were evaluated at test tube scale. Parallel test tubes loaded with 100 mg of dried PHA, with or without added solvent, were incubated isothermally for selected times. Samples were incubated for up to 50 min in the sealed glass test tubes (Hach™ LZP065) at 160 and 180 °C (Grant-Bio QBH2). After heat treatment, samples were dried in a vacuum oven (48 h at 40 °C with N₂ atmosphere). Dried heat treated samples were dissolved in dimethyl carbonate for intrinsic viscosity $[\eta]$ measurements as previously described (Werker et al., 2023). Molecular weight loss as a function of temperature and incubation time (t) was compared by a decomposition number (N_d) and an average decomposition rate (r_d) was determined as follows:

$$N_d(t) = \frac{[\eta](t=0)}{[\eta](t)} - 1 \quad (1)$$

$$r_d = \frac{N_d(t)}{t} \quad (2)$$

2.5. Polymer and gel characterization

2.5.1. Thermogravimetric analysis and pyrolysis GCMS

Thermogravimetric analysis (TGA) was performed (Mettler Toledo, TGA 2) to estimate sample PHA content, volatile and inorganic fractions, and PHA thermal stability as described previously (Chan et al., 2017; Werker et al., 2023). Thermal stability (T_d) is reported for the maximum rate of PHA decomposition with a 10 °C/min heating rate. Approximately 8 mg dried samples were used to determine PHA content of dried samples, and solvent content was assessed on gel samples of 25–30 mg. Gravimetric analyses were also conducted to assess solvent loss rates as a function of temperature with the help of a drying scale (Satorius MA37). Gel granulate samples were brought to constant weight defined by less than 0.1 % weight loss over 1 min for the temperature range from 45 to 160 °C. In a similar way, TGA was also used for isothermal incubations to a constant dry weight. For TGA determination of the gel solvent content, a representative gel sub-sample mass was quickly placed into a tare weighed crucible and the measurement was started directly without any delay to mitigate the risk for unrecorded solvent evaporation.

A combined TGA assessment of solvent content and dried polymer purity/quality was performed for fresh gel samples. A fresh gel mass of 25–30 mg was directly inserted into a tare weighed crucible and then the TGA, which was preheated to 80 °C with a nitrogen flow of 50 mL/min.

The TGA analysis was initiated without delay. The sample was heated (10 °C/min) to 130 °C, and held for 90 min. Weight loss from initial mass to the end of the isothermal stage was interpreted as being due to 2-butanol evaporation. Following isothermal drying, the sample was heated at 10 °C/min to 550 °C, at which point the atmosphere was changed to air (50 mL/min), and the sample was held at 550 °C for 30 min. This second heating ramp and the bake out at 550 °C was used to assess for total volatile and inorganic solid fractions, as well as polymer purity and thermal stability, as previously described (Chan et al., 2017).

Polymer monomer composition was estimated by methods of Pyrolysis Gas Chromatography with Mass Spectrometry (Py-GCMS) based on similar published methods (Gonzalez et al., 2005; Khang et al., 2021; Torri et al., 2014) that were adapted for the available analytical equipment as previously described (Werker et al., 2023).

2.5.2. Differential scanning calorimetry (DSC)

Polymer melt and crystallization properties in dry and gel forms were assessed by DSC (DSC 3+, Mettler-Toledo) as previously described (Chan et al., 2017; Werker et al., 2023). For thermoreversible gelation analysis, nominally 30 mg of fresh gel grab samples were placed into 100 µL tare weighed crucibles (Mettler-Toledo nr. 26929) that were sealed directly. DSC analysis for gels was carried out with an initial 5-min isothermal stage at 10 °C followed by heating and cooling cycles at 10 °C/min (50 mL/min nitrogen purge gas flow) to and from a maximum temperature and back to 10 °C. The requisite maximum temperature was between 145 and 195 °C. It was adjusted depending on gel solvent content (less solvent content required a higher maximum temperature). Estimated enthalpies of integrated melt and crystallization (gelation) peaks, during heating and cooling, were referenced to the mass of PHA in the sample.

2.5.3. Melt and solution rheology analyses

PHA solution and melt rheological properties were assessed (Anton Paar MCR 102). Solution rheology (Anton Paar CC17) was performed on 5 mL aliquots of PHA dissolved in dimethyl carbonate (nominally 15 mg PHA/mL DMC). Solution viscosity was measured at 60 °C with 75 s⁻¹ shear rate from which the intrinsic viscosity was estimated as previously described (Werker et al., 2023). Changes in the PHA weight average molecular mass were therefore followed with respect to the estimated intrinsic viscosity $[\eta]$ (dL/g).

Melt rheology analysis was performed on dried PHA samples using a parallel plate configuration (Anton Paar PP25) with the same rheometer. Weighed aliquots of dried powder or flakes of PHA of nominally

0.3 g were used wherein the mass was pre-formed into standard 25 Ø mm coupons by means of a stainless-steel mould. The standard coupons were formed by pressing at room temperature with five metric tons pressure for 5 min. Polymer in pellet form (nominally 3 Ø mm x 3 mm) was similarly evaluated with 0.3 g weighed sample mass. Pellets could not be cold pressed into coupons and were melt-pressed directly in the rheometer when the sample mass was first compressed before a measurement. The polymer mass was first compressed in the rheometer after heating to 195 °C with a 25 N normal force for 2 min. Melt rheology was performed in three measurement stages with 10 N compressive force and 2 % maximum strain: 1) isothermal shear at 195 °C and 1 Hz for 2.25 min, 2) 0.1–100 Hz frequency sweep at 195 °C over 10 min, and 3) quenching from 195 to 15 °C at 1 Hz over 12.5 min. Viscoelastic properties were logged with a 7.5 s time averaged signal.

3. Results

3.1. Gel solvent content for feeding and mass transport control for extrusion

Initial findings underscored an impact of gel solvent content on gel properties and processing methods. The steps of pilot scale gel processing during the PHA recovery process (Fig. 1) could influence the final gel granulate morphology as shown in Fig. 3. A freshly prepared PHA gel typically contained in the order of 95 wt% 2-butanol given an extraction filtrate discharge of about 50 gPHA/L. The gel was subjected to mechanical compression to exude solvent by applying up to 2.3 bar pressure and this led to a compact cake with about 90 wt% solvent. The compact cake that was processed by mechanical grating resulted in a gel granulate of between 0.8 and 2 mm particle size. Such a granulate morphology was found to be readily achievable with gels containing less than or equal to about 85 wt % 2-butanol. Solvent content after gel pressing was lowered as necessary for the study objectives by a controlled time for solvent evaporation in a vacuum oven.

Gel solvent content was reduced to less than about 90 wt% in order to ensure consistent flow without agglomeration of the soft particulate matter during feeding to the extruder. At higher solvent content, the gel was found to agglomerate into a paste-like morphology. This morphology was not possible to feed consistently into the extruder with either of the two available standard Rondol feeders. This standard setup required feeding into a hopper that gave steady outflow into the extruder barrel naturally flowing by gravity. Alternate, better adapted feeding and extruder delivery methods, even for gel pastes, are anticipated to be possible and remain part of ongoing investigation.

The feeders were calibrated as a function of screw speed (Supplementary Information – S1). The feeding rate for the gel could be consistently controlled, but the feeder transport was not a linear function in mass transport rates with increased screw speeds (Fig. S1):

$$\dot{m}_f = a_1 v_f + a_2 v_f^2 \quad (3)$$

where a_1 and a_2 are empirical constants, \dot{m}_f is the feeder output rate of gel (g/h), and v_f is the feeder screw speed (rpm). From linear regression, a_1 and a_2 were found to be 1.9 ± 0.3 and -0.004 ± 0.002 , respectively. In contrast, the feeder gave an output directly proportional to screw speed for a 500 µm LDPE powder with a_1 and a_2 equal to 4.0 ± 0.1 and 0, respectively. Thus, the available feeders were also not specifically well-adapted to the delivery of soft particles like gel granulate. Compression of the soft gel particles at higher screw rates may explain the non-linear response. Conditions for consistent and stable flow of a gel granulate into the extruder were nevertheless predictable for the purposes of the present investigation.

A maximum allowable feeder operating screw rate, for this particular system, could be established and hopper granulate mass hold up could be avoided with respect to extruder screw rate (Supplementary Information - SI2). The allowable maximum feeder screw rate to avoid hold up is defined by the extruder barrel screw rate (Fig. S2):

$$v_f \leq b_1 v_b \quad (4)$$

where b_1 is an empirical constant and v_b is the barrel screw rate (rpm). b_1 was estimated to be 1.06 ± 0.01 based on feeding LDPE powder. Given that the gel mass flow is always less than the LDPE powder for the same v_f , equation (4) conditions would be conservative for settings of feed and barrel screw rate combinations for the gel extrusion experiments.

3.2. Extruder barrel residence time control and solvent evaporation

Residence time (t_b) for gel transport in the extruder from the barrel inlet to the die was characterized for this system. t_b can influence properties for polymer extrusion in general. For the present work, it also served needs for solvent evaporation and its recovery. Predictable gel solvent content at the die was important to relate to die temperature selection for stable extrusion and extrudate quality. t_b is inversely proportional to barrel screw speed (v_b) and screw pitch (P), and it is directly proportional to barrel length (L) with a proportionality constant. All constants together define a composite geometry constant for the system.

Gel feeding and transport in the barrel were studied without the die attached. With the die removed from the barrel, t_b was measured in practical mass balance experiments (Fig. 4) with v_b ranging from 10 to 300 rpm. Transport rates of LDPE pellets (2 mm particle size), LDPE powder (nominally 500 µm average particle size), and a PHB gel-granulate (800 µm average particle size) were measured and the data were fit by non-linear least squares regression to the generalized equation, of all the constants together, for the system:

$$t_b = \frac{c_1}{v_b} + c_2 \quad (5)$$

where c_1 and c_2 are barrel mass transport constants for the specific setup. The gel granulate was transported in the barrel more like the dry LDPE powder, for which c_1 and c_2 were estimated to be 3921 ± 115 rpm

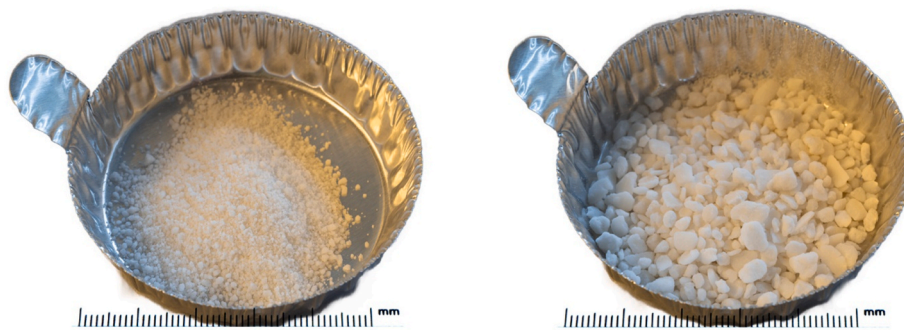


Fig. 3. Distinct gel granulates produced from the same PHB source. A PHB solution was formed in 2-butanol and then solidified under quiescent conditions (≈ 95 wt % solvent), the gel was mechanically pressed to a compact cake (≈ 90 wt% solvent), and granulated with a grater.

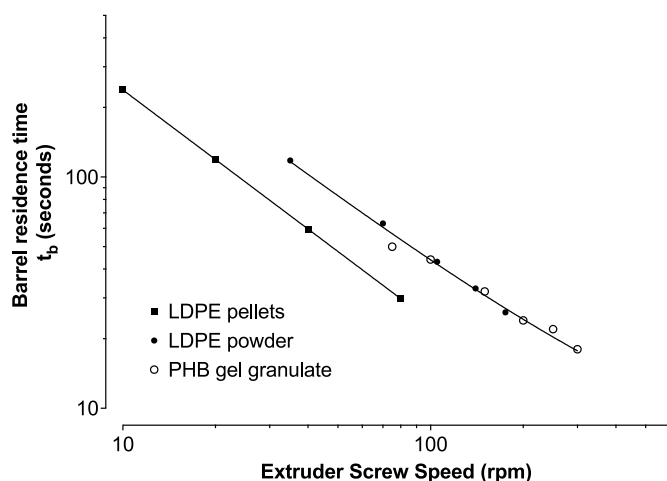


Fig. 4. Barrel residence time (t_b) of LDPE pellets, LDPE powder and PHB gel granulate as a function of extruder screw speed and fit to Equation (5).

s and 4.7 ± 1.4 s, respectively. The pellet t_b is significantly shorter for the same v_b and predictable with c_1 and c_2 equal to 2383 rpm s and 0 s, respectively. c_2 was small but significant for the granulate and may represent a dead time in the inlet zone.

Fig. 5a shows convective drying rates that were estimated for a PHA gel starting with 80 wt% 2-butanol (4 g-solvent/g-polymer). The drying rate is driven by the bulk gel temperature difference with respect to the surrounding temperature, and the bulk gel temperature is a function of the heat transfer from the surrounding environment together with the effects of evaporative cooling (Incropera and De Witt, 1981). It is not constant in time and slows down from a maximum rate (Fig. 5a and 6a) as the material heats up and shrinks with reduced solvent content before reaching an endpoint dryness that is a function of the applied temperature (Fig. 5b). Average convective drying rates as a function of bulk air temperature approached a maximum by about 140 °C. This maximum is presumably due to the bulk gel temperatures approaching the solvent boiling point, causing limiting conditions. In the convective gel drying experiments, granulate was found to become increasingly more compact, sintered, and melted with increased applied drying temperatures (Supplementary information - SI3).

Average conductive drying rates in the extruder are a function of the barrel temperature and barrel screw speed. The higher barrel screw speed means less time for drying, but drying times only ranged from about 30 s to 1 min for v_b from 300 down to 150 rpm. PHA gel granulate (67 wt% 2-butanol or 2.03 g-solvent/g-polymer) was fed at 100 g/h at different extruder screw speeds (150, 200, 250 and 300 rpm) to establish mass balance results with a range of t_b and as a function of isothermal barrel temperatures (Zones 2 to 8 set at 70, 90, 110 or 140 °C). Solvent contents of barrel output samples were measured and the average evaporation rate was corrected for the estimated drying time in the 7

heated zones (Equation (5)). Drying rates were significantly higher in the extruder due to conductive heat transfer as expected. At 140 °C the gel became effectively dried (8.2 ± 3.6 mg-solvent/g-polymer) within the barrel retention time, and so the estimated solvent removal rate is not representative in this case. Barrel temperature determined an average drying rate while screw speed (v_b) established t_b and resulted in a relatively minor influence on the material dryness for the gel mass entering the die (Fig. 6b). From such a system characterization, for a given input gel solvent content, the solvent content at the die can be readily controlled to have solvent contents from 10 to 1 wt%.

3.3. Gel solvent content and PHA melting temperature

Gel samples exiting the extruder barrel without the die attached were collected and evaluated for solvent content. The respective sample polymer melt characteristics were assessed by DSC using sealed crucibles (Figs. 7 and 8). The gel solvent content significantly lowers the melting temperature (Fig. 8b). An increase from 5 to 86 wt% 2-butanol corresponded to a melt temperature decrease from 170 to 114 °C, as may be expected from the thermodynamics of polymer solutions (Billmeyer and Wiley, 1984). Solvent content also influenced crystallization (gelation) temperatures. Thus, solvent content enables polymer-gel melting at lower temperatures and a delay of crystallization upon cooling (Werker et al., 2023). Melting temperatures of PHAs can be further influenced by the polymer (or polymer blend) crystallinity, blend composition, and/or molecular weight distribution. For co-polymer blends, melting behaviour may also be influenced by the respective crystallinity of the blend fraction(s) (Fig. 8a). The sensitivity to 2-butanol content of the estimated average melting temperature was found to be most significant from 0 to about 50 wt% solvent from this study on the two distinctly different types of PHA (Fig. 8b).

3.4. Solvent, temperature, and PHA decomposition rates

Melt processing (time, temperature, pressure) will promote some molecular weight decomposition by random chain scission. Therefore, polymer degradation rates were evaluated with or without the presence of solvent. Parallel samples, with and without added 2-butanol, were incubated in sealed tubes at 160 and 180 °C. For samples with added solvent, a 66 wt% solution/gel solvent content was targeted. In the presence of 2-butanol, PHA melted and formed a viscous solution. Constant decomposition rates were estimated in both cases based on the trend of decrease in intrinsic viscosity (equations (1) and (2)) over 1 h as shown in Fig. 9. There was no statistically significant influence of the presence of 2-butanol. Decomposition rates increased similarly significantly with temperature as expected (Grassie et al., 1984a; Kunioka and Doi, 1990) and increased sixfold from 160 to 180 °C. This result suggests that presence of the solvent should not contribute to polymer decomposition during extrusion. Pressure in the test tubes with 2-butanol are expected to be about 6.4 and 10.4 bar, respectively, for 160 and 180 °C

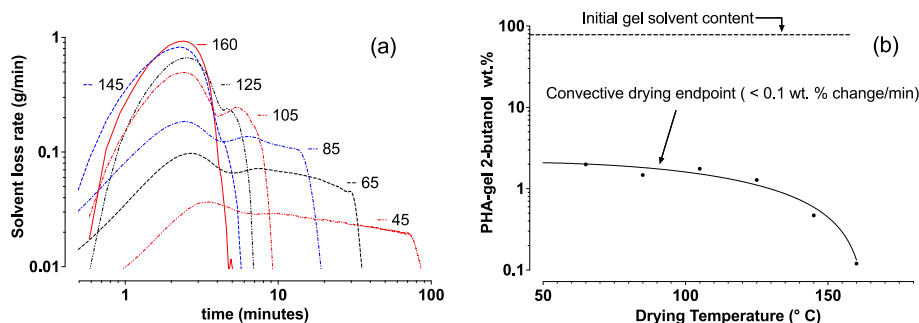


Fig. 5. Convective drying rates as a function of time for drying PHA gels as a function of temperature (°C) as indicated (a). 2-Butanol mass remaining at the endpoint as a function of the drying temperature (b).

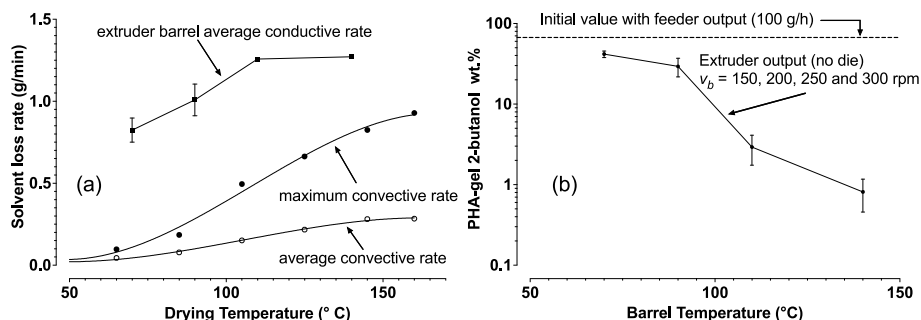


Fig. 6. Convective and conductive average (and maximum) drying rates for PHA gels as a function of applied isothermal temperature (a). The estimated average drying rate at 140 °C was not representative because exit material was dried. Gel output was dried to an extent that was most influenced by barrel temperature. Error bars (not all are large enough to show) show variability in dryness due to different v_b (150, 200, 250, and 300 rpm) (b).

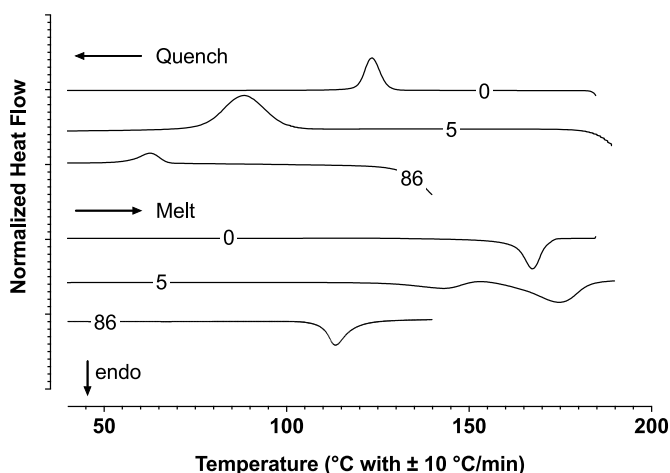


Fig. 7. Melt and crystallization trends for heating and cooling PHB samples (± 10 °C/min) with 0, 5 and 86 wt% 2-butanol content. The double peak for melting PHB (5 wt% 2-butanol) may reflect a heterogeneous distribution of butanol in the gel.

from published Antoine equation parameters (Ambrose and Townsend, 1963). Since the presence of solvent did not influence the decomposition rate, the data further suggest that the difference in pressure did not influence that rate either.

An opportunity for extrusion of gels at reduced temperatures compared to the neat PHA can further help to reduce risk for molecular weight losses in processing. For a given gel solvent content, if temperature along with added effects of shear and pressure are sufficient, the

polymer will melt at a reduced temperature. For example, from the characterization and evaluations presented above (Fig. 8), 150 °C will be sufficient to melt a PHB gel with about 10 wt% solvent content in a closed vessel. The 2-butanol vapour pressure at 150 °C in a closed vessel is expected to be about 5 bar.

3.5. Gel extrusion and solvent recovery

With the Rondol extruder setup in the present investigation, a barrel temperature of 100 °C with an extruder screw speed of 250 rpm yields nominally 10 wt% 2-butanol content at the die (Fig. 6b). This outcome was targeted with an input fed gel with 70 wt% solvent (PHB and PHBV batches with $D_{50} \approx 800$ μ m). Here, the powder feeder was used at screw rates between 100 and 125 rpm achieving feeder output (barrel input) mass flow rates of 150–250 g-gel/h. Fig. 10 is illustrative of the system mass balance analysis. While processing 1140 g PHBV gel with 70 wt% 2-butanol the average extrudate production rate was monitored by weighing filament segments cut every 15 min. Cut segments were pelletized into 3 mm length pellets. Pellet solvent content was measured on grab samples. The cumulative produced solvent condensate was collected and weighed. From the 1140 g gel fed, 328 g PHA extrudate and 615 g 2-butanol condensate were recovered. The extrudate output rate (50 g/h) closely matched the effective input rate of PHBV mass (neglecting solvent) from the feeder output. With the system running well in this way under steady state conditions, a 96 % mass closure was obtained between PHA mass fed and mass recovered. About 77 wt% of 2-butanol mass fed with the gel was recovered as condensate.

3.6. Die temperature settings, die pressure, and extrudate quality

In a set of experiments with Zone 1 set to 25 °C, zones 2 to 8

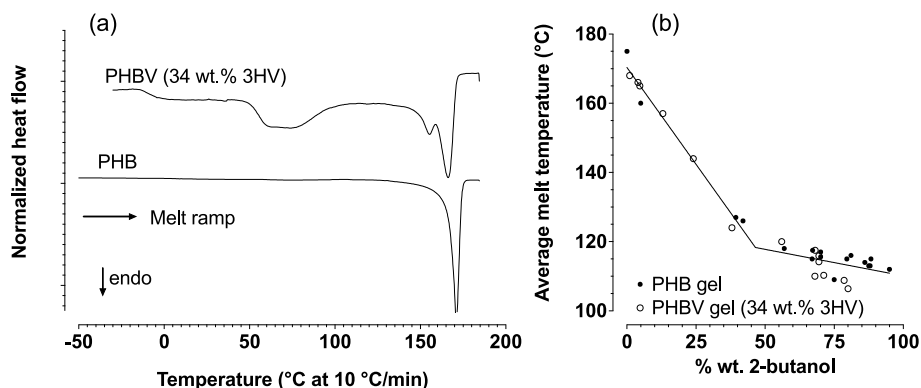


Fig. 8. Melting of PHAs as dried polymer and as gels. (a) DSC heat flow showing endothermic melting peaks for the neat dried PHB and a PHBV with 34 wt% 3HV (0 wt% 2-butanol). (b) Trend of average melt temperatures of gels for PHB and the co-polymer blend of PHBV from a) and as a function of wt.% 2-butanol. Data were fit to a two segment line by least squares regression.

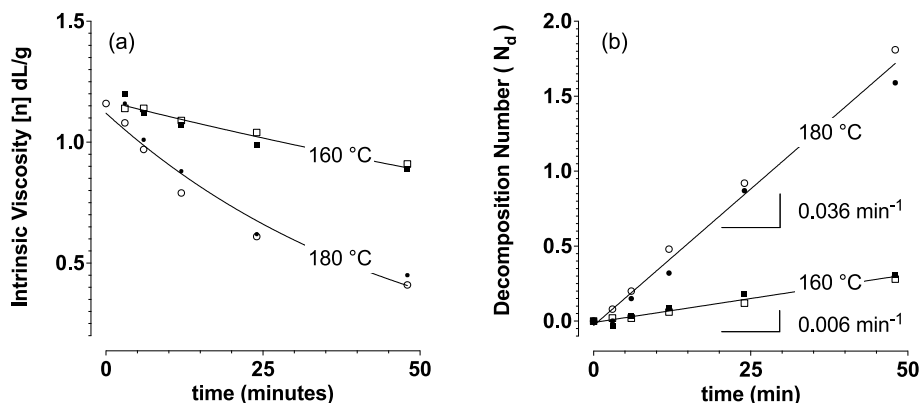


Fig. 9. PHBV thermal decomposition with and without added 2-butanol. (a) Trend of the polymer molecular weight (intrinsic viscosity) for incubation of the same PHBV at 160 (squares) versus 180 (circles) °C given dried (open symbols) versus the gel melted polymer in 2-butanol (filled symbols). (b) Decomposition number and rate assessed (equations (1) and (2)) with results of no significant influence of decomposition rate due to presence of the solvent.

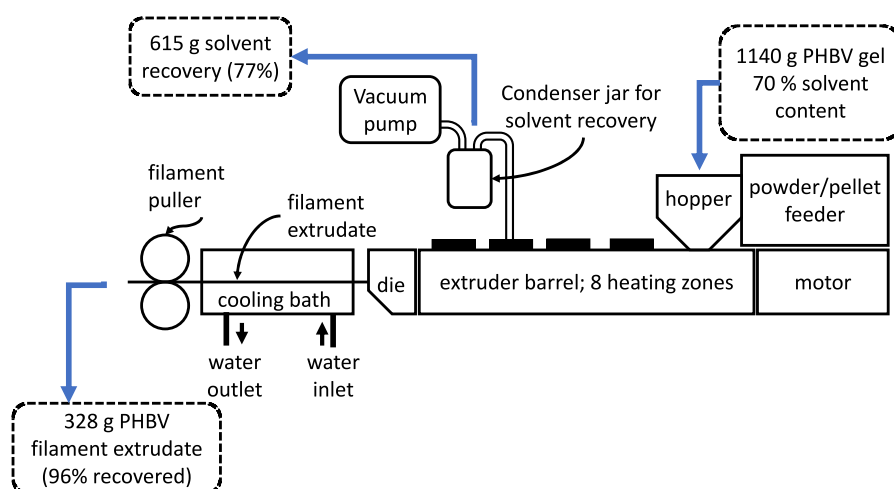


Fig. 10. Extrusion mass balance for solvent and PHA during processing 1140 g-PHA gel granulate.

temperatures were operated over a range of selected temperatures from 75 to 120 °C while otherwise maintaining steady state operating conditions. In so doing, gel drying was controlled to deliver gel to the die over a range, respectively, from 40 down to 10 wt% 2-butanol. The objective was to explore the influence of gel solvent content on feasible die temperatures as well as the influence of the set die temperature on resulting extrusion operating pressures. The goal, notwithstanding the input gel solvent content, was still to produce a filament extrudate containing less than 1 wt% remaining solvent. Studies were performed by conservatively starting with a die temperature of 190 °C and then lowering temperature in 10 °C steps while monitoring and logging operating parameters (temperatures, torque, pressure). Mass balances for the polymer and solvent were also made. A summary of applied and resulting conditions for the PHB and PHBV gel granulate extrusion runs is given in Tables 1 and 2, respectively. Trends of die pressures as a function of applied die temperature as obtained from the instrument log data are shown in Fig. 11.

While stepping down in die temperatures, and assessing the log file during periods of quasi-steady state operations, a point was reached when pressures increased rapidly. At this point further steps of die temperature decrease were not possible. A lower barrel temperature delivering a gel with higher solvent content at the die, enabled sustained stable extrusion down to lower die temperatures while keeping lower die pressures. A barrel temperature of 120 °C would effectively dry the gel before it reached the die (Fig. 11). For a PHB gel, the die pressure

Table 1

Extruder operating conditions for a PHBV gel granulate with 68 wt% 2-butanol using ventilation with 500 ± 20 mm-Hg applied vacuum. Barrel zone 1 setpoint was 25 °C. Feeder gel output is the gel mass fed into the extruder barrel. SME (specific mechanical energy) demand (addressed in section 3.8) is given on the basis of polymer output, and total product mass output (polymer and solvent) in brackets.

Feeder gel output	Barrel screw rate and temperature (Zone 2–8)	Die temperature and Pressure		Extrudate	Mass output rate	SME
(g/h)	(rpm) °C	°C	bar	wt.% 2-butanol	g/h	kJ/kg
85	250	120	184	5.1	0.7	27.2
85	250	120	138	25.9	1.2	27.3
85	250	105	184	5.2	1.1	27.3
85	250	105	137	15.3	1.2	27.3
164	250	105	130	20.2	0.8	51
110	250	90	175	5.2	1.2	36
85	250	90	183	4.7	1.8	27.5
85	250	90	123	28.7	1.5	27.4
85	250	75	184	5.0	4.1	28.1
85	250	75	105	25.0	3.7	28.0

Table 2

Extruder operating conditions for a PHB gel granulate with 65 wt% 2-butanol using ventilation with 300 ± 20 mm-Hg applied vacuum (SME = specific mechanical energy demand). Feeder gel output is the gel mass fed into the extruder barrel. Barrel zone 1 setpoint was 25 °C. SME (specific mechanical energy) demand (addressed in section 3.8) given on the basis of polymer output, and total product mass output (polymer plus solvent) in brackets.

Feeder gel output	Barrel screw rate and temperature (Zone 2–8)	Die temperature and Pressure	Extrudate	Mass output rate	SME
(g/h)	(rpm) °C	°C bar	wt.% 2-butanol	g/h	kJ/kg
100	250 120	190 6.7	1.4	35.4	7.3 (3.1)
100	250 120	167 23	1.5	35.5	6.7 (2.9)
100	250 75	190 8	14.4	40.8	5.1 (2.6)
100	250 75	144 4.4	25.0	46.6	3.6 (2.2)

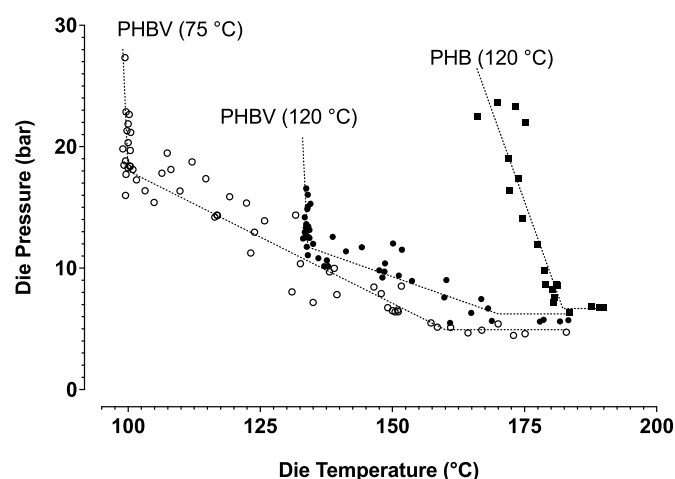


Fig. 11. Die pressure versus die temperature from log files during PHB (squares) and PHBV (circles) gel extrusion (Tables 1 and 2). Development of die pressure was monitored while lowering die setpoint temperature from 190 °C. Results are shown for operations with barrel temperature (Zones 2 to 8) at 120 (closed symbols) and 75 (open symbols) °C.

started from 6.7 bar at above 180 °C and it increased rapidly with die temperature cooling to 170 °C. Contrary to PHB gel, a gel of a relatively less crystalline PHBV (34 wt% 3-hydroxyvalerate), when dried in the barrel at 120 °C, could be extruded down to a limiting temperature of 140 °C. At lower barrel temperatures, the higher resulting gel solvent content at the die inlet permitted extrusion with significantly reduced die temperatures down to 100 °C before die pressures became too high.

Barrel and die temperature coupling influenced the die temperature operating window, the residual solvent content in the extrudate, and solvent recovery performance. Extrusion parameter combinations, with die temperatures (from 180 down to 130 °C) and barrel temperatures (from 90 up to 120 °C), consistently resulted in PHA extrudates containing less than 2 wt% solvent content, and resulting in about 75 wt% of the 2-butanol in the fed gel being recovered as a condensate. However, lower barrel temperatures (≈ 75 °C) and lower die temperatures (between 100 and 120 °C), yielded PHA extrudates with higher solvent contents (Tables 1 and 2).

The combinations of barrel and die temperatures influenced extrudate quality. Within a window of operating conditions, smooth and defect-free surface qualities were obtained. Examples of changes in surface quality for extruded filaments with selected barrel and die temperatures are shown (Figs. 12 and 13). Higher barrel temperatures (120 °C) with die temperatures from 90 to 120 °C resulted in extrudates

of better surface finish quality. Shark skin defects were seen in some cases such as at 150 °C die temperature. Lower barrel temperatures (e.g., 75 °C) combined with the die at 180 °C lead to defects of inconsistent filament dimensional quality and trapped gas bubbles. Bubbles were considered to be due to solvent boiling after the pressure decrease for the extrudate upon exiting the die. Good quality could be obtained even with reduced drying rates due to lowered barrel temperature. Fairly good PHBV dimensional stability was obtained for 75 °C (barrel) and 150 °C (die). Lowering die temperature to 150 °C apparently reduced effects of extrudate vapour production from its entrapment for the hardened strand. Thus “sweet spots” may exist for this processing approach and any benefits of a reduced extrusion temperature will need to be coupled to context of demands placed on the needed extrudate quality. Reduced extrudate aesthetic quality may be acceptable when making intermediate formulations such as compounded bioplastic pellets. Lower temperatures may especially be helpful when compounding PHA with temperature sensitive additives, including but not limited to cellulose, and/or where minimal risk for PHA decomposition is required during compounding. Therefore, what is optimal in quality depends on the context of type of solvent, the type of PHA, and the extrusion objectives. Surface quality will be influenced by the material dryness at the die coupled to the applied die temperature and pressure. For example, shark skin effects may come from the material becoming too dry at the die in combination with its extrusion through the die at too low a temperature. What is optimal for the parameters in a production context may need to be determined heuristically, case by case.

3.7. Dry versus wet extrusion and polymer decomposition rates

By selecting combinations of barrel and die temperatures, extrusion conditions were created with more or less dried material at the die, leading to higher or lower die pressures. The extrudate and input PHA molecular weights (intrinsic viscosities) were compared. In replicate evaluations (Tables 3 and 4), polymer decomposition was found to be insensitive to processing conditions tuned to deliver gels with higher or lower solvent content at the die inlet, and with corresponding need for lower or higher die temperatures.

A second case study was undertaken for the PHBV with 34 wt. 3HV (Fig. 8a) extracted from a PHA-rich biomass. The purpose of this study was to compare the influence of wet versus dry processing on the resulting polymer quality. The granulate dried solids were 98.4 % dry wt. PHBV with a thermal decomposition temperature (T_d) of 302 °C (Fig. 14a). The gel granulate was divided into two batches for drying by vacuum oven (40 °C, 0.2 bar, 3.5 L/min N_2 gas flow). One batch was reduced to 66 wt % solvent content, and the other to 4 wt % solvent. The batches were melt extruded as wet (gel) or dry polymer (Table 5). Conditions were selected to give similar extrudate filament output rates and solvent content. Barrel zone temperatures were respectively selected for processing the gel versus dry polymer granulate. Die temperatures were varied similarly to establish four steady state periods of extruder operation. Die temperatures during these steady state periods were in the range from 180 down to 150 °C. Rondol pellet (20–35 rpm rate) and powder feeders (100–125 rpm rate) were used for gel and dry PHBV feeding, respectively. Barrel screw rate was 250 rpm in both cases. Results of gel versus dry feed on extrudate polymer properties were compared and are presented below.

A typical example of the polymer assessment for a comparison using melt rheology is shown in Fig. 14b–15 (Materials and methods, 2.6.3) for the fed PHBV. For the isothermal time-sweep stage-1 (195 °C, 1 Hz and 2 % strain), complex viscosity decreases over time due to thermal decomposition of the melt (Fig. 15a). The second stage (isothermal frequency sweep) indicates an expected trend of complex viscosity $|\eta^*|$ towards a zero-shear viscosity (η_0) (Fig. 15b). The asymptote for this trend may be estimated based on Cross (1979). The third quench stage illustrates that this particular PHBV had a well-defined crystallization temperature at 106 °C.



Fig. 12. Extrudate strand surface finish as a function of barrel (B) and die (D) temperatures ($^{\circ}\text{C}$) for PHBV gel processing (Table 1). White bar scale indicates 5 mm.

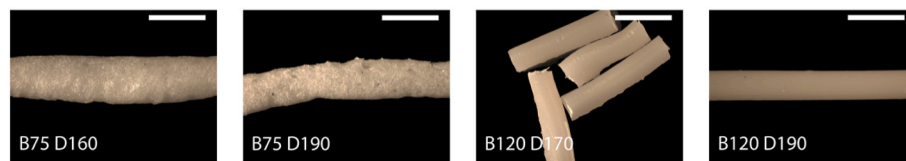


Fig. 13. Extrudate strand surface finish as a function of barrel (B) and die (D) temperatures ($^{\circ}\text{C}$) for PHB gel processing (Table 2). White bar scale indicates 5 mm.

Table 3

Processing of PHBV gel granulate (68 wt% 2-butanol) with outcomes of molecular weight decomposition (Feed rate 85 g/h and barrel screw speed 250 rpm). Fed PHBV polymer intrinsic viscosity was 1.17 ± 0.02 dL/g.

Zones 2-8	Die temperature and Pressure		Extrudate	Mass output rate	[η]	N_d
$^{\circ}\text{C}$	$^{\circ}\text{C}$	bar	wt.% 2-butanol	g/h	dL/g	
120	184	5.1	0.7	27.2	0.96 ± 0.1	0.23
75	105	25.0	3.7	28.0	0.92 ± 0.1	0.28

Table 4

Processing of PHB gel granulate (65 wt% 2-butanol) with outcomes of molecular weight decomposition (Feed rate 100 g/h and barrel screw speed 250 rpm). Fed PHB polymer intrinsic viscosity was 1.77 ± 0.02 dL/g.

Zones 2-8	Die temperature and Pressure		Extrudate	Mass output rate	[η]	N_d
$^{\circ}\text{C}$	$^{\circ}\text{C}$	bar	wt.% 2-butanol	g/h	dL/g	
120	190	6.7	1.4	35.4	1.17 ± 0.08	0.52
75	144	4.4	25.0	46.6	1.17 ± 0.01	0.52

Zero-shear viscosity (η_0) is proportional to molecular mass (Mezger, 2023). However, it has also been shown that, for the same PHA during thermal decomposition, changes in the weight average molecular mass (M_w) are linearly proportion to complex viscosity (Malengreux, 2008):

$$M_w = a \cdot |\eta^*|_{(T,f)} + b \quad (7)$$

where a and b are constants of proportionality and “(T,f)” are the conditions of temperature and frequency for the melt rheology measurement. Decrease in complex viscosity between the end of stage-1 and the beginning of stage-3 (Figs. 15 and 195 $^{\circ}\text{C}$, 1 Hz and 2 % strain) are further indicative of thermal decomposition during the time of measurement. Changes in the complex viscosity at the end of stage-1 were used as a reference (avoiding an extrapolation) for comparing relative differences in molecular weight before and after extrusion given the same PHBV (Fig. 16). The feed and extrudate polymer was also assessed for intrinsic viscosity by solution rheology and these levels were found to be directly proportional to selected reference measurements of complex viscosity for the same samples.

Dry or gel extrusion die temperature did not influence operating conditions of torque for similar extrudate output rates and at the same barrel screw speed (Fig. 16a). Die pressure did decrease with increased die temperature as it might be expected to do. Die pressures decreased more with higher die temperatures for gel extrusion. The molecular weight of the gel fed extrudate was slightly lower (Fig. 16b). At the same time, extrudate molecular weight was insensitive to conditions of die temperature and/or the corresponding changes in die pressure. Presence of solvent, under the influence of temperature and or pressure changes, was found to have no measurable influence on the polymer decomposition rate (Results, 3.2). However, in this extrusion practical testing comparison, there was an aspect of the solvent or solvent chemistry that did promote an outcome of slightly higher decomposition.

3.8. Specific mechanical energy demand

Outcomes for specific mechanical energy (SME) demand for PHBV and PHB gel extrusion trials were estimated (Tables 1 and 2). SME expresses the mechanical energy applied to produce a unit mass of extrudate (de Margerie et al., 2021; Domenech et al., 2013; Fayose and Huan, 2014). SME demand includes factors of input material properties, feed rate, extruder screw speed, and temperature (barrel and die):

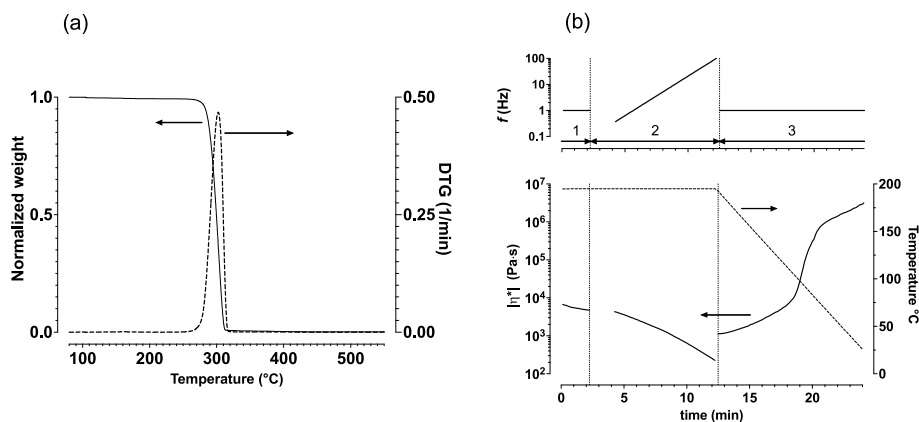


Fig. 14. Results of TGA (a) and melt rheology analyses (b) on the PHBV used for comparing dry versus gel melt extrusion methods. The PHBV had a thermal decomposition of 302 °C given a 10 °C/min heating rate. Melt rheology complex viscosity ($|\eta^*|$) was assessed over three measurement stages: 1-isothermal time sweep, 2-isothermal frequency sweep, and 3-quench time-sweep.

Table 5

Operating parameters for dry versus gel extrusion of PHBV (34 %HV, Fig. 7). Standard deviations reported for extrudate production rate and solvent content based on 4 measurements over respective steady state operation periods for the 4 die temperatures tested in order of 180, 170, 160 and 150 °C.

Extrusion Method	Zone 1–8 Set Temperature	Zone 1–8 Actual Temperature	Extrudate Production	Feed solvent content	Extrudate solvent content
	Zone 1 - Zone 2 - ... (°C)	Zone 1 - Zone 2 - ... (°C)		wt. %	wt. %
Dry	25 - 25-180 - 170-160 - 150-140 - 130	66 - 123-180 - 170-160 - 150 - 140 - 130	71 ± 2	4	1.0 ± 0.6
Gel	25 -100 -100 -100 - 100 -100 - 100 - 100	72 -100 -100 -100 - 100 -100 - 100 - 100	64 ± 7	66	1.5 ± 0.4

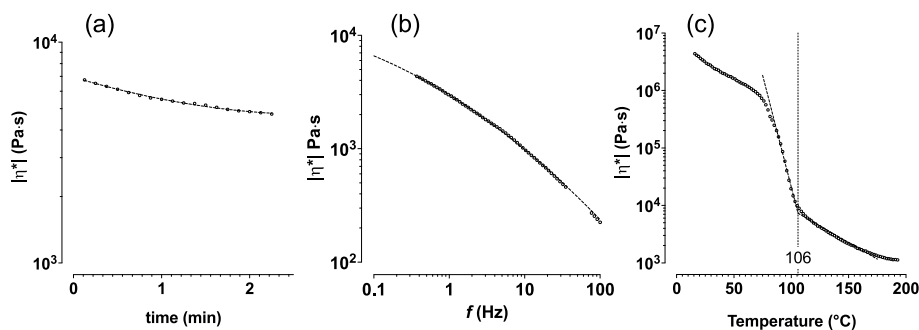


Fig. 15. With reference to Fig. 13b, respective complex viscosity ($|\eta^*|$) trends during measurement stages 1 (a), 2(b) and 3 (c) shown with respect to time, frequency and temperature. Crystallization onset temperature during quenching was estimated to be 106 °C (c).

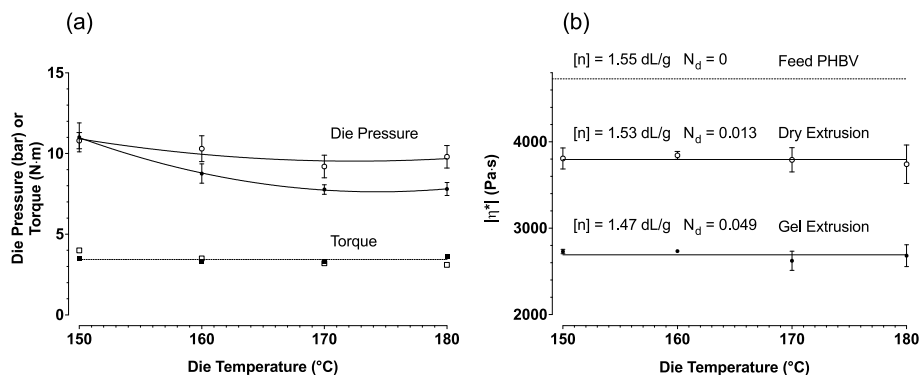


Fig. 16. Outcome of extrusion for dry (open symbols) versus gel (closed symbols) PHBV extrusion (Table 5). (a) Die pressure (circles) and torque (squares) resulting from changes in die temperature. Averages values with standard deviations from replicate measurements ($n = 9$) based on extruder conditions in a window of 10 min steady state operation for respective die temperatures. Standard deviations for torque are too small to show. (b) Dry and gel extrudate complex viscosity $|\eta^*|$ and intrinsic viscosity $[\eta]$ with scission number (N_d) reported as a function of die temperature and with respect to input feed $|\eta^*|$. Melt rheology data are shown with median and range from measurements made in duplicate.

$$SME = K^* \frac{v_b^* \tau}{\text{Extrudate output rate}} \quad (8)$$

where K is a system dependent constant, v_b is the barrel screw speed and τ is the applied barrel torque. Added compounding ingredients may alter SME due to change in the extruded material properties, and mass processing rates. Typically for processing just neat polymer, feed and output mass flow rates under steady state operations will be the same. For gel extrusion, the mass input rate will be higher than the extrudate output mass rate due to the significant solvent mass removal.

Equation (8) can express a ratio of SME values (SME_{dry}/SME_{gel}) for dry (neat) polymer and gel extrusion. This ratio is influenced by the solvent-to-polymer mass ratio (r) for the gel, the overall solvent recovery efficiency (n), and the screw torque ratio (τ_{dry}/τ_{gel}):

$$\frac{SME_{dry}}{SME_{gel}} = (1 + (n^*r))^* \frac{\tau_{dry}}{\tau_{gel}} \quad (9)$$

From the campaigns of extrusion runs made for the present investigation, torque values for dry and gel extrusion processing were similar, varying between 3.5 and 4.5 Nm. Thus, the ratios (τ_{dry}/τ_{gel}) fell between minimum 0.77 and maximum 1.28. If the processing torques may therefore be assumed to be approximately the same ($\tau_{dry}/\tau_{gel} \approx 1$) then:

$$\frac{SME_{dry}}{SME_{gel}} \approx 1 + n^*r \quad (10)$$

SME_{dry} versus SME_{gel} demand of dry versus gel (60–70 wt% 2-butanol solvent) PHA extrusions were made for operations at the same barrel screw speed (250 rpm) and with a similar PHA extrudate output rate (80 g/h). To obtain these comparable PHA extrudate mass output rates, feeder screw rates were adjusted accordingly. Naturally more gel mass is processed in the same time compared to the dry PHA extrusion given similar output rates. Thus, based on feed rate, SME demand for processing of gel material will always be lower compared to the dry PHA extrusion. However, considering recovered solvent also as a production output, SME in gel processing can still be significantly less compared to dry processing. From equation (10), SME demand for gel processing ($r = 1.63$) can be 40–65 % less compared to the SME applied during dry PHA extrusion. The reduced specific demand depends on extent of solvent recovery. Gel extrusion, over conventional dry processing, include benefits due to outcomes of consistent extrudate quality and the efficiency of concurrent solvent recovery.

4. Discussion

Standard melt extrusion equipment was applied for this unconventional method of polyhydroxyalkanoate processing. The applied methods were adapted for, but also constrained by, the available equipment. Solvent-rich PHA gel was fed into the hopper of the extruder with the Rondol standard feeders. The best feeder type to use depended on the gel morphology. In these trials the gel contained less than 95 wt% butanol, and successful processing of a gel granulate was possible between 5 and 90 wt% 2-butanol. Granulate flowability by gravity was necessary for the available feeder and hopper arrangement. Feeder rates could not be in excess of the barrel transport rates to avoid build-up and jamming of gel granulate in the small hopper (Figure S1 and Figure S2). Further advancement in these methods would benefit from well-adapted feeding methods that work robustly to different kinds of gel morphologies (pastes or granulates), and convey polymer gel mass into the extruder at a controlled rate. Feeder gel mass flow rate decreased with feeder screw speed (Fig. S1). Thus other methods of granulate feeder transport to the barrel are required. Factors influencing gel morphology, gel rheology, and methods of feeding of soft particles or pastes are a part of ongoing investigation.

Conventional practice is to separate volatile emissions from the melt in the extrusion processes with a focus on degassing and removal

(Kohlgrüber et al., 2022), but not on solvent recovery. The Rondol extruder standard ports for volatile emission venting with vacuum pump and condensation cup were not intended in their design to be a solvent recovery system. Still, most of the solvent (77 %) was recovered. Improvements to the solvent capture efficiency are required due to considerations of safety and the fact that a high degree of solvent recovery is critical for an extraction process economic viability (Bengtsson et al., 2017). The feeder, and the interface between feeder and extruder barrel were open to the surroundings. To manage the risks associated with flammable solvents (as discussed further below) and to enable maximal solvent recovery, fugitive emissions must be avoided. In the present work an extractor ventilation system was used to manage volatile emissions from the feeder and extruder input (hopper) zones. Ideally, a closed input system is required. It should include the gel input reservoir, the optimal gel feeding mechanism, and its coupling to the extruder. Methods for improved evaporated solvent mass capture are anticipated to be possible by adding multiple venting ports, having overall system enclosure, and creating optimized solvent condensation conditions.

The current work has been focused on technical proof of principle for effective concurrent solvent recycling with melt processing of PHA gels. Such gels are inherently formed in so-called PHA-poor solvents like 2-butanol, after cooling the hot polymer rich solutions generated by the PHA extraction (Werker et al., 2020). A techno-economic evaluation of PHA-poor solvent based PHA extraction and recovery was part of a previous study with details reported (Bengtsson et al., 2017). Cost estimates at that time (2016) were made for a 5000 ton/year PHA extraction facility. The extraction facility represented just over 50 percent of the CAPEX and OPEX with an estimated production cost of about 2.1 €/kg PHA produced and recovered as a dried purified powder. The economic and environmental cost evaluations suggested a PHA selling price of 4.5 €/kg and a net positive benefit in the life cycle analysis (LCA). Mass and energy balances predicted that solvent recovery (with the polymer drying) accounted for 60 percent of the heat (with 11 bar steam) and 70 percent of the electricity demands for the overall extraction process. Sensitivity analysis also showed that the LCA was most influenced by solvent use. One strategy to make both environmental and economic gains in the polymer production alone is to use less net input solvent. The present investigation suggests that another strategy is to derive more environmental and economic value from the input solvent that is anyway used and mostly recovered. Effective savings are expected, although unproven, if extraction is extended to include solution and gel processing.

The market price for PHA depends on how much polymer is ordered from the supplier. It is estimated to be between 5 and 10 €/kg (Vandi et al., 2018). According to Vandi et al. (2018), an approach to leverage the high material costs, while still benefiting from the polymer properties and its biodegradability, is to produce composite materials with a high fraction of a lower cost composite. Post extraction solution blending or low temperature gel blending enables efficient compounding and homogenous mixing before the solvent removal. Wet melt processing of formulations still permit recycling of the solvent. Preliminary work with gel blending PHAs and compounding with nanocellulose show promising outcomes for nucleating agents (unpublished data). An LCA and/or full techno-economic evaluation was beyond the scope of the present investigation. The goal of this work was to motivate any deepened technical and techno-economic studies based on successful technical outcomes. Future techno-economic evaluations will be most meaningful if the context and scale are both clearly specified in such critical studies. For example, combined gel and melt processing can be used to make formulated pellets for sale to downstream businesses. These pellets may be sold to stakeholders who undertake further melt-processing and conversion. However, results suggest that formulated gels can be processed all the way into final bioplastic articles for final sale and application. The infrastructure, the product value, and the boundary conditions for the business cases, and for the LCA outcomes may change significantly due to context and the identified avoided

environmental impacts in the selected production context (Heimersson et al., 2014).

Many non-halogenated solvent types (alcohols, ketones, carbonates, etc.) have long before been identified for PHA extraction from biomass (Liddell, 1996). For gel melt-processing, the PHAs must be thermo-reversibly soluble and form gels with a morphology that is processable at elevated temperatures. Risks with a flammable solvent must also be managed. A screening with testing of other potentially suitable solvents for gel-extrusion processing was beyond the scope of the present investigation. Such screening with practical experimental work is complicated by the fact that each solvent has to be duly assessed for its health and safety risks. The equipment and the working environment must be safe and suitable. A professional risk management assessment was made for 2-butanol for this research work given the infrastructure used for extraction and processing (Pol, 2021). The health and safety considerations (presented below in summary) are illustrative to the necessary assessment that needs to be taken for any flammable solvent use.

The equipment surfaces must not be allowed to become warmer than the minimum ignition temperature for the flammable solvent. The ignition temperature for 2-butanol (390 °C) is almost double the maximum heated zone temperatures used for the extrusion process (180 °C). Equipment used in hazardous areas should comply with the gas group that corresponds with the properties of the solvent. 2-Butanol is in gas group IIA which makes it relatively safer with a minimum ignition energy of 200 μ J. Risks for ignition sources need to be nevertheless mitigated and this prevention includes relative speeds in mechanical equipment to be lower than 1 m/s. For the 10 mm extruder screws operated at a maximum 300 rpm, the relative velocity between surfaces would not have exceeded 0.16 m/s.

An explosion may occur with a flammable substance given enough oxygen/air present and a source of ignition. 2-Butanol has a lower and upper explosion limit (LEL and UEL) in air of 1.7 and 9.8 % vol, respectively. As discussed above, the input system comprising the gel reservoir, with feeder and coupling to the extruder barrel should be a closed system. In that closed system it is an objective to maintain any head space above the UEL in order to avoid the risk for an explosive atmosphere in the equipment. It is also an objective to sustain constant gel properties (solvent content) before extrusion.

The atmosphere in the extrusion barrel needs to be controlled for purposes of efficient solvent recovery and for managing the solvent risks. A strategy is to ventilate the barrel with enough, but not too high air flow rates, that maintains an atmosphere well above the UEL. Conservative air flow rates into the barrel may be estimated from a mass balance and the ideal gas law. For example, consider a gel feeder output of 100 g/h with 85 wt% 2-butanol. Assuming an extrudate of 1 wt% solvent, the average solvent evaporation rate will be about 85 g/h. With a factor of safety of 5 for the UEL, the solvent vapour extraction air flow rate into the barrel should not exceed about 0.5 m³/min (25 °C, 1 atm).

The working environment around the equipment furthermore needs to be ventilated to maintain conditions well below LEL to avoid ignition hazards. For occupational health and safety, levels need to be lower than the derived no effect level (DNEL). This level is about 100 ppm for 2-butanol. Organic solvent sensors with alarms, and automated equipment shut-down control will form part of the safety evaluation and implemented operating checks and protocols.

After health and safety, production quality control is critical. PHA degradation rates are significant as temperatures increase over 170 °C (Grassie et al., 1984b). An Arrhenius relationship for decomposition rate means logarithmic increase in rate with temperature (Kunioka and Doi, 1990). Shear stresses also contribute to the polymer decomposition rate (Pachekoski et al., 2013). Thus, recommendations in PHA melt processing include using as short a time as possible at the polymer melting temperature, and a reverse temperature gradient after the melting zone with temperatures still above the crystallization temperature (Krishnaswamy et al., 2009; Zhang et al., 2004). Polymer molecular

weight losses influence melt and crystallization behaviour, microstructure and, as such, final article mechanical properties (Grassie et al., 1984b). In the present work it was surprising to observe that lowering the die temperature, causing some increase in die pressure, did not significantly influence the extent of decomposition for either gel or dry PHBV melt extrusion, with all other factors being the same. At the same time, the presence of solvent did not influence decomposition rates but processing of gel versus dried PHBV did result in slightly lower molecular weights, independent of die temperatures over a wide range from 150 to 180 °C. The presence of trace levels of water in the solvent could not be ruled out. Trace water content can promote hydrolysis and decomposition of PHAs during melt processing (Gigante et al., 2020). In addition trace amounts of water in solvent can increase decomposition rates during PHA extraction and recovery (Werker et al., 2023). It is anticipated that solvent water content requires to be monitored and maintained as low as possible also for gel based extrusion methods.

Well-tuned processing conditions and appropriately selected additives are essential to process PHA into articles with targeted thermal and mechanical properties and with limited effects of aging (Gigante et al., 2020). Many research works address challenges involved with efficient processing of PHA, PHA based blends, and/or PHA composite materials (Bugnicourt et al., 2014; Collet et al., 2022; Montano-Herrera et al., 2014; Puppi et al., 2019). For extrusion of neat polymers or PHBV wood-fibre biocomposites, PHBV molecular weight loss extent can be mitigated by optimizing processing parameters but it will not be completely eliminated (Vandi et al., 2019). This documented know-how coupled to gel processing is untested. Gel processing can include methods to “cold” blend and then melt process PHA bioplastics with added compounding or composite materials at reduced processing temperatures. Reduced processing temperatures would be especially advantageous for those kinds of additives or composite materials that are less thermally tolerant or are reactive with PHA at higher temperatures. Blending with other kinds of biopolymers or composite materials should enhance properties or maintain properties as fillers, to add additional value (Vandi et al., 2018). Other kinds of biodegradable polymers can include poly (lactic acid) (Abdelwahab et al., 2012; Armentano et al., 2015; Arrieta et al., 2014; Zhang and Thomas, 2011), poly (butylene succinate) (Ma et al., 2012), poly (ϵ -caprolactone) (Gassner and Owen, 1994), and poly (butylene adipate-co-terephthalate) (Jiang et al., 2006). Composites can be formed with cellulose (Chiulan et al., 2016), lignin (Mousavioun et al., 2013), and starch (Parulekar and Mohanty, 2007) to serve various kinds of applications (Emaimo et al., 2022). Cross-linking agents can be applied in extrusion blown starch/PHA composites films for improved thermal stability (Sun et al., 2018). In all these cases it is critical to homogeneously mix the compounded formulation and it is advantageous to form the homogeneous blend without the need for elevated temperatures. In the proposed workflow (Fig. 1), formulation additives and composite materials can be blended with the polymer homogeneously during the process of extraction before gelation, and or mixed in with the gel material before introducing the matrix as a paste or gel granulate into the extruder. Given a potential for lower extrusion temperatures, and homogenous blending, gel processing can provide a degree of freedom to process and side step challenges for producing PHA composite materials within shorter applied time or with lower temperatures during melt compounding.

Processing temperatures may be lowered in principle for melt extrusion of less crystalline co-polymers of PHA, for example co-polymers of poly (3-hydroxybutyrate-co-3-hydroxyvalerate), or PHBV (Rivera-Briso and Serrano-Aroca, 2018). However, these PHAs are often also inherently blends of random co-polymers for which a component of the blend can still be, like PHB, more crystalline (Laycock et al., 2014; Pei et al., 2025). Therefore, in traditional polymer melt processing, complete melting of complex co-polymer blends may still require a period at higher temperatures (180–185 °C) for completely melting the most crystalline of the blend components (Fig. 7). Gel processing of PHB

facilitated reduced die temperatures and manageable die pressures. Similarly reduced die temperatures were not possible to apply, to our experience, with the same equipment when melt processing neat PHB. Other factors out of the scope of the present investigation are important to consider in ongoing investigation. During melt processing, some molecular weight loss does not necessarily mean loss of mechanical properties while other operating parameters influencing the melt consolidation will (Vandi et al., 2019).

Technological feasibility exists to produce PHBVs from a wide range of possible waste organic supplies (Estevez-Alonso et al., 2021). However, each waste source will most likely not make the same grade of PHBV (Pei et al., 2025). An efficiency for managing quality in supplies of disparate sources of PHA from different waste streams is not well-established. Centralized extraction with solution blending and masterbatches of PHAs from different “PHA-rich biomass” sources is seen as a possible means to facilitate supply chains that can generate masterbatches of PHBV blends of targeted qualities. PHA is valued because it is biobased and biodegradable while offering potential property specifications for a range in kinds of applications (Pandey et al., 2022). Biodegradation gives PHA a unique selling point in applications, such as with controlled release fertilizers (Majeed et al., 2015). However, even for single use applications like packaging, PHAs are interesting because they are also recyclable (Popa et al., 2022; Vu et al., 2020). EU policy frameworks are increasingly aimed at ensuring that all future packaging should be designed for reuse, and mostly derived from recycled post-consumer feedstocks, especially biowaste (European Commission, 2023). This goal means that there is a target to remove fossil-based plastics from recyclable packaging and to increasingly support sustainable practices for society, health and environment. Mechanical recycling of PHAs is challenged by molecular weight losses for every cycle (Dedieu et al., 2023; Main et al., 2023). Economics of packaging materials may further dictate that the good barrier properties of PHA are best exploited as a coating on cellulose based packaging (Kumari and Singh, 2023). The underlying context for the purposes of the present investigation has been centralized PHA recovery facilities extracting PHA (at least 5000 tPHA/yr) from masterbatches of PHA-rich biomass produced and supplied regionally from a distribution of available waste derived organic substrates (Werker et al., 2020). If centralized recovery facilities have merit, then such centralized facilities may become logically placed locations for synergy with solvent based PHA-recycling. Recycled PHA-based bioplastics can be formulated together with the virgin polymer extraction from PHA-rich dried biomass. In this way, additives and composite materials in those recycled bioplastics may be efficiently recovered and reused in the process. The recycled polymer formulations can be gel-reprocessed into renewed masterbatches avoiding a step of melt processing with molecular weight losses for each recycling iteration.

5. Conclusions

PHB and PHBV extraction can be integrated with downstream melt extrusion and solvent recovery by directly processing the intermediate recovered extraction gel mass. Gel granulate melt processing with quality control of the PHA extrudate was accomplished with concurrent recovery of the extraction solvent. Combinations of barrel and die temperatures, with barrel residence time, controls solvent content at the die. These combinations are to be optimized for the type of PHA and extrudate quality objectives. Optimal conditions will vary due to the crystallinity of different PHA-types including co-polymers or blends thereof. Molecular weight loss of the extrudate was found to be insensitive to extrusion processing conditions. Thus, decomposition rates were not found to be significantly influenced by the gel solvent content. More than 98 % solvent was consistently removed from the gel wherein 77 wt% was recovered as condensate using the primitive setup in the present work as a first proof of concept for technical feasibility. From 40 to 65 % less specific mechanical energy, including both PHA extrudate

and recovered solvent as outputs, was applied during the gel processing as compared to extrusion of dried PHA. This study motivates method developments of unconventional processes and specialized equipment alongside their critical evaluations for techno-economic efficiency towards production of higher-value bioplastic products with quality control and at reduced production costs.

CRediT authorship contribution statement

Sanjay Pal: Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Philip Kridiotis:** Investigation. **Ana Jiménez Vergel:** Investigation. **Zarja Medved:** Writing – review & editing, Investigation. **Raquel Barbosa:** Writing – review & editing, Supervision, Project administration. **Alan Werker:** Writing – original draft, Visualization, Validation, Supervision, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of generative AI and AI-assisted technologies in the writing process

Author(s) used standard Microsoft Word tools for identifying typographical, grammatical and spelling errors. The author(s) have reviewed and edited the content as needed and take full responsibility for the content and generation of own original work intended for peer reviewed scientific publication.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Alan Werker reports a relationship with Promiko AB that includes: consulting or advisory. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2025.145818>.

Data availability

Data will be made available on request.

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